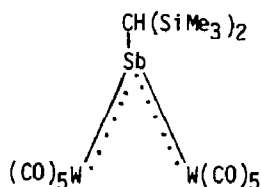ANTIMONY

ANNUAL SURVEY COVERING THE YEAR 1986

LEON D. FREEDMAN AND G.O. DOAK

Department of Chemistry, North Carolina State University, Raleigh, North Carolina, 27695-8204 (U.S.A.)
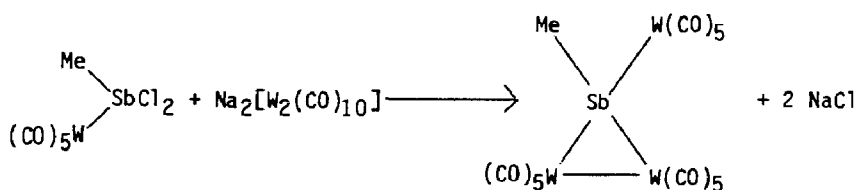
The preparation, reactions, and properties of organoantimony(V) compounds containing three C-Sb bonds have been thoroughly reviewed in a new volume of the *Gmelin Handbook of Inorganic Chemistry* [1]. A short (eleven page) overview of organoantimony chemistry has been included in a recent textbook on organometallic compounds [2]. In addition, information about organoantimony compounds has been given in surveys of recent publications on the main-group elements [3], on the main-group elements of Groups IV and V [4], on the main-group elements of Group V [5], and on organic derivatives of arsenic, antimony, and bismuth [6]. Ashe [7] has written an interesting account of work, mainly from his own laboratory, on distibines and related compounds. Organoantimony compounds have also been briefly mentioned in review articles on the following subjects: Mössbauer spectroscopy of antimony compounds [8], multiple bonding between main-group V and transition elements [9-11], double bonding between the heavier elements of main-group IV or V [12], new ring systems of elements of main-group IV or V [13], diffraction studies of organometallic compounds [14], p-π conjugation in aromatic compounds containing Group V or VI elements [15], reactions of metal carbonyls with Group V and VI donor ligands [16], π bonding to main-group elements [17], and fluxional cyclopentadienyl compounds of main-group elements [18]. A few organoantimony compounds have been discussed in a book on the IR and Raman spectra of inorganic and coordination compounds [19], and the *Second Supplement* of the *Dictionary of Organometallic Compounds* has several pages devoted to organoantimony compounds [20].

A dark blue stibinidene complex of tungsten has been prepared in 57% yield by the interaction of bis(trimethylsilyl)methyldichlorostibine and the disodium salt $Na_2[W(CO)_5]$ in THF [21]. Mass spectrometry and IR spectroscopy indicated the presence of $W(CO)_5$ and $(Me_3Si)_2CHSb$ moieties in the complex, while X-ray crystallography proved that the substance had the following "open" structure:

$$\begin{array}{c} CH(SiMe_3)_2 \\ | \\ Sb \\ \diagup \quad \diagdown \\ (CO)_5W \qquad W(CO)_5 \end{array}$$
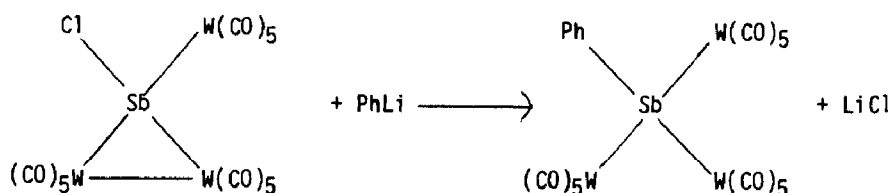
Each tungsten atom (bonded to five terminal carbonyl ligands and the central antimony atom) adopted an octahedral geometry. Within experimental error, the sum of bond angles at the antimony atom was 360°; hence the stibinidene geometry was trigonal-planar. The W-W separation was 4.907(1)Å and was thus well outside the normal range of distances associated with W-W single bonding. This observation (together with the trigonal-planar antimony geometry) clearly established the complex as a member of the "open" dinuclear structure class.
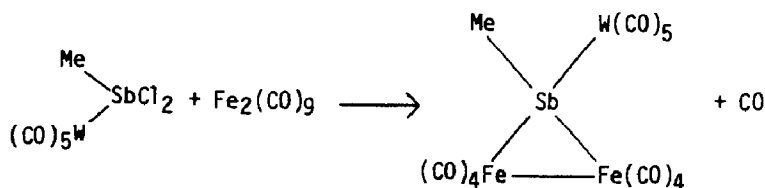
A dark red trinuclear derivative of antimony has been obtained in 22% yield by means of the following reaction [22]:

$$\begin{array}{c} Me \\ \diagdown \\ \quad SbCl_2 + Na_2[W_2(CO)_{10}] \longrightarrow \\ (CO)_5W \diagup \end{array} \qquad \begin{array}{c} Me \qquad W(CO)_5 \\ \diagdown \quad \diagup \\ Sb \\ \diagup \quad \diagdown \\ (CO)_5W \text{———} W(CO)_5 \end{array} \quad + \; 2 \; NaCl$$

A similar phenyl compound was prepared in 11% yield by the reaction of another trinuclear derivative:

$$\begin{array}{c} Cl \qquad W(CO)_5 \\ \diagdown \quad \diagup \\ Sb \\ \diagup \quad \diagdown \\ (CO)_5W \text{———} W(CO)_5 \end{array} \quad + \; PhLi \longrightarrow \begin{array}{c} Ph \qquad W(CO)_5 \\ \diagdown \quad \diagup \\ Sb \\ \diagup \quad \diagdown \\ (CO)_5W \qquad W(CO)_5 \end{array} \quad + \; LiCl$$

An antimony derivative containing both iron and tungsten was obtained in 12% yield by the following reaction:

$$\begin{array}{c} Me \\ \diagdown \\ \quad SbCl_2 + Fe_2(CO)_9 \longrightarrow \\ (CO)_5W \diagup \end{array} \qquad \begin{array}{c} Me \qquad W(CO)_5 \\ \diagdown \quad \diagup \\ Sb \\ \diagup \quad \diagdown \\ (CO)_4Fe \text{———} Fe(CO)_4 \end{array} \quad + \; CO$$

The substances thus prepared were studied by spectroscopy (IR, PMR, and UV) and were compared with similar phosphorus and arsenic compounds.

Organic compounds containing rings of six antimony atoms have been obtained by the slow air oxidation of bis(trimethylsilyl)phenylstibine dissolved in 1,4-dioxane, benzene, or toluene [23]:

$$6 \text{ PhSb}(SiMe_3)_2 + 3 \text{ O}_2 + \text{solvent} \longrightarrow (PhSb)_6 \cdot \text{solvent} + 6 \text{ } (Me_3Si)_2O$$
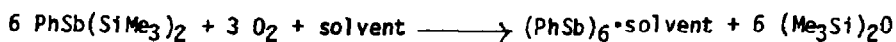
(where the solvent was 1,4-dioxane, PhH, or PhMe)

X-ray crystal structures of the cyclic compounds showed that the three solids were isomorphous. The centrosymmetric Sb_6 rings had the chair conformation, and the phenyl groups were equatorial. The Sb-Sb distances (284 pm) were similar to those found in distibines; and the Sb-C distances (216 pm) were in the usual range reported for organoantimony compounds. The Sb-Sb-Sb angles were about 90°. The crystal structures were characterized by stacks of $(PhSb)_6$ molecules with short Sb···Sb interactions (420 pm). The solvent molecules were required for optimum packing of these stacks. When a solution of bis(trimethylsilyl)phenylstibine in pentane was stirred in air for 4 h, siloxy compounds were formed:
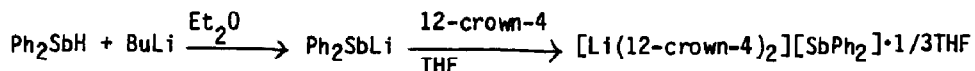
$$2 \text{ PhSb}(SiMe_3)_2 + 2 \text{ O}_2 \longrightarrow Ph_2SbOSiMe_3 + (Me_3SiO)_3Sb$$

Under similar conditions, trimethylsilyldiphenylstibine was also oxidized to a siloxy compound:

$$Ph_2SbSiMe_3 + 1/2 \text{ O}_2 \longrightarrow Ph_2SbOSiMe_3$$
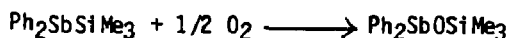
The siloxy compounds were studied by IR, PMR, and mass spectrometry. Elemental analyses were reported for all the substances prepared in this investigation.

The Ph_2Sb^- and $Ph_4Sb_3^-$ species have been included in a study of the isolation and structural characterization of solvated lithium salts of main-group V anions [24]. The diphenylstibide ion was obtained from the corresponding secondary stibine:

$$Ph_2SbH + BuLi \xrightarrow{\text{Et}_2O} Ph_2SbLi \xrightarrow[\text{THF}]{\text{12-crown-4}} [Li(12\text{-crown-4})_2][SbPh_2] \cdot 1/3THF$$

The X-ray crystal structure of the resulting dark-red complex showed the presence of three dissimilar Ph_2Sb groups. The C-Sb-C angles were 96.8 (4)°, 97.6(4)°, and 102.4(4)°; the six C-Sb distances ranged from 2.129(12) Å to 2.157(10)Å. The $Ph_4Sb_3^-$ was unexpectedly formed by the treatment of triphenylstibine with lithium powder in THF. After a dark-gray precipitate was removed by filtration, the addition of 12-crown-4 and

the concentration of the resulting solution gave orange-red crystals of [Li(12-crown-4)$_2$][Sb$_3$Ph$_4$]·THF. According to the X-ray diffraction study, the anion had the following structure:

$$Ph_2Sb \diagdown \overset{Sb^-}{\diagup} \diagdown SbPh_2$$
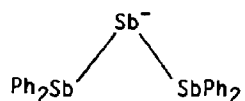
The C-Sb distances were 2.166(11)Å and 2.190(12)Å, values similar to those reported for other organoantimony compounds. The C-Sb-C angles of 92.7(4)° were also not unusual, but the Sb-Sb-Sb angle, 88.8(1)°, was rather acute. The Sb-Sb distance of 2.761(1)Å was significantly shorter than the corresponding values in distibines. The distance between the terminal antimony atoms in the anion was 3.864(1)Å; this value ruled out significant bonding interactions between these atoms.

The following examples have been included in a study of exchange reactions of the tetramethyldipnictogens [25]:

$$Me_2SbSbMe_2 + Me_2EEMe_2 \rightleftharpoons 2\ Me_2SbEMe_2$$
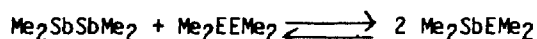
(where E was As or Bi)

Rapid exchange was found to take place at 25°C both in benzene-d_6 and in the absence of solvent. PMR spectra of the reaction mixtures showed signals for the parent compounds and for the products. The relative concentration of each species was determined from the integration of the PMR signals assigned to that species. The equilibrium constants were calculated by using the following expression:

$$K = \frac{[Me_2SbEMe_2]^2}{[Me_4Sb_2][Me_4E_2]}$$

The equilibrium constants for the formation of the Sb-As and Sb-Bi species in benzene-d_6 were 0.9 and 1.2, respectively, and were thus significantly smaller than the value of 4 expected on the basis of simple probability considerations. There was no evidence of an exchange reaction between tetramethyldistibine and tetramethyldiphosphine. Even after heating mixtures of the two substances at 80°C for 4h or allowing them to stand at 25°C for six days, no new signals were observed in the PMR spectrum. Raman spectroscopy proved to be useful for characterization of the interpnictogen compounds. Thus, mixtures of tetramethyldistibine and tetramethyldiarsine showed new bands at 218 and 231 cm^{-1}, which were assigned to Sb-As stretching frequencies. Similarly, samples obtained by mixing tetramethyldistibine and tetramethyldibismuthine showed new bands at 128 and 163 cm^{-1}, which were

assigned to the Sb-Bi stretch. As expected, the bands assigned to a heterodipnictogen bond occurred at frequencies intermediate between the bands of the corresponding symmetrical tetramethyldipnictogens. The mobility of the equilibrium between the tetramethyldipnictogens frustrated attempts to obtain pure samples of the mixed compounds. However, a pure sample of an arsinostibine was obtained by the following exchange reaction carried out in THF-d_8:
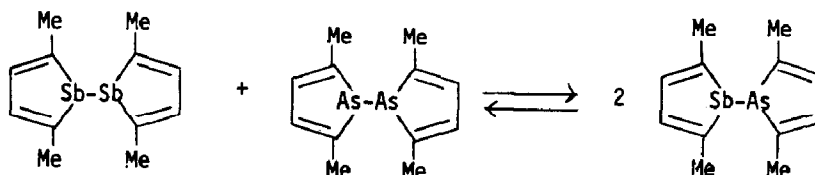

Integration of the PMR signals gave an equilibrium constant of 6.6. Removal of the solvent yielded a dark residue, which on slow sublimation gave three crystalline solids: golden crystals of the biarsole, violet crystals of the bistibole, and red crystals of the mixed compound. Like the bistibole (but unlike the biarsole), the mixed compound exhibited thermochromism and a large red shift between solution and solid. Crystallographic-quality crystals of the mixed compound could not be obtained, and thus it was not possible to determine whether or not the substance crystallized with stacking along its Sb-As bond axis (as has been found for the bistibole).

In a paper devoted mainly to the interaction of tetrapropyldibismuthine and chalcogens, the following exchange reaction has been reported [26]:

$$Me_2SbSbMe_2 + Pr_2BiBiPr_2 \rightleftarrows 2 Me_2SbBiPr_2$$
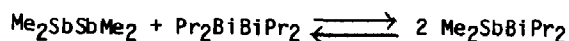
The equilibrium constant in benzene at 25 °C was found to be about 0.7. Although the mixed compound could not be isolated, the mass spectrum of the reaction mixture clearly showed the molecular ion of this species as well as several fragments that contained the SbBi bond.

Ten compounds containing SbS, SbSe, or SbTe bonds have been prepared by the interaction of distibines and dichalcogenides [27]:

$$R_2SbSbR_2 + R'AAR' \longrightarrow 2 R_2SbAR'$$
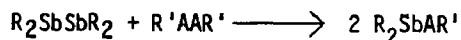
(where R was Me or Et, R' was Me or Ph, and A was S, Se, or Te)

The reactions were conducted either at room temperature (for tetramethyldistibine) or at -40 °C (for tetraethyldistibine). All of the reactions appeared to go to completion in a few minutes. The products were obtained analytically pure in quantitative yield as air-sensitive liquids or solids

and were said to have faint, pleasant odors. Even when these substances were heated, there was no evidence of reversion to starting materials. There was, however, some tendency (especially pronounced for the diethyl-stibino derivatives) for heating to cause decomposition to the trialkylsti-bine and a compound of the type $RSb(AR')_2$. The two tellurium compounds prepared ($Me_2SbTeMe$ and $Et_2SbTeMe$) were found to be thermochromic. Thus, the dimethylstibino derivative (a red liquid at room temperature) solidi-fied at about -52°C to a red solid, which became yellow-orange at about -80°C. A similar color change was observed when the compound was dissolved in deuterated chloroform. The other tellurium derivative was an orange liquid at 25°C and solidified at -80°C to a green-yellow solid. Freezing a solution of this substance in deuterated chloroform produced a similar change in color. All ten compounds were studied by PMR, IR, and mass spectrometry. The IR spectra exhibited a strong band at 340 or 345 cm^{-1} for the Sb-S stretching vibration and a medium or strong band at 220 or 230 cm^{-1} for the Sb-Se stretching vibration. No IR band, however, was assigned to the Sb-Te bond. The mass spectra exhibited relatively intense molecular ions (M+). The base peaks of the dimethylstibino derivatives corresponded to $(M-Me)^+$. The SbA^+ peak was observed in all of the mass spectra; in two cases ($Et_2SbTeMe$ and $Et_2SbSePh$) it was the base peak. The PMR spectra were in all cases consistent with the structures assigned to the ten compounds.

NMR, Raman, and mass spectrometry have been used to study the exchange reactions of tetramethyldipnictogens with dimethyldichalcogenides at 25°C [28]:

$$Me_2EEMe_2 + MeAAMe \rightleftharpoons 2 \, Me_2EAMe$$
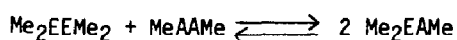
(where E was P, As, Sb, or Bi and A was S, Se, or Te)

The relative concentration of each species present at equilibrium was determined by integration of the PMR signals. The equilibrium constants for the interaction of tetramethyldistibine and dimethyldiselenide or dimethylditelluride were greater than 10^3; the equilibrium constant for the formation of (dimethylstibino)methylsulfide was 200. It was found that the Sb-A stretching vibrations gave rise to intense and easily identifiable Raman peaks at frequencies intermediate between the Sb-Sb bands of tetra-methyldistibine and the A-A bands of the corresponding dimethyldichalcoge-nide. The mass spectra of the Me_2SbAMe compounds exhibited strong mole-cular ions and the characteristic daughter ions Me_2SbA^+, $MeSbA^+$, SbA^+, Me_2Sb^+, Sb^+, MeA^+, and A^+.

Two aminostibines have been found to undergo a transamination reaction with diphenylamine at 100°C [29]:

$$R_2SbNEt_2 + Ph_2NH \longrightarrow R_2SbNPh_2 + Et_2NH$$
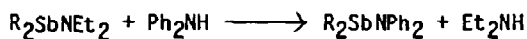
(where R was Et or Ph)

Reactions between the two aminostibines and diethylphosphine, diphenylphosphine, or diphenylarsine, however, took a different course and led to the formation of symmetrical compounds:

$$2\ R_2SbNEt_2 + 2\ R'_2EH \longrightarrow R_2SbSbR_2 + R'_2EER'_2 + 2\ Et_2NH$$

(where R' was Et or Ph when E was P; and where R' was Ph when E was As)

The interaction of diethylbromostibine and lithium diphenylphosphide also failed to produce the desired phosphinostibine:

$$2\ Et_2SbBr + 2\ LiPPh_2 \longrightarrow Et_2SbSbEt_2 + Ph_2PPPh_2 + 2\ LiBr$$
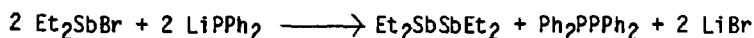
On the other hand a substance that gave the correct elemental analysis for the desired unsymmetrical compound was obtained by the reaction between an aminostibine and diphenylarsine:

$$Ph_2SbNEt_2 + Ph_2AsH \longrightarrow Ph_2SbAsPh_2 + Et_2NH$$

It was not definitely established, however, that the isolated substance was a pure compound and not a 1:1 molar mixture of tetraphenyldistibine and tetraphenyldiarsine. The new antimony compounds prepared in this investigation (and a number of related substances containing the Sb-N or Sb-Sb bond) were studied by [121]Sb Mössbauer spectroscopy at 42K. All of the isomer shifts were in a very narrow range (-4.0 to -4.6 mm/s relative to InSb). This result was interpreted to mean that the s-character of the Sb-Sb, Sb-As, and Sb-N bonds was essentially the same in the entire series of compounds. The positive values found for the quadrupole coupling constants and the magnitude of these values suggested that the lone pair electrons (on the antimony atoms) had considerable p-character. The variation in asymmetry parameters (which ranged from 0.0 to 0.9 relative to InSb) was attributed to possible changes in the p-character of the antimony-ligand bonds.

Electron diffraction has been employed to investigate the gas-phase molecular structure of tetramethyldistibine at 74°C [30]. Although it was concluded that gauche and anti conformations of the molecule were probably present, it was not possible to determine the rotomeric composition because of the small relative scattering from the torsion-sensitive distances. Most of the observed bond distances and bond angles were not remarkable. The Sb-Sb distance, 281.8(4) pm, however, appeared to be significantly

shorter than in the crystal, where the Sb-Sb distance had been reported to be 286.2(2)pm or 283.1(1)pm. The longer distance observed in crystalline tetramethyldistibine was attributed to electron delocalization along the linear chains of Sb-Sb···Sb-Sb atoms. It was also suggested that Sb-Sb bond shortening probably occurred in the liquid phase, where the rupture of the chains of antimony atoms by the melting process was accompanied by a color change from deep red to pale yellow.

Dimesitylhalo- and mesityldihalostibines have been prepared by heating a mixture of trimesitylstibine and the appropriate antimony trihalide [31]:

$$2 \ Ar_3Sb + SbX_3 \longrightarrow 3 \ Ar_2SbX$$

$$Ar_3Sb + 2 \ SbX_3 \longrightarrow 3 \ ArSbX_2$$
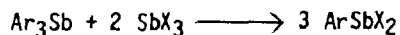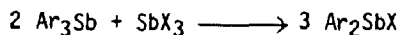
(where Ar was $2,4,6\text{-}Me_3C_6H_2$ and X was Cl or Br)

The tertiary stibine was synthesized by the Grignard reaction:

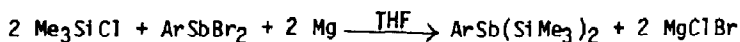$$3 \ ArMgBr + SbCl_3 \xrightarrow[Et_2O]{THF} Ar_3Sb + 3 \ MgClBr$$
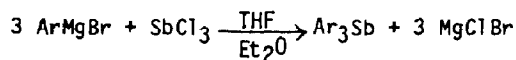
When the Grignard reagent was allowed to react with an excess of antimony trichloride or tribromide at low temperatures, however, trimesitylantimony dihalides were obtained. Presumably, the following sequence of reactions was involved:

$$3 \ ArMgBr + SbX_3 \longrightarrow Ar_3Sb + 3 \ MgXBr$$
$$Ar_3Sb + 2/3 \ SbX_3 \longrightarrow Ar_3SbX_2 + 2/3 \ Sb$$
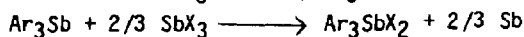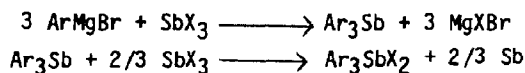
Trimesitylantimony dibromide was also prepared (in 96% yield) by halogenation of the tertiary stibine:

$$Ar_3Sb + Br_2 \xrightarrow{Et_2O} Ar_3SbBr_2$$
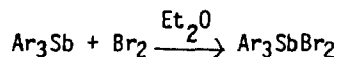
Silylstibines were obtained by the dehalogenation of a mixture of trimethyl-chlorosilane and dimesitylbromo- or mesityldibromostibine:

$$Me_3SiCl + Ar_2SbBr + Mg \xrightarrow{THF} Ar_2SbSiMe_3 + MgClBr$$

$$2 \ Me_3SiCl + ArSbBr_2 + 2 \ Mg \xrightarrow{THF} ArSb(SiMe_3)_2 + 2 \ MgClBr$$

In the absence of the chlorosilane, the interaction of the bromostibine and magnesium yielded a distibine:

$$2 \ Ar_2SbBr + Mg \xrightarrow{THF} Ar_2SbSbAr_2 + MgBr_2$$

The distibine was a yellow, crystalline solid, which was quite soluble in organic solvents. It was remarkably sensitive to oxygen and readily formed an oxide on exposure to air:

$$Ar_2SbSbAr_2 + 1/2\ O_2 \longrightarrow Ar_2SbOSbAr_2$$
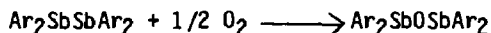
The reaction of mesityldibromostibine with magnesium yielded tetramesityl-tetrastibetane:

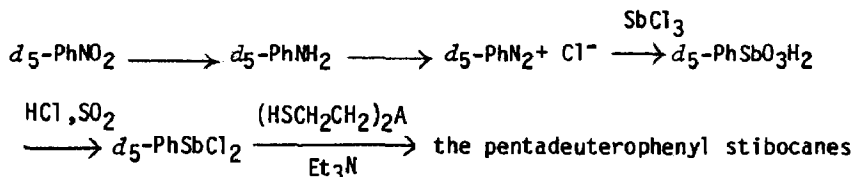$$4\ ArSbBr_2 + 4\ Mg \xrightarrow{\ THF\ } (ArSb)_4 + 4\ MgBr_2$$
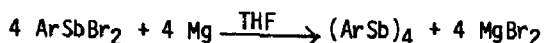
When the THF was removed by vacuum distillation and the residue treated with benzene or toluene, crystals of the composition $(ArSb)_4 \cdot PhH$ or $(ArSb)_4 \cdot PhMe$ were obtained. The PMR spectra of the various organoantimony compounds obtained in this investigation were reported and discussed. In most cases, mass spectra were also recorded.

A study has been reported of the IR and Raman spectra in the 3200-100cm^{-1} region of 5-phenyl-1-oxa-4,6-dithia-5-stibocane and 2-phenyl-1,3,6-trithia-2-stibocane [32]:
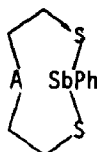

(where A was 0 or S)

The spectra of both compounds were very similar. Inclusion of the penta-deuterophenyl analogs in this study made it possible to identify signals originating from vibrations of the phenyl groups, of the aliphatic parts of the rings, and of the coordination polyhedra around the antimony atoms. These analogs were synthesized in five steps from nitrobenzene-d_5:

$$d_5\text{-PhNO}_2 \longrightarrow d_5\text{-PhNH}_2 \longrightarrow d_5\text{-PhN}_2^+\ Cl^- \xrightarrow{\ SbCl_3\ } d_5\text{-PhSbO}_3H_2$$

$$\xrightarrow{\ HCl,SO_2\ } d_5\text{-PhSbCl}_2 \xrightarrow[Et_3N]{(HSCH_2CH_2)_2A} \text{the pentadeuterophenyl stibocanes}$$

The vibrational spectra of a number of related tin, lead, and bismuth dithiolates were also described.

The addition of a chromium complex of phenyldiiodostibine to a THF solution of 18-crown-6 and potassium at -80°C has been found to yield an orange-red iodide complex [33]:

$$(CO)_5Cr(PhSbI_2) \xrightarrow[18\text{-crown-6}]{K} [K(18\text{-crown-6})][(PhSbI_2)_4I]$$
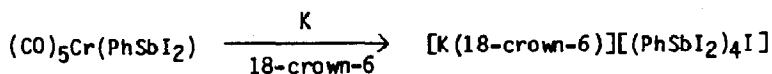
An X-ray structural analysis showed that the central iodide ion of the anion was coordinated to four phenyldiiodostibine molecules in a square-planar fashion:
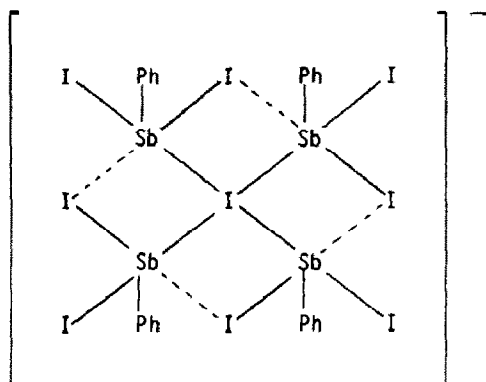

The SbI_2 parts of the ligands were arranged so as to give an almost planar matrix via unsymmetrical SbISb bridges. The phenyl groups of the centrosymmetric anion protruded from either side of this plane. It was concluded that the unconventional square-planar coordination of the iodide ion was partly due to lattice effects and was stabilized by four 2-electron donor ligands.

Diphenyl(8-quinolinethiolato)stibine has been prepared by the following metathetical reaction [34]:

$$Ph_2SbCl + NaSQ \xrightarrow{EtOH} Ph_2SbSQ + NaCl$$
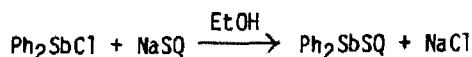
(where QSH was 8-mercaptoquinoline)

An X-ray diffraction study of this substance showed that the antimony atom was a member of a chelate ring:
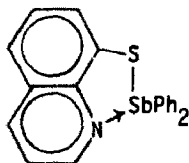
The Sb-N distance was significantly longer than the sum of the covalent radii of antimony and nitrogen, whereas the Sb-C and Sb-S bond lengths agreed fairly well with the corresponding sums of the covalent radii. Each molecule had a short Sb···Sb contact [2.884(1)Å] to a neighboring molecule. Since the van der Waals radius of antimony has been estimated to be about 2.09Å, the observed Sb···Sb distance indicated weak intermolecular interaction. If the antimony atom of the neighboring molecule was assumed to

form part of the coordination sphere of each antimony atom, then a distorted pyramid was present with one phenyl carbon in the apical position and with the basal plane containing a carbon atom from the other phenyl group plus the sulfur atom, the nitrogen atom, and the neighboring antimony atom. The stereochemically active $5s$ electron pair presumably occupied the position opposite the apical carbon atom. It was therefore possible to view the antimony as being in the center of a distorted octahedron. The interaction between the neighboring antimony atoms could be rationalized as a consequence of an overlapping of the lone pair of one antimony atom and an empty orbital of the other antimony atom and *vice versa* so that weak four-electron two-center bonding resulted.

Bis(ethanethioato)phenylstibine has been prepared by the following metathetical reaction [35]:

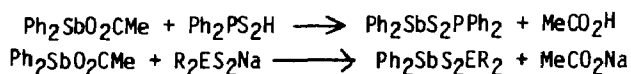$$PhSbCl_2 + 2\ KSAc \xrightarrow{\ EtOH\ } PhSb(SAc)_2 + 2\ KCl$$
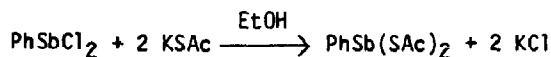
(where Ac was the acetyl group)

The compound was fully characterized by single crystal X-ray diffraction. The AcS groups were found to bond primarily via sulfur; the Sb-S distances were 2.451 and 2.471Å. Substantial Sb···O interactions, however, led to a bis-chelate structure. Isolated molecules were considered to have distorted square-pyramidal geometry in which the phenyl group was apical. The sulfur atom with the longer bond to antimony also formed a weak intermolecular Sb···S contact (3.802Å) *trans* to the phenyl group, and hence dimers were present in the solid state. The IR and mass spectra of the compound also provided evidence that the AcS groups were bonded primarily through sulfur rather than through oxygen. Attempts to prepare (ethanethioato)-diphenylstibine from diphenylchlorostibine led to disproportionation:

$$2\ Ph_2SbCl + 2\ KSAc \longrightarrow PhSb(SAc)_2 + Ph_3Sb + 2\ KCl$$
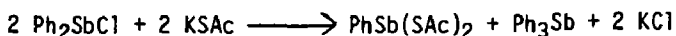
The apparent instability of the desired substance was surprising in view of the ease of preparation of the acetato compound Ph_2SbOAc. The diacetato compound $PhSb(OAc)_2$ could not, however, be obtained either by the interaction of phenyldichlorostibine and sodium acetate or from stibosobenzene, (PhSbO), and acetic anhydride. In both cases, only acetatodiphenylstibine was isolated. Possible reasons for the instability of Ph_2SbSAc and $PhSb(OAc)_2$ were considered.

Dithiophosphinate and dithioarsinate derivatives of antimony(III) have been prepared from diphenylacetatostibine and either the free acid or the sodium salt of the appropriate dithiophosphinic or dithioarsinic acid [36]:

$$Ph_2SbO_2CMe + Ph_2PS_2H \longrightarrow Ph_2SbS_2PPh_2 + MeCO_2H$$

$$Ph_2SbO_2CMe + R_2ES_2Na \longrightarrow Ph_2SbS_2ER_2 + MeCO_2Na$$

(where E was P and R was Me,Et, or Pr; or where
E was As and R was Me or Ph)

The six products thus obtained could be recrystallized without decomposition and were characterized by elemental analysis and by IR and PMR spectroscopy. X-ray structures were determined for the two compounds of the type $Ph_2SbS_2EPh_2$. These substances were found to be isostructural. The dithiophosphinate and dithioarsinate ligands were basically unidentate, and the geometry about each antimony atom could be considered pyramidal with angles ranging from 92.5 to 94.4°. The C-Sb and Sb-S distances were similar to other reported values. The two E-S distances in each molecule corresponded to the values expected for a single and a double bond. Each antimony atom in both compounds, however, exhibited longer contacts to two additional sulfur atoms; these contacts were significantly shorter than the sum of the antimony and sulfur van der Waals radii. One of these contacts was intermolecular and led to dimerization and the formation of eight-membered $Sb_2S_4E_2$ rings; the other contact was an intramolecular (trans-annular) interaction between an antimony atom and the double-bonded sulfur:
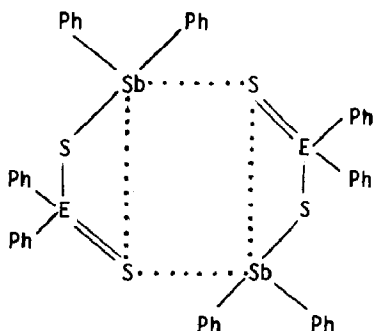
The presence of these weak Sb··S interactions made it possible to consider the sulfur and antimony atoms as being effectively three- and five- coordinate, respectively. The geometry about the antimony atom would then be described as distorted square-pyramidal. The basal atoms of the pyramid would be the three sulfur atoms (to which each antimony atom was linked) and one of the carbon atoms bonded to the antimony. The other carbon atom bonded to the antimony would occupy the apical position. It was also concluded that the lone pair of electrons on the antimony was *not* sterically active.

The structural investigation summarized in the above paragraph has been extended to a diphenylphosphinate and a diphenylmonothiophosphinate

derivative of trivalent antimony [37]. The two compounds were prepared by the interaction of diphenylacetatostibine and the appropriate acid:

$$Ph_2SbO_2CMe + Ph_2P(X)OH \longrightarrow Ph_2SbO(X)PPh_2 + MeCO_2H$$

(where X was O or S)

The thiophosphinate derivative was also obtained from the ammonium salt of diphenylthiophosphinic acid:

$$Ph_2SbO_2CMe + Ph_2P(S)ONH_4 \longrightarrow Ph_2SbO(S)PPh_2 + MeCO_2NH_4$$

Both compounds were white solids, which were recrystallized from acetonitrile. The thiophosphinate was sensitive to moisture; if the compound was stored in contact with the atmosphere, the sulfur was slowly replaced by oxygen. The IR spectra of both compounds suggested that the phosphinate and thiophosphinate ligands were behaving as either chelate or bridging groups. X-ray crystallography showed that the two substances had a polymeric structure in which diphenylantimony(III) groups were linked into chains by bridging phosphinate or thiophosphinate ligands. The coordination around the antimony could be considered trigonal-bipyramidal with the two bonding phenyl groups and the lone pair in equatorial positions (and the oxygen and sulfur atoms of the ligands in axial positions). An alternative approach was discussed that did not require stereochemical activity for the antimony $5s$ electrons.

Esters (mixed anhydrides) of carboxylic acids and appropriate thiohydroxamic acids have been found to react with tris(phenylthio)stibine at room temperature to give high yields of nor-alcohols [38-40]:
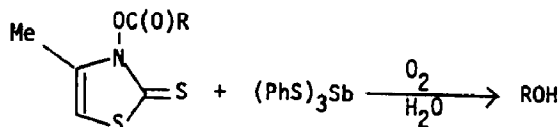

(where R was primary, secondary, or tertiary)

The reaction appeared to follow a simple radical chain mechanism in which a carbon radical attacked the stibine and formed an oxygen-sensitive organoantimony compound:

$$R\cdot + (PhS)_3Sb \longrightarrow RSb(SPh)_2$$

References p. 56

Aerial oxidation and subsequent hydrolysis of the oxidized substance pre-
sumably produced the nor-alcohol and antimony(III) oxide, which was recov-
ered almost quantitatively from the reaction mixture.

Certain heteroelement-substituted ethenes have been found to undergo
1,3-cycloaddition reactions with 1,3-diphenyl-2-azaallyllithium [41]:

$$Li[PhCH\overset{..}{=}N\overset{..}{=}CHPh] \xrightarrow[\text{2) H}_2\text{O}]{\text{1) CH}_2\text{=CHG}}$$
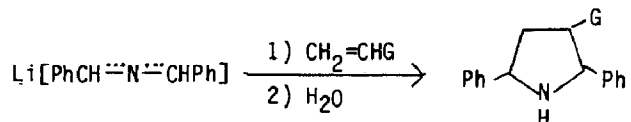
[where G was PhS, PhSe, Ph_2P, Ph_2As, Ph_3Si, Ph_3Ge, $Ph_2P(O)$, or $Ph_2As(O)$]

In contrast, no cycloaddition was observed between the azaallyllithium
compound and either ethenyldiphenylstibine or any other compound studied in
which the heteroelement belonged to the fifth or sixth period of the perio-
dic table. The tendency of these elements to undergo exchange reactions
with lithium might have been involved in the failure of these cycloaddition
reactions to occur.

The addition of freshly generated solutions of iodine azide or iodine
isocyanate to triarylstibines has been found to give good yields of stable,
crystalline triarylantimony(V) compounds [42]:

$$Ar_3Sb + IX \xrightarrow[\text{-10}^\circ\text{C}]{CCl_4} Ar_3SbIX$$
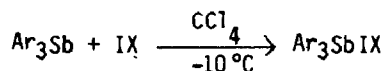
(where Ar was Ph, $4\text{-MeC}_6\text{H}_4$, $4\text{-ClC}_6\text{H}_4$, or $4\text{-FC}_6\text{H}_4$ and X was N_3 or NCO)

No traces of aryl halides or diarylpseudohalostibines were detected in any
of the reaction mixtures. Tetrazole derivatives were obtained by the
interaction of tri-4-tolylantimony iodide azide and phenyl isocyanate or
isothiocyanate:

$$Ar_3SbIN_3 + PhN=C=Y \xrightarrow{110^\circ C} Ar_3Sb(I)-N\underset{N}{\overset{Y=C-N-Ph}{\diagdown\diagup}}N$$
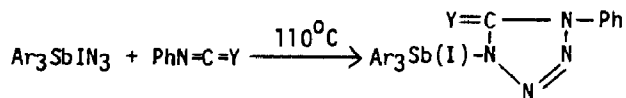
(where Ar was $4\text{-MeC}_6\text{H}_4$ and Y was O or S)

No reaction was observed when the triarylantimony iodide pseudohalides were
treated with either silver thiocyanate or isocyanate, or when tri-4-tolyl-
antimony iodide azide was refluxed with an excess of carbon disulfide for
8h. The structure of the tetrazoles was confirmed by a study of their IR
and UV spectra. The molar conductance of the other antimony(V) compounds
(in $10^{-3}M$ acetonitrile solutions) ranged from 8.56 to 11.24 ohm^{-1} mol^{-1} cm^2,
values that indicated that the substances were non-electrolytes. Their
monomeric nature was established by cryoscopic molecular weight determina-

tions in benzene. The IR spectra of the compounds in the solid state exhibited absorptions characteristic of the aryl groups and of covalently bonded N=C=O or N=N=N groups. The PMR spectrum of tri-4-tolylantimony iodide azide contained two doublets centered at δ 7.98 and δ 7.27 ppm (assigned to the 12 aromatic protons) and a singlet at δ 2.37 ppm (assigned to the 9 methyl protons). It was concluded that the antimony(V) compounds had trigonal-bipyramidal structures in which the aryl groups occupied the equatorial positions.

The use of iodine pentafluoride for the oxidative difluorination of trivalent derivatives of arsenic, antimony, and bismuth has been investigated [43]. Tributylstibine and four triarylstibines were found to give good yields of the corresponding difluorides at -35 to 0°C:

$$5 \ R_3Sb + 2 \ IF_5 \xrightarrow{\text{MeCN}} 5 \ R_3SbF_2 + I_2$$
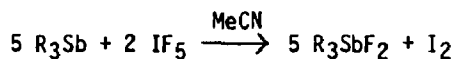
(where R was Bu, Ph, C_6F_5, p-FC_6H_4, or p-$CF_3C_6H_4$)

They were purified by distillation, sublimation, or recrystallization. The triarylantimony difluorides were characterized by IR, Raman, ^{13}C NMR, ^{19}F NMR, and mass spectrometry. Spectral information for tributylantimony difluoride (a previously described compound) was not reported in this paper. Treatment of diphenylchlorostibine with iodine pentafluoride at -78°C gave a 21% yield of diphenylantimony trifluoride:

$$10 \ Ph_2SbCl + 6 \ IF_5 \xrightarrow{CH_2Cl_2} 10 \ Ph_2SbF_3 + 3 \ I_2 + 5 \ Cl_2$$
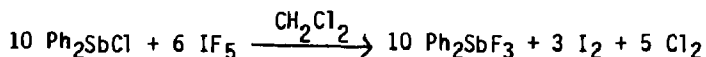
Some C-Sb bond cleavage accompanied this reaction, and the trifluoride was not obtained analytically pure. It was identified by mass spectrometry, which exhibited the molecular ion and typical fragmentation peaks. The interaction of phenyldichlorostibine and iodine pentafluoride at 0°C gave no identifiable organoantimony compound. It was suggested that this reaction initially yielded phenyldifluorostibine:

$$5 \ PhSbCl_2 + 2 \ IF_5 \xrightarrow{CH_2Cl_2} 5 \ PhSbF_2 + I_2 + 5 \ Cl_2$$
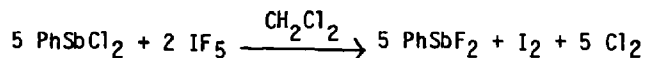
This substance apparently reacted further with iodine pentafluoride to give antimony trifluoride and iodobenzene. It was also reported that the ^{19}F NMR spectrum of the reaction mixture showed the presence of a small amount of an antimony(V)-fluorine derivative.

Triphenylstibine has been used as a reducing agent in the following reaction [44]:
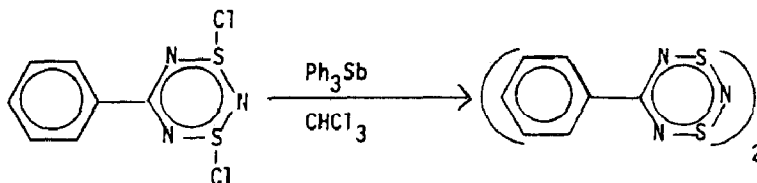
Triphenylantimony dichloride was presumably also formed, but it apparently was not identified. The crystal and molecular structure of the dimeric product was determined by single-crystal X-ray diffraction. It was found to consist of a cofacial arrangement of two 5-phenyl-1,3,2,4,6-dithiatriazine units linked by two long (2.527Å) S·····S interactions.

The oxidation of a variety of organic derivatives of trivalent phosphorus, arsenic, and antimony at a platinum anode has been studied by a number of electrochemical methods [45]. Seven tertiary stibines were included in this investigation. It was proposed on the basis of the results obtained that the electrochemical oxidation of all the compounds studied proceeded via the formation of radical cations, which then underwent fast reactions with nucleophilic components of the solutions.

A simple, rapid, and sensitive iodometric method has been described for the micro or submicro determination of triphenylphosphine, -arsine, or -stibine [46]. The method involved oxidation of the sample with an excess of periodate in buffered acidic or alkaline media. The oxidations appeared to obey the following type of equation:

$$Ph_3E + KIO_4 \longrightarrow Ph_3EO + KIO_3$$

(where E was P, As, or Sb)

Triphenylstibine oxide, mp 295°C, was in fact obtained by the interaction of triphenylstibine and potassium periodate in alkaline solution. It appeared to be identical (mp, mixed mp, and TLC) to an authentic sample of the oxide, the synthesis of which was not described.

A study of the microdetermination of carbon and hydrogen in organoantimony compounds has been reported [47]. It was found that the presence of halogens in these substances caused serious errors when the usual combustion methods were employed. When a 2-cm plug of quartz wool or polyurethane foam was placed in the cool beak-end of the combustion tube, however, excellent results were obtained even when the organoantimony compounds contained nitrogen and/or halogens.

An organoantimony compound believed to be a dipolar ion has been obtained by the thermal decomposition of a bismuth(V) derivative in the presence of triphenylstibine [48]:
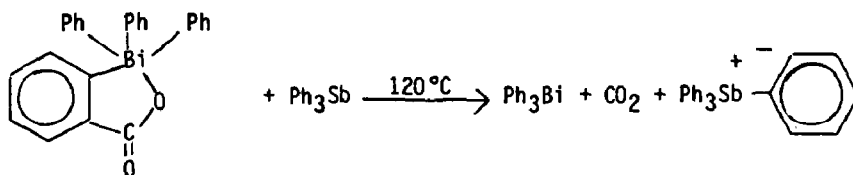
The same substance was produced by the interaction of triphenylstibine and diazotized anthranilic acid. It was suggested that benzyne was an intermediate in both cases. Treatment of the product with hydrochloric acid resulted in the formation of tetraphenylantimony chloride. When the putative betaine was heated with the above bismuth(V) compound at 120°C, a heterocyclic derivative of antimony was obtained. One of the C–Sb bonds in this substance was cleaved by treatment with hydrochloric acid:
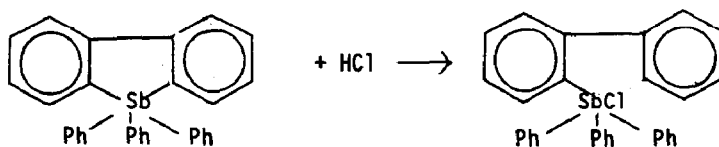
Bis(hexafluoroacetylacetonato)copper(II) has been found to be an efficient homogeneous catalyst for the conversion of certain diazo compounds to stibonium ylides by the following types of reactions [49]:
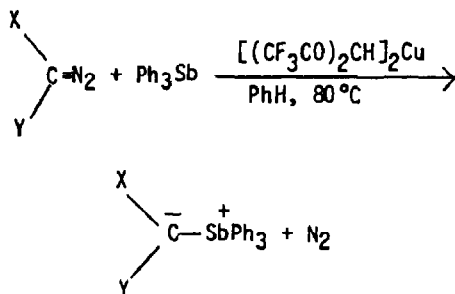
[where X and Y were $PhSO_2$, $4\text{-}MeC_6H_4SO_2$, or $MeC(O)$; or where X was $MeC(O)$ and Y was $PhC(O)$]
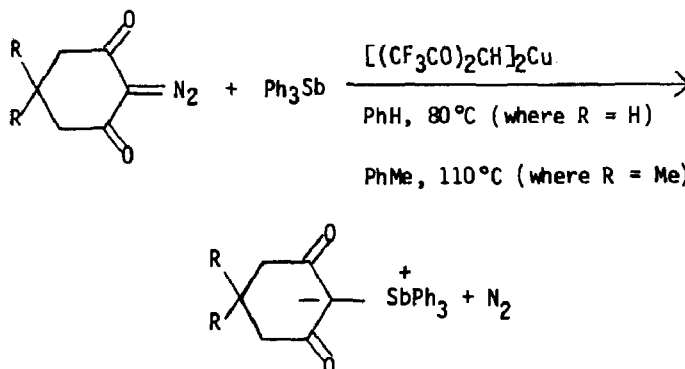
The copper compound also catalyzed the conversion of triphenylstibine and diazotetraphenylcyclopentadiene to the previously reported triphenylstibonium tetraphenylcyclopentadienylide. Diazomalonic esters, ethyl diazoacetoacetate, diazoacetophenone, and ethyl diazoacetate did not, however, yield stibonium ylides u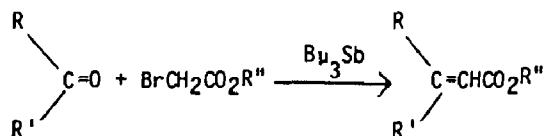nder the conditions used in the present investigation. It was concluded that stibonium ylides were formed only if the substituents on the diazo compounds were more electron-withdrawing than ester groups. The catalyst was thought to serve as a template in which the reactants were coordinated at cis sites in a six-coordinate intermediate. Ylide formation was also catalyzed by bis(acetylacetonato)copper(II), but this compound was much less effective. No catalysis at all was provided by the rhodium(II) acetate dimer in which the two coordination sites were apparently too far apart. The interaction of the dimer and triphenylstibine yielded red solutions that presumably contained the adduct $Rh_2(O_2CMe)_2(SbPh_3)_2$. The new stibonium ylides prepared in this study were colorless (or nearly so) and appeared to be indefinitely stable in a dry atmosphere. They were fairly basic and were protonated by trifluoroacetic acid. In protic solvents they were slowly cleaved to give triphenylstibine oxide and the corresponding methylene compound, $e.g.$:

$$(PhSO_2)_2\overset{-}{C}\text{-}\overset{+}{S}bPh_3 + H_2O \longrightarrow (PhSO_2)_2CH_2 + Ph_3SbO$$

The structures of the ylides were confirmed by elemental analysis, by mass, IR, and PMR spectra, and in the case of $(PhSO_2)_2\overset{-}{C}\text{-}\overset{+}{S}bPh_3$ by X-ray crystallography. Like their arsonium analogues, the ylides did not appear to take part in Wittig reactions, even with reactive aldehydes such as 2,4-dinitrobenzaldehyde.

Tributylstibine has been used to mediate the olefination of eight aldehydes and three ketones with esters of bromoacetic acid [50]:

$$\begin{array}{c} R \\ \diagdown \\ C=O \\ \diagup \\ R' \end{array} + BrCH_2CO_2R'' \xrightarrow{\ Bu_3Sb\ } \begin{array}{c} R \\ \diagdown \\ C=CHCO_2R'' \\ \diagup \\ R' \end{array}$$

(where R was an alkyl, aryl, or vinylic group, R' was H or alkyl, and R" was Me or Et)

The convenient one-pot process was carried out without the use of any added base, and the products were exclusively in the E form. No solvent was required, and the yields were not significantly affected by the presence of solvents such as hexane, benzene, THF, or acetonitrile. Bromoacetophenone, bromomalonic ester, and chloroacetonitrile were also used for the olefination of carbonyl compounds, but details of these reactions have not yet been published.

Trimethyl phosphite, triphenylarsine, and triphenylstibine have been shown to add to the benzylidene carbon of certain tungsten complexes and thereby to form new phosphorus, arsenic, and antimony ylide complexes [51]:

$$(CO)_5W=C\begin{array}{c}Ar\\ \\H\end{array} + R_3E \quad \rightleftharpoons \quad (CO)_5\overset{-}{W}-\overset{\overset{+}{E}R_3}{\underset{H}{C}}-Ar$$
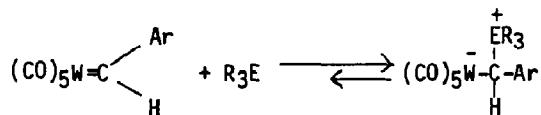
(where Ar was Ph or 4-MeC$_6$H$_4$ and R$_3$E was (MeO)$_3$P, Ph$_3$As, or Ph$_3$Sb)

The complexes thus obtained were yellow solids, which were moderately soluble in polar solvents but insoluble in non-polar solvents. They were quite stable in the solid state at room temperature and only slightly sensitive to air. On exposure to light, however, the antimony complex quickly became dark brown. All three new compounds were characterized by elemental analysis and by IR, PMR, and mass spectrometry.

The proton affinities (*i.e.* basicities) of triphenylamine, -phosphine, -arsine, and -stibine have been determined in the gas phase [52]. A bracketing technique was used in which the reactant ions were monitored by a combination of gas chromatography and chemical ionization mass spectrometry (GC/CIMS). The proton affinities of the four triphenyl compounds were shown to be in the order Ph$_3$N < Ph$_3$P > Ph$_3$As > Ph$_3$Sb. Triphenylstibine was found to have a proton affinity of 846± 8 kJ mol^{-1}.

The cone angle (a steric characteristic expressing the degree of filling out by the ligand of the coordination sphere of a transition metal) has been calculated for 610 ligands [53]. Among the ligands studied were a number of tertiary amines, phosphines, arsines, stibines, and bismuthines. As the atomic number of the ligand atom in a group increased, the cone angle was found to decrease. For neighboring elements of Group IVA and VA, however, the cone angles were equal or nearly so.

Tantalum(V) chloride has been found to catalyze the polymerization of 1-(trimethylsilyl)-1-propyne, MeC CSiMe$_3$ [54], and 4,4,7,7-tetramethyl-4,7-disila-2-octyne, MeC CSiMe$_2$CH$_2$CH$_2$SiMe$_3$ [55]. When certain cocatalysts (*e.g.* triethylsilane, tetrabutyltin, triphenylstibine, or triphenyl-bismuthine) were added in a 1:1 ratio to the tantalum compound, the molecular weights of the polymers obtained were considerably higher. Thus, when triphenylstibine was the cocatalyst, the weight-average molecular weight increased from 8.4 x 10^5 to 3.6 x 10^6 for poly[1-(trimethylsilyl)-1-propyne] and from 1.5 x 10^5 to 3.2 x 10^5 for poly(4,4,7,7-tetramethyl-4,7-disila-2-octyne).

Triaryl derivatives of phosphorus, arsenic, and antimony have been employed in an investigation of the effects of photographic supersensitizers on the polarographic reduction of oxygen in aqueous alcohol solutions [56]. Tributylstibine has been included in a study of the effect of polar

organic compounds on an oxidized iron surface in relation to the hard-soft acid-base [HSAB] principle [57].

Trimethylstibine has been used as the antimony source for the production of thin alloy films of indium, arsenic, and antimony [58], gallium, aluminum, and antimony [59], gallium, indium, and antimony [59], and gallium, indium, arsenic, and antimony [60]. Antimony-doped n-type films of lead, tin, and tellurium have been produced by incorporating trimethyl-stibine into the reactant mixtures employed in the pyrolytic process known as metalorganic chemical vapor deposition [61]. Triarylstibines have been employed as ingredients of charge-providing materials used for electrostatic image development [62,63], as hardening accelerators in the preparation of transparent fire-resistant resins [64], and in the manufacture of epoxy resin acrylates [65].

There have been a number of recent articles that mentioned the use of tertiary stibines as ligands in transition metal complexes. The metals coordinated to the antimony in these complexes included chromium [66], cobalt [67], copper [68,69], gold [70,71], iridium [72], iron [67,73,74], manganese [75], molybdenum [66,76-83], nickel [84,85], osmium [86], palladium [87-93], platinum [94], rhodium [95,96], ruthenium [74,97-99], and tungsten [66,79-83]. No reaction was observed between triphenylphosphine, -arsine, or -stibine and the platinum(II) complex [Pt(mal)(dppe)], where mal was the malonate ion and dppe was 1,2-ethanediylbis(diphenylphosphine) [100].

An Indian patent has described the preparation of the drug urea stibamine for the treatment of kala-azar [101]. It was prepared by washing p-MeCONHC$_6$H$_4$SbO$_3$H$_2$ with aqueous Na$_2$CO$_3$, and then treating the purified acid with urea.

Akiba and coworkers [102] have found that Ph$_3$SbBr$_2$ and Me$_3$SbCl$_2$ were excellent oxidizing agents for the conversion of α-hydroxyketones to the corresponding dicarbonyl compounds. The oxidations were carried out in the presence of two equivalents of a base, Et$_3$N or DBU. The solvents employed were CH$_2$Cl$_2$ or CDCl$_3$, and although the reaction times were long (up to 2 days), the yields were excellent. The α-hydroxyketones oxidized by this procedure were of the type RCHOHCOR', where R = R'= Ph, 4-MeC$_6$H$_4$, 2-furyl, or 2-thienyl, R = Ph, R' = 2-furyl, Me, or OEt, R = Me, R' = Et. In one case (R = R'= 4-MeC$_6$H$_4$), the Sb compound used was Me$_3$SbCl$_2$, the yield of 4-MeC$_6$H$_4$COCOC$_6$H$_4$Me-4 was 89%, and the reaction was carried out for 19 hours. The Me$_3$Sb formed in the reaction was not isolated. In all other cases the oxidizing agent was Ph$_3$SbBr$_2$, and the resulting Ph$_3$Sb was recovered in yields up to 84%. Since Ph$_3$Sb is readily oxidized to Ph$_3$SbBr$_2$ by either Br$_2$ or a bromine donor, the authors tried the oxidation with catalytic amounts of either Ph$_3$Sb or Ph$_3$SbBr$_2$ with the addition of one equivalent of the bromine donor, ethyl 2,3-dibromo-3-phenylpropionate. With

4-MeC$_6$H$_4$CHOHCOC$_6$H$_4$Me-4, but using only catalytic amounts of Ph$_3$SbBr$_2$, a 97% yield of (4-MeC$_6$H$_4$CO)$_2$ was obtained with this procedure. The base employed was 2,6-lutidine (2 equivalents). Similar results were found with catalytic amounts of Ph$_3$Sb. In this case the reaction rate was found to increase with increasing amounts of Ph$_3$Sb (from 0.1 to 0.5 equivalent). The authors suggested two different reaction pathways to account for their results.

In the previous paper it was shown that organoantimony(V) compounds, Ph$_3$SbBr$_2$ or Me$_3$SbCl$_2$, were efficient oxidizing agents for converting α-hydroxyketones to the corresponding diketones. In a somewhat similar reaction, Huang and coworkers [103] found that Ph$_3$Sb(OAc)$_2$ oxidized benzoin to benzil in high yield under mild conditions. However, neither Ph$_3$Sb(OAc)$_2$ nor other organoantimony(V) compounds (Ph$_3$SbBr$_2$, Ph$_2$SbBr$_3$, and Ph$_3$SbS) would oxidize benzyl alcohol in the presence of a base. The authors did find, however, that benzyloxy(diphenyl)stibine was readily converted to benzaldehyde on the addition of bromine:

$$Ph_2SbOCH_2Ph + 2 Br_2 \longrightarrow PhCHO + Ph_2SbBr_3 + HBr$$
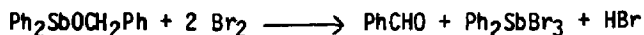
It was also found that the starting compound Ph$_2$SbOCH$_2$Ph was readily prepared from bromodiphenylstibine and benzyl alcohol:

$$Ph_2SbBr + PhCH_2OH \xrightarrow{\text{Et}_2NH} Ph_2SbOCH_2Ph + Et_2NH_2Br$$
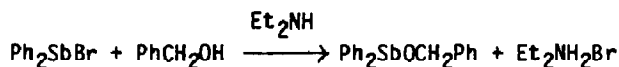
It was then found possible to combine the two reactions, *i.e.* to add bromine after formation of the stibine, to obtain the aldehyde. In this manner, the authors prepared a series of substituted benzaldehydes, XC$_6$H$_4$CHO (where X was H, 4-F, 4-Cl, 4-Br, 4-MeO, 4-NO$_2$, 4-Me, 2-Me, or 3-Me). The yields varied from 40% (X = 4-NO$_2$) to 86% (X = 3-Me). With 1-phenylethanol, however, only a 28% yield of acetophenone was obtained. The reaction conditions employed were extremely mild. The benzyl alcohol (2 equivalents), bromodiphenylstibine (2.8 equivalents), and diethylamine were stirred together in benzene for 2 hours, after which bromine (5 equivalents) in benzene was added at 5-10°C and the mixture stirred a further 10 minutes. After removal of the precipitated amine salt, the benzene was evaporated and the product purified by distillation. The authors suggested a mechanism for the reaction.

Raj and coworkers [104] have prepared a number of organoantimony(V) compounds of the types R$_3$Sb(SeCN)$_2$, R$_4$Sb(SeCN), and (R$_3$SbOSbR$_3$)(SeCN)$_2$, where R was Me, Ph, or a substituted aryl group. Compounds of the type R$_3$Sb(SeCN)$_2$ were obtained from the corresponding dichloride or dibromide by metathasis with KSeCN in the presence of the phase transfer catalyst 18-crown-6:

$$R_3SbX_2 + 2 \ KSeCN \xrightarrow[\text{PhH}]{\text{18-crown-6}} R_3Sb(SeCN)_2 + 2 \ KX$$
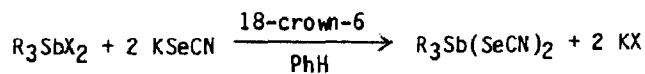
(where X was Cl or Br, and

R was Me, Ph, C_6F_5, p-MeC_6H_4, p-ClC_6H_4, or p-FC_6H_4)

Two compounds, $Ph_4SbSeCN$ and $Ph_3(CH_2=CHCH_2)SbSeCN$, were obtained in a similar manner from Ph_4SbX or $Ph_3(CH_2=CHCH_2)SbX$ and KSeCN. Four compounds of the type $(R_3SbOSbR_3)(SeCN)_2$, where R was Ph, p-MeC_6H_4, p-ClC_6H_4, or p-FC_6H_4, were obtained from the halides $(R_3SbOSbR_3)X_2$ and KSeCN. All of these metathetical reactions were carried out in the presence of 18-crown-6. In the absence of this catalyst, the yields of the selenocyanates were considerably lower. The compound $Ph_3(CH_2=CHCH_2)SbBr$, which had not been previously described, was prepared from triphenylantimony dibromide and allylmagnesium bromide and was characterized by elemental analysis. All of the new organoantimony(V) selenocyanates were characterized by elemental analyses and by their IR spectra. NMR results were reported only for $(p$-$MeC_6H_4)_3Sb(SeCN)_2$. On the basis of molecular weight determinations cryoscopically in benzene (results not reported), it was stated that all of the compounds were monomolecular. Molar conductances of representative compounds in nitrobenzene or acetonitrile showed that they were non-electrolytes in these solvents. On the basis of their IR spectra, it was concluded that they possessed the iso-structure, $i.e.$, $Ph_{5-n}Sb(N=C=Se)_n$. All of the new selenocyanates were moisture sensitive and slowly decomposed on storage. They were either white or colored, possessed repulsive odors, and caused headaches on exposure. Representative compounds were found to possess significant bactericidal and fungicidal activities.

The preparation of a number of trimethyl- and triphenylantimony disulfonates, as well as a number of triphenylbismuth disulfonates, has been described by Rüther and coworkers [105]. The compounds were of the type $R_3Sb(O_3SR')_2$, where R was Me and R' was Me, CF_3, CH_2CH_2OH, Ph, or 4-MeC_6H_4, and where R was Ph and R' was Me, CH_2CH_2OH, Ph, 4-MeC_6H_4, or $2,4$-$(NO_2)_2C_6H_3$. With the exception of $Me_3Sb(O_3SCH_2CH_2OH)_2$, which was obtained only as an oil, all of the compounds were crystalline solids. Most of the compounds were prepared from $Me_3Sb(OH)_2$ or $(Ph_3SbO)_2$ and the corresponding sulfonic acid. The reactions were carried out in a mixture of acetone and 2,2-dimethoxypropane. The triphenylantimony compounds separated from solution in crystalline form, whereas the trimethylantimony compounds separated only after the addition of diethyl ether. The triphenylstibine oxide was prepared by the oxidation of triphenylstibine with hydrogen peroxide in acetone solution. The compound $Me_3Sb(O_3SCF_3)_2 \cdot 2H_2O$ was obtained from $Me_3Sb(OH)_2$ and CF_3SO_3H without the use of a solvent. For two of the compounds, benzene was used as the solvent and $HO_3SCH_2CH_2OH$ was added in methanol solution. For the compound $Ph_3Sb[O_3SC_6H_3(NO_2)_2$-$2,4]_2$, water formed in the reaction was removed by azeotropic distillation with benzene.
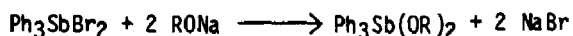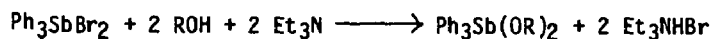
The reaction between $(Ph_3SbO)_2$ and CF_3SO_3H gave $(Ph_3SbO_3SCF_3)_2O$ as the only product. The trimethyl- and triphenylantimony disulfonates were generally soluble in $CHCl_3$, MeOH, and EtOH. The trimethyl compounds dissolved in water but were converted to oxy compounds of the type $(Me_3SbO_3SR)_2O \cdot 2H_2O$. Several of the compounds were hygroscopic, and $Me_3Sb(O_3SCF_3)_2 \cdot 2H_2O$ could be handled only in a nitrogen atmosphere. Most of the compounds were mono-molecular in $CHCl_3$ solution, but the two compounds $Me_3Sb(O_3SPh)_2$ and $Ph_3Sb(O_3SPh)_2$ were completely dissociated in methanol solution. Two of the compounds, $Me_3Sb(O_3SCF_3)_2 \cdot 2H_2O$ and $Me_3Sb(O_3SCH_2CH_2OH)_2$ were not suffic-iently soluble for molecular weight determinations. However, on the basis of their IR spectra, it was concluded that these two compounds were ionic. The structure $[Me_3Sb(OH_2)_2][O_3SCF_3]_2$ was suggested for one of these com-pounds. By contrast, the IR and Raman spectra of the other compounds were interpreted in terms of a pentacovalent antimony, *i.e.* a trigonal bipyramid with unidentate axial sulfonato groups. The benzene sulfonates reacted with ethanolic HCl with cleavange of the Sb-O bonds:

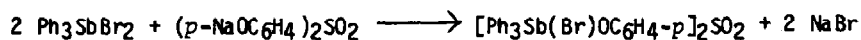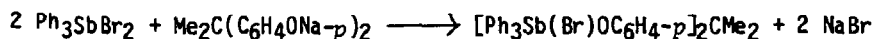$$R_3Sb(O_3SPh)_2 + 2\ Cl^- \longrightarrow R_3SbCl_2 + 2\ PhSO_3^-$$

The compound $Me_3Sb(O_3SPh)_2$ reacted with aqueous NaCl in a similar manner to give Me_3SbCl_2.

The crystal structure of the one of the compounds, $Ph_3Sb(O_3SPh)_2$, was determined by X-ray diffraction. The molecular structure was that of a trigonal bipyramid with two axial sulfonato groups and three equatorial phenyl groups. However, the equatorial angles were somewhat distorted and one of the contact distances between the Sb atom and a non-bonding oxygen atom was somewhat shortened. These results suggested a weak interaction between the Sb atom and a second oxygen atom.

Triphenylantimony(V) compounds of the type $Ph_3Sb(OR)_2$, where ROH was 2,4,6-tribromophenol, 2,4,6-trichlorophenol, or pentachlorophenol, have been prepared by Jha and coworkers [106]. They were obtained from tri-phenylantimony dibromide and either the phenol in the presence of Et_3N, or from the sodium salt of the phenol:

$$Ph_3SbBr_2 + 2\ ROH + 2\ Et_3N \longrightarrow Ph_3Sb(OR)_2 + 2\ Et_3NHBr$$

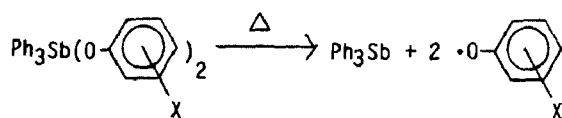$$Ph_3SbBr_2 + 2\ RONa \longrightarrow Ph_3Sb(OR)_2 + 2\ NaBr$$

In addition to the above compounds, two other compounds of a similar type were obtained as follows:

$$2\ Ph_3SbBr_2 + Me_2C(C_6H_4ONa\text{-}p)_2 \longrightarrow [Ph_3Sb(Br)OC_6H_4\text{-}p]_2CMe_2 + 2\ NaBr$$

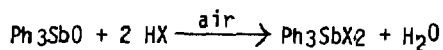$$2\ Ph_3SbBr_2 + (p\text{-}NaOC_6H_4)_2SO_2 \longrightarrow [Ph_3Sb(Br)OC_6H_4\text{-}p]_2SO_2 + 2\ NaBr$$
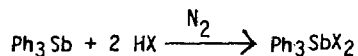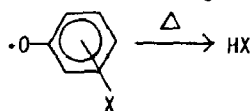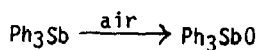
The compounds obtained in all cases were crystalline solids, stable to
moisture, and non-ionic as shown by conductances carried out in acetoni-
trile. Molecular weight determinations in benzene showed that they were
monomeric. They were characterized by elemental analyses, PMR, and IR
spectroscopy. It was concluded on the basis of the spectral results that
the configuration around each Sb atom was that of a trigonal bipyramid with
axial Sb-O bonds.

Because some organoantimony(V) compounds have shown promise as flame
retardents for organic polymers, the authors studied the thermal behavior
of their new compounds by means of thermogravimetric analysis, both in air
and in a nitrogen atmosphere. It was found that the thermal decomposition
proceeded in two steps. The maximum decomposition temperature of the first
step was structure sensitive, whereas that of the second slow step was the
same for all of the compounds. It was also found that the energy of
activation, calculated from the kinetics of the thermal decomposition, was
different for the first step of the reaction for each compound. On the
basis of these results the authors suggested a mechanism for the first step
of the thermal decomposition:

$$Ph_3Sb(O\text{—}C_6H_4\text{—}X)_2 \xrightarrow{\Delta} Ph_3Sb + 2 \cdot O\text{—}C_6H_4\text{—}X$$

(where X = Cl or Br)

$$Ph_3Sb \xrightarrow{air} Ph_3SbO$$

$$\cdot O\text{—}C_6H_4\text{—}X \xrightarrow{\Delta} HX$$

$$Ph_3Sb + 2 HX \xrightarrow{N_2} Ph_3SbX_2$$

$$Ph_3SbO + 2 HX \xrightarrow{air} Ph_3SbX_2 + H_2O$$

It was further suggested that unreacted Ph_3Sb or Ph_3SbO underwent thermal
decomposition in the second step of the reaction to give antimony metal (in
nitrogen) or Sb_2O_3 (in air).

When Me_3SbCl_2 and $SbCl_3$ in equimolar amounts are mixed in dichloro-
methane and the solution cooled, the complex $Me_3SbCl_2 \cdot SbCl_3$ crystallizes
from solution. The structure of this complex has previously been deter-
mined by X-ray diffraction [107]. It consisted of a chain structure with
the two apical chlorine atoms of the Me_3SbCl_2 serving as chlorine bridges

to the Sb atoms of $SbCl_3$. These chains are further cross-linked by one-half of the bridging chlorine atoms. The crystal thus contained three types of chlorine atoms, terminal chlorines on $SbCl_3$ and two types of bridging chlorine atoms. The ratio of the three types of chlorine atoms was therefore 3:1:1. There were also two types of antimony atoms in a ratio of 1:1. De Bock and coworkers [108] have now attempted to distinguish between these three different types of Cl and two different types of Sb atoms by means of ESCA and NQR spectroscopy. The ESCA spectra of the complex exhibited only a single Sb and a single Cl signal, and there was no substantial increase in the FWHM values for the complex as compared with those in Me_3SbCl_2 alone. The complexation shifts

$$\Delta E_c = E_b(\text{complex}) - E_b(Me_3SbCl_2)$$

(where E_b was the ESCA bonding energy and ΔE_c was the complexation shift)

were within the range of the average standard deviations.

The NQR spectra of the three compounds $SbCl_3$, Me_3SbCl_2, and $Me_3SbCl_2 \cdot SbCl_3$ were reported, and the complexation shifts

$$\Delta \nu = \nu(\text{complex}) - \nu(\text{starting compounds})$$

(where ν was the NQR frequency)

were calculated. The NQR spectra did not distinguish between the two types of bridging chlorine atoms, although the two types of Sb atoms and the bridging and terminal chlorine atoms were easily distinguished. The authors speculated on the electronic effects of the complexation as indicated by the complexation shifts in the NQR spectrum of the complex.

Yanaga and coworkers [109] have carried out Mössbauer, ^{13}C NMR, and ^{1}H NMR spectroscopic studies on a small series of organoantimony(V) halides, Me_3SbX_2 (X = F, Cl, Br, or I) and Ar_3SbX_2 (Ar = Ph or p-MeC_6H_4, and X = Cl, Br, or I). Isomer shifts, quadrupole coupling constants (e^2q_zQ), and halfline widths were reported as well as chemical shifts for the ^{1}H and ^{13}C atoms. It was found that the absolute value of the isomer shift decreased as the electronegativity of the halogen atom increased for all three types of organoantimony compounds (Me_3SbX_2, Ph_3SbX_2, and $(p$-$MeC_6H_4)_3SbX_2$) studied. Since the isomer shift is proportional to the electron density at the Sb atom, this trend showed that the s electron density decreased as the electronegativity of the halogen increased. The observed large positive electric field gradient eq_z meant that the p electron density along the X and Y axis was greater than along the Z axis. Thus, both the isomer shifts and the quadrupole coupling constants showed that the electron attraction by halogen increased as the electronegativity

difference between Sb and halogen increased. It was also noted that for the same halogen atom the absolute values of the isomer shifts were in the order $Me_3SbX_2 > (p-MeC_6H_4)_3SbX_2 > Ph_3SbX_2$.

The authors also compared the [121]Sb Mossbauer results with the ^{1}H and ^{13}C NMR data. For the methyl compounds both the ^{1}H and ^{13}C shifts occurred at higher fields with increasing electronegativity of the halogen. A plot of the Mössbauer isomer shift vs. the ^{1}H chemical shift showed a smooth decrease in isomer shift with a decrease in chemical shift. Similar results were obtained for the ^{13}C chemical shifts of the carbon atom attached to the Sb atom. The chemical shift values for the o- and p- carbon atoms, however, shifted to lower fields with increase in electro- negativity of the halogen, while the chemical shift values for the m-carbon atoms remained constant. All of the results thus suggested that the elec- tron cloud around the Sb atom spread along the X and Y axes with an increasing withdrawal of electron density from the Sb atom along the Z axis.

The use of Ph_3SbBr_2 and three compounds of the type $Ph_3Sb(OAr)_2$, where Ar was $2,4,6-Br_3C_6H_2$, $2,4,6-Cl_3C_6H_2$, or Cl_5C_6, as flame retarding agents for polypropylene has been investigated by Jha and coworkers [110]. Tri- phenylantimony dibromide was found to be a highly efficient flame retardent at low levels and was superior to the other three compounds tested. A mechanism for the action of Ph_3SbBr_2 as a flame retardent was suggested. This mechanism involved radical formation by pyrolytic cleavage:

$$Ph_3SbBr_2 \xrightarrow{\Delta} Ph_3Sb\overset{\bullet}{Br} + \overset{\bullet}{Br}$$
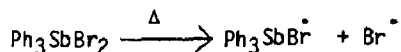
These radicals then served as quenching agents for the radicals formed by the pyrolysis of polypropylene. By contrast, the pyrolysis of the com- pounds of the type $Ph_3Sb(OAr)_2$ was believed to occur by cleavange of an Sb-O bond without the formation of radicals.

Another paper [111] from the same laboratory presented further techni- cal data on the same four organoantimony compounds as flame retardents for polypropylene.

Triphenylantimony dichloride was one of several organometallic com- pounds used as catalysts for the polymerization of ethylene carbonate [112]. Partial decarboxylation of the ethylene carbonate occurred during the polymerization, which was carried out at 150 °C.

Previous studies by electronic, PMR, and Mössbauer spectroscopy on the degree to which the nitrogen atom coordinates to the antimony atom in complexes of type I have given conflicting results. The problem has now

I
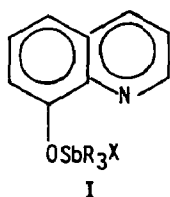
(where X was Cl, Br, or another 8-quinolinolato group)

been investigated by a combination of ^{15}N, ^{1}H, and ^{13}C NMR, and electron spectroscopy; the results were then compared with related tin quinolinolato complexes [113]. The antimony(V) compounds studied were R_3SbClQ, Me_3SbBrQ, Me_3SbQ_2, and Et_3SbQ_2, where R was Me, Et, or Ph and Q was the 8-quinolino-lato group. The last two compounds, which had not been previously des-cribed, were prepared from sodium 8-quinolinolate and R_3SbBr_2 (R = Me or Et), and were characterized by elemental analyses and by electronic and NMR spectroscopy. On the basis of the spectroscopic results and a comparison of these results with those for similar tin compounds, the following con-clusions were reached. The two compounds Me_3SbQ_2 and Et_3SbQ_2 contained largely 5-coordinate antimony in the solutions studied. With Ph_3SbQ_2, however, 6-coordination made a greater contribution to the structure of the compound. With the compounds R_3SbXQ (where X was Cl or Br), still more coordination between the nitrogen and the antimony atoms was present, particularly where R was Ph. Coordination, however, was less for any of the antimony(V) compounds than was the case for the tin compounds, R_3SnQ, R_2SnClQ, and R_2SnQ_2, all of which were largely chelated. The authors also considered the fluxionality of the compounds. The compound Me_3SbQ_2 gave only one signal for the methyl protons when the compound was cooled to 183 K in CH_2Cl_2 solution. This result was in agreement with previous studies on quinolinolato antimony(V) compounds.

A normal coordinate analysis, using a generalized valence force field, for the compounds $[Ph_3ECl][SbCl_6]$, where E was N, P, As, or Sb, has been performed by the method of Fadini [114]. All vibrations of $[Ph_3SbCl][SbCl_6]$ were found to be skeletal vibrations.

Although triphenylstibine oxide has been known for many years, its structure has been the subject of considerable controversy. It has been reported in crystalline form, mp 221-223 °C, and as an amorphous powder with a wide range of melting points. Furthermore, the crystalline form has been described both as a monomer in equilibrium with a more highly associated form and as a dimer. Bordner and coworkers [115] have now used X-ray diffraction to delineate the structure of the crystalline form. These studies showed clearly that this form of the compound was dimeric in the solid state. The antimony and oxygen atoms formed a four-membered planar ring. The Sb atoms were trigonal bipyrimidal with one equatorial and one axial oxygen atom, and with two equatorial and one axial phenyl group. The

IR spectrum and molecular weight data in solution were in accord with the dimeric structure for this compound in solution.

An amorphous form of triphenylstibine oxide had been reported by a number of investigators as formed by the oxidation of Ph_3Sb with hydrogen peroxide in acetone solution. In all such reports the product of the oxidation had been treated with benzene. In the only reported oxidation not using benzene, a peroxide-containing antimony compound of unknown structure had been obtained. Bordner and coworkers have now shown that an unstable triphenylantimony(V) compound in which a mole of acetone was incorporated into the molecule, was formed in the oxidation reaction. This compound possessed the following structure as shown by X-ray diffraction:
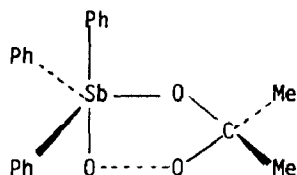

When this compound was treated with various organic solvents such as benzene, $CHCl_3$, CCl_4, or $CDCl_3$, a mole of acetone was lost and an amorphous form of triphenylstibine oxide was formed. The progressive loss of acetone could be readily seen in the PMR spectrum of the compound in $CDCl_3$ which initially showed methyl signals for both acetone and the peroxide-containing compound. In addition to this latter compound, a second oxidation product was obtained by the oxidation of Ph_3Sb with hydrogen peroxide in acetone solution. This crystalline material, m.p. 285-290°C, was obtained when the mother liquors from the oxidation reaction were allowed to stand for several weeks. This product proved to be identical (IR spectrum and mixed m.p.) with a compound previously prepared by McEwen and coworkers [116] by heating crystalline triphenylstibine oxide in xylene or dioxane with exclusion of oxygen. They believed this compound was the anhydride of diphenylstibinic acid, $Ph_2Sb(O)OSb(O)Ph_2$. Bordner and coworkers, however, determined the structure of this compound by X-ray diffraction and showed it to be a complex tricyclic compound with four antimony and six oxygen atoms in the rings.

It has been found that triphenylstibine oxide will oxidize thiols [117]. Furthermore, a mixture of triphenylstibine and triphenylstibine oxide catalyzed this oxidation under aerobic conditions.

Preut and coworkers [118] have noted that the Sb-O-Sb angle in compounds of the type $(R_3SbY)_2O$ may be either linear or bent, as shown by X-ray diffraction studies on several compounds of this type. Thus, the Sb-O-Sb angle in $(Ph_3SbN_3)_2O$ is bent, whereas in $(Ph_3SbO_3SCH_2CH_2OH)_2O$, the angle is linear. The authors have now prepared and determined the crystal struc-

tures of two new compounds, $(Ph_3SbO_3SPh)_2O$ and $(Ph_3SbO_3SCF_3)_2O$, by X-ray diffraction. In both of these compounds the configuration around the Sb atom was that of a distorted trigonal bipyramid; the Sb-O-Sb angle for the first compound was 139.8°, for the second compound 136.5°. There appeared to be no relationship between Sb-μ-O distances with the presence of bent or of linear Sb-O-Sb bridges. The authors suggested that the differences between the linear Sb-O-Sb angle (and also the Sb-O-S angle) in the compound $(Ph_3SbO_3SCH_2CH_2OH)_2O$ and the bent Sb-O-Sb angles in the two compounds described in the present paper were probably caused by crystal packing effects.

A number of complexes of the type $[C_5H_5Fe(CO)_2(R_3EY)][BF_4]$ (where C_5H_5 was cyclopentadienyl, R was Ph or an alkyl group, Y was S or Se, and E was P, As, or Sb) have been prepared by means of the following reaction [119]:
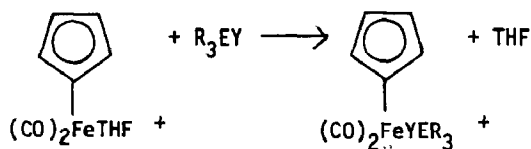
The antimony compounds prepared were those in which R was Me or Ph and Y was S, and where R was Ph and Y was Se. The compounds were characterized by elemental analyses as well as by ^1H and ^{13}C NMR data and by IR data for the CO groups. It was concluded that the R_3EY compounds were strong donors of the ylide type. The relative donor strengths were in the order $R_3PY > R_3SbY > R_3AsY$. This order was interpreted in terms of $(Y{\rightarrow}E)_\pi$ bonding.

A Japanese patent stated that triarylstibine oxides improved toners for the development of electrostatic images [120]. Another Japanese patent described the use of halogenated organoantimony compounds such as $(p\text{-}MeC_6H_4)_3SbCl_2$ for the same purpose [121]. Yet another Japanese patent described the use of organoantimony(V) compounds of the type Ar_3SbY_2, where Y was a group such as halogen, OH, CN, or SCN, in photographic developers [122]. The developers gave high resolution, gradation images without fog, and showed good durability. A toner for the development of electrostatic images containing a triarylstibine oxide, a butyl acrylate-styrene copolymer, and a low molecular weight polyethylene wax, was the subject of a Japanese patent [123].

The polymerization of propene by $TiCl_3\text{-}Et_2AlCl$, modified with $P(OBu)_3$, has been studied by Karayannis and coworkers [124]. The addition of Ph_3SbS to this system gave an even more effective catalyst, as did the addition of $(Bu_3Sn)_2S$.

Two hexamethoxides, $W(OMe)_6$ and $Mo(OMe)_6$, and two ionic hexamethoxy antimony compounds, $[Me_4Sb][Sb(OMe)_6]$ and $[Me_4Sb][Sb(OCD_3)_6]$, have been

prepared by Tatzel and coworkers [125] in order to study the vibrational spectrum and to calculate the force constants for the M(OMe)$_6$ species. The antimony compounds were prepared from Me$_4$SbOMe (or Me$_4$SbOCD$_3$) and [Sb(OMe)$_5$]$_2$ (or [Sb(OCD$_3$)$_5$]$_2$) in methylene chloride at room temperature. Both compounds were obtained in crystalline form with mp's of 154-156 and 152-154°C, respectively. They were characterized by elemental analyses and PMR spectra. IR and Raman spectra of all four compounds were also determined and assignments of the bands were made. Stretching force constants for both W-O and Sb-O were found to be identical, but other parts of the valence force field were markedly different.

The reaction between tetraphenylantimony chloride and either bis(triphenylgermyl)cadmium or bis(triphenylgermyl)mercury led to the formation of a compound containing an antimony-germanium bond [126]:

$$Ph_4SbCl + (Ph_3Ge)_2M \longrightarrow Ph_4SbGePh_3 + Ph_3GeMCl$$

$$(where\ M = Hg\ or\ Cd)$$
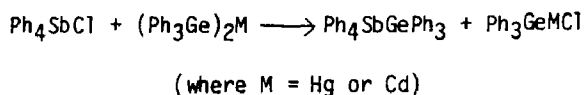
This was the first example of a compound containing a bond between Sb(V) and Ge. When heated in toluene for 4 hours at 220°C, the new compound decomposed to give triphenylstibine and tetraphenylgermane. When treated with acetic acid, the Sb-Ge bond was also cleaved; tetraphenylantimony acetate and triphenylgermane were the reaction products.

In a paper on the acidic properties of tetrakis(trifluoromethylthio)-pyrrole, a number of derivatives of the corresponding anion have been prepared [127]. Thus, the potassium salt of tetrakis(trifluoromethylthio)-pyrrole reacted with tetraphenylantimony chloride to form the tetraphenylantimony derivative of the pyrrole. It was characterized by its ^{19}F NMR spectrum and by elemental analysis.

In a paper mainly devoted to the thermodynamic properties of [Ph$_4$As]-[Ph$_4$B], the preparation of [Ph$_4$Sb][Ph$_4$B] from Ph$_4$SbCl and [Ph$_4$B]Na was described [128]. The partitioning of thermodynamic quantities of [Ph$_4$As]-[Ph$_4$B] was discussed by comparing its standard free energies of transfer from water to a variety of organic solvents with those for [Ph$_4$Sb][Ph$_4$B]. It was concluded that the use of [Ph$_4$As][Ph$_4$B] as a reference electrolyte for the single ion thermodynamic study required a certain asymmetric partition that was primarily attributable to the size difference between the cation and the anion.

The condensation of mono-substituted oxiranes with isocyanates leads readily to the formation of 3,5-disubstituted 2-oxazolidinones:
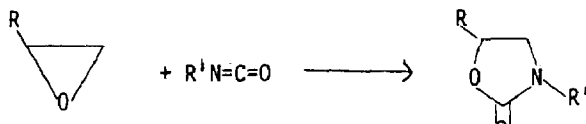
Although a number of catalysts have been used in this reaction, the 3,5-disubstituted product has been obtained almost exclusively. Baba and coworkers [129] have now found that when Ph_4SbI was used as the catalyst the 3,4-disubstituted product was produced in addition (usually) to the 3,5-disubstituted product. The ratio between the two products depended largely on the solvent employed in the reaction. Thus, when in the above equation R = Ph, R' = Me, and the solvent was THF, the 3,4:3,5 ratio was 50:50, whereas with CH_2Cl_2 as the solvent, the ratio was 80:20. Various other solvents gave different ratios, with CH_2Cl_2 and benzene usually giving the largest yields of the 3,4-disubstituted product. When R = Et, R' = Ph or Bu, and CH_2Cl_2 was the solvent, the yields of the 3,4-disubstituted products were 100%. Not only was Ph_4SbI preferred for this reaction, but it was found to be effective catalytically under much milder conditions than when other catalysts were used for the condensation. Tetraphenyl-antimony bromide was also effective as a catalyst for producing the 3,4-disubstituted product, but Ph_4SbOAc and Ph_3Sb failed to effect any condensation. It was also found that the formation of the 3,4-disubstituted product did not involve rearrangement of the 3,5-product. Thus, when the oxazolidinone (R = Me, R' = Ph) was heated with Ph_4SbI in benzene solution, the 3,4-product was recovered unchanged. In only one case did the condensation fail, namely with 2,2-dimethyloxirane and phenyl isocyanate; neither the 3,4- nor the 3,5-disubstituted product was obtained.

The temperature dependence of the ^{127}I quadrupole coupling constants in compounds of the type R_4EIO_4, where R was Et or Ph and E was P, As, or Sb, has been studied by Klobasa and coworkers [130]. For Et_4PIO_4 and Et_4AsIO_4, the quadrupole coupling constants showed normal temperature coefficients, but for Ph_4PIO_4, Ph_4AsIO_4, and Ph_4SbIO_4, there was a complicated temperature dependence of the ^{127}I quadropole interaction with phase transitions, and there were anomalous positive temperature coefficients. Suggestions were made to explain the anomalous results.

Cyclic carbonates have been prepared from oxiranes and carbon dioxide at room temperature and atmospheric pressure by the use of catalysts comprising a metal halide and a Group V onium salt [131]. Among the catalysts used was a $ZnCl_2/Ph_4SbBr$ mixture.

The use of tetraaryl or alkylaryl quaternary salts of Group V elements, including stibonium salts, in silver halide photographic materials with improved contrast has been claimed in a Japanese patent [132].

REFERENCES

1   M. Wieber, *Gmelin Handbook of Inorganic Chemistry, 8th Edition, Sb Organoantimony Compounds, Part 4,* Springer-Verlag, Berlin, 1986.

2   I. Haiduc and J.J. Zuckerman, *Basic Organometallic Chemistry,* Walter de Gruyter, Berlin, 1985, pp. 205-216.

3   A.T. Hutton, *Annu. Rep. Prog. Chem., Sect. B: Org. Chem.,* 82 (1986) 223.

4   P.G. Harrison, *Annu. Rep. Prog. Chem., Sect. A: Inorg. Chem.,* 82 (1986) 107.

5   M.F.A. Dove and D.B. Sowerby, *Coord. Chem. Rev.,* 75 (1986) 297.

6   J.L. Wardell, *Organomet. Chem.,* 14 (1986) 141.

7   A.J. Ashe, III, AFOSR *Report* (1985) 1-11; *Chem. Abstr.,* 105 (1986) 237384c.

8   J.G. Stevens, *Chem. Mössbauer Spectrosc.* [*Proc. Symp. Twenty-Five Years Chem. Mössbauer Spectrosc.*], (1985) 319; *Chem. Abstr.,* 105 (1986) 87594e.

9   A.H. Cowley, *Phosphorus Sulfur,* 26 (1986) 31.

10   G. Huttner, *Pure Appl. Chem.,* 58 (1986) 585.

11   G. Huttner and K. Evertz, *Acc. Chem. Res.,* 19 (1986) 406.

12   A.H. Cowley and N.C. Norman, *Prog. Inorg. Chem.,* 34 (1986) 1.

13   R.R. Holmes, R.O. Day, V. Chandrasekhar, S. Shafeizad, J.J. Harland, D.N. Rau, and J.M. Holmes, *Phosphorus Sulfur,* 28 (1986) 91.

14   D.R. Russell, *Organomet. Chem.,* 14 (1986) 415.

15   I.P. Romm and E.N. Gur'yanova, *Usp. Khim.,* 55 (1986) 225.

16   D.A. Edwards, *Organomet. Chem.,* 14 (1986) 196.

17   P. Jutzi, *Advan. Organomet. Chem.,* 26 (1986) 217.

18   P. Jutzi, *Chem. Rev.,* 86 (1986) 983.

19   K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds, 4th Edition,* Wiley-Interscience, New York, 1986.

20   J.E. Macintyre, editor, *Dictionary of Organometallic Compounds, Second Supplement,* Chapman and Hall, London, 1986, pp. 310-316.

21   A.M. Arif, A.H. Cowley, N.C. Norman, and M. Pakulski, *Inorg. Chem.,* 25 (1986) 4836.

22   H. Lang, G. Huttner, B. Sigwarth, U. Weber, L. Zsolnai, I. Jibril, and O. Orama, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.,* 41B (1986) 191.

23   H.J. Breunig, A. Soltani-Neshan, K. Häberle, and M. Dräger, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.,* 41B (1986) 327.

24   R.A. Bartlett, H.V. Rasika Dias, H. Hope, B.D. Murray, M.M. Olmstead, and P.P. Power, *J. Am. Chem. Soc.,* 108 (1986) 6921.

25   A.J. Ashe, III and E. G. Ludwig, Jr., *J. Organomet. Chem.,* 303 (1986) 197.

26 H.J. Breunig and D. Müller, Z. *Naturforsch., B: Anorg. Chem., Org. Chem.,*
    41B (1986) 1129.

27 H.J. Breunig and S. Gülec, Z. *Naturforsch., B: Anorg. Chem., Org. Chem.,*
    41B (1986) 1387.

28 A.J. Ashe, III and E.G. Ludwig, Jr., *J. Organomet. Chem.,* 308 (1986)
    289.

29 J.G. Stevens, J.M. Trooster, H.F. Martens, and H.A. Meinema, *Inorg.*
    Chim. Acta, 115 (1986) 197.

30 A.G.Császár, L. Hedberg, K. Hedberg, E.G. Ludwig, Jr., and
    A.J. Ashe, III, *Organometallics,* 5 (1986) 2275.

31 M. Ates, H.J. Breunig, A. Soltani-Neshan, and M. Tegeler, Z. *Naturforsch.,*
    B: Anorg. Chem., Org. Chem., 41B (1986) 321.

32 H.M.Hoffmann, M. Dräger, B.M. Schmidt, and N. Kleiner, *Spectrochim.*
    Acta, Part A, 42A (1986) 1255.

33 J.V. Seyerl, O. Scheidsteger, H. Berke, and G. Huttner, *J. Organomet.*
    Chem., 311 (1986) 85.

34 H. Preut, U. Praeckel, and F. Huber, *Acta Crystallogr., Sect. C:*
    Cryst. Struct. Commun., C42 (1986) 1138.

35 M. Hall, D.B. Sowerby, and C.P. Falshaw, *J. Organomet. Chem.,*
    315 (1986) 321.

36 C. Silvestru, L. Silaghi-Dumitrescu, I. Haiduc, M.J. Begley, M. Nunn
    and D.B. Sowerby, *J. Chem. Soc., Dalton Trans.,* (1986) 1031.

37 M.J. Begley, D.B. Sowerby, D.M. Wesolek, C. Silvestru, and I. Haiduc,
    J. Organomet. Chem., 316 (1986) 281.

38 D.H.R. Barton, D. Bridon, and S.Z. Zard, *J. Chem. Soc., Chem. Commun.,*
    (1985) 1066.

39 D.H.R. Barton. and S.Z. Zard, *Pure Appl. Chem.,* 58 (1986) 675.

40 D.H.R. Barton, D. Bridon, and S.Z. Zard, *Tetrahedron Lett.,* 27 (1986)
    4309.

41 T. Kauffmann, H. Ahlers, K.-J. Echsler, H. Schulz, and H.-J. Tilhard,
    Chem. Ber., 118 (1985) 4496.

42 P. Raj, K. Singhal, and R. Rastogi, *Polyhedron,* 5 (1986) 677.

43 H.J. Frohn and H. Maurer, *J. Fluorine Chem.,* 34 (1986) 129.

44 R.T. Boeré, C.L. French, R.T. Oakley, A.W. Cordes, J.A.J. Privett,
    S.L. Craig, and J.B. Graham, *J. Am. Chem. Soc.,* 107 (1985) 7710.

45 A.S. Romakhin, E.V. Nikitin, O.V. Parakin, Yu.A. Ignat'ev, B.S.
    Mironov, and Yu. M. Kargin, *Zh. Obshch. Khim.,* 56 (1986) 2597.

46 Y.A. Gawargious, A. Besada, M.E.M. Hassouna, *Microchem.J.,* 33 (1986)
    116.

47 Y.A. Gawargious, A.-F. B. Farag, H.N.A. Hassan, and M.E.M. Hassouna,
    Analyst (London), 111 (1986) 845.

48 V.V. Sharutin, V.T. Bychkov, O.P. Bolotova, and V.I. Kuzina,
    Zh. Obshch. Khim., 56 (1986) 330.

58

49   C. Glidewell, D. Lloyd, and S. Metcalfe, *Tetrahedron*, 42 (1986) 3887.

50   Y. Huang, Y. Shen, and C. Chen, *Tetrahedron Lett.*, 27 (1986) 2903.

51   H. Fischer and J. Schmid, *J. Organomet. Chem.*, 306 (1986) 203.

52   T.T. Vinh and B. Munson, *Org. Mass Spectrom.*, 21 (1986) 41.

53   N.S. Imyanitov, *Koord. Khim.*, 11 (1985) 1171; *Chem. Abstr.*, 104 (1986)
     101126s.

54   T. Masuda, E. Isobe, T. Hamano, and T. Higashimura, *Macromolecules*,
     19 (1986) 2448.

55   E. Isobe, T. Masuda, T. Higashimura, and A. Yamamoto, *J. Polym. Sci.*,
     Part A: Polym. Chem., 24 (1986) 1839.

56   B.I. Shapiro, A.I. Poloznikov, and L.G. Kurkina, *Zh. Nauchn. Prikl.*
     Fotogr. Kinematogr., 31 (1986) 339; *Chem. Abstr.*, 105 (1986) 235631g.

57   K. Higashi, H. Nishihara, and K. Aramaki, *Boshoku Gijutsu*, 34 (1985)
     599; *Chem. Abstr.*, 105 (1986) 118875d.

58   R.M. Biefeld, *J. Cryst. Growth*, 77 (1986) 392.

ゝ   G.J. Bougnot, A.F. Foucaran, M. Marjan, D. Etienne, J. Bougnot,
     F.M.H. Delannoy, and F.M. Roumanille, *J. Cryst. Growth*, 77 (1986)
     400.

60   M.J. Cherng, H.R. Jen, C.A. Larsen, G.B. Stringfellow, H.Lundt, and
     P.C. Taylor, *J. Cryst. Growth*, 77 (1986) 408.

61   H.M. Manasevit, R.P. Ruth, and W.I. Simpson, *J. Cryst. Growth*, 77
     (1986) 468.

62   K. Tanaka and H. Fukumoto, Jpn. Kokai Tokkyo Koho JP 61 147,
     259 [86 147, 259]; *Chem. Abstr.*, 106 (1987) 93610u.

63   K. Tanaka and H. Fukumoto, Jpn. Kokai Tokkyo Koho JP 61 147,
     263 [86 147, 263]; *Chem. Abstr.*, 106 (1987) 58914z.

64   S. Suzuki and J. Sakamoto, Jpn. Kokai Tokkyo Koho JP 60 221,
     701 [85 221, 701]; *Chem. Abstr.*, 104 (1986) 187744b.

65   Mitsubishi Gas Chemical Co., Inc., Jpn. Kokai Tokkyo Koho JP
     60 120, 715 [85 120, 715]; *Chem. Abstr.*, 105 (1986) 7373u.

66   U. Kunze, H. Jawad, and E. Boziaris, *J. Organomet. Chem.*, 312 (1986) 67.

67   H. Schumann, *J. Organomet. Chem.*, 304 (1986) 341.

68   A. Bell, R.A. Walton, D.A. Edwards, and M.A. Poulter, *Inorg. Chim. Acta*,
     104 (1985) 171.

69   D. Makanova and G. Ondrejovic, *Proc. Conf. Coord. Chem.*, 10th, (1985)
     263; *Chem. Abstr.*, 105 (1986) 34482k.

70   R. Usón, A. Laguna, A. Navarro, R.V. Parish, and L.S. Moore, *Inorg. Chim.*
     Acta, 112 (1986) 205.

71   J. Vicente, A. Arcas, M. Mora, X. Solans, and M. Font-Altaba,
     J. Organomet. Chem., 309 (1986) 369.

72   J.C. Rodriguez, C. Claver, and A. Ruiz, *J. Organomet. Chem.*, 293
     (1985) 115.

73   J. Schneider, M. Minelli, and G. Huttner, *J. Organomet. Chem.*, 294
     (1985) 75.

74   S. Aime, R. Gobetto, G. Nicola, D. Osella, L. Milone, and E. Rosen-
     berg, *Organometallics*, 5 (1986) 1829.

75   H.-J. Haupt, G. Lohmann, and U. Flörke, *Z. Anorg. Allg. Chem.*, 526
     (1985) 103.

76   C.G. Young and J.H. Enemark, *Aust. J. Chem.*, 39 (1986) 997.

77   R.S. Herrick and J.L. Templeton, *Inorg. Chem.*, 25 (1986) 1270.

78   A.D. Hunter and P. Legzdins, *Organometallics*, 5 (1986) 1001.

79   P.K. Baker and S.G. Fraser, *Polyhedron*, 5 (1986) 1381.

80   P.K. Baker and S.G. Fraser, *J. Coord. Chem.*, 15 (1986) 185.

81   P.K. Baker and S.G. Fraser, *Transition Met. Chem. (Weinheim, Ger.)*,
     11 (1986) 34.

82   P.K. Baker and S.G. Fraser, *Transition Met. Chem. (Weinheim, Ger.)*,
     11 (1986) 273.

83   P.K. Baker and S.G. Fraser, *Inorg. Chim. Acta*, 116 (1986) L1.

84   J.-P. Gehrke, R. Taube, E. Balbolov, and K. Kurtev, *J. Organomet. Chem.*,
     304 (1986) C4.

85   R. Taube, J.-P. Gehrke, and U. Schmidt, *Makromol. Chem., Macromol. Symp.*,
     3 (1986) 389.

86   A. Casoli, A. Mangia, G. Predieri, and E. Sappa, *Anal. Chim. Acta*,
     176 (1985) 259.

87   W. Gaube and H. Stegemann, *J. Prakt. Chem.*, 326 (1984) 947.

88   S. Takahashi, M. Uno, and K. Seto, Jpn. Kokai Tokkyo Koho JP 60
     197,650 [85 197,650]; *Chem. Abstr.*, 104 (1986) 88318j.

89   S. Takahashi, M. Uno, and K. Seto, Jpn. Kokai Tokkyo Koho JP 60 204, 753
     [85 204, 753]; *Chem. Abstr.*, 104 (1986) 68627f.

90   S. Takahashi, M. Uno, and K. Seto, Jpn. Kokai Tokkyo Koho JP 61 17, 553
     [86 17, 553]; *Chem. Abstr.*, 105 (1986) 60428s.

91   S. Takahashi, M. Uno, and K. Seto, Jpn. Kokai Tokkyo Koho JP 61 103, 861
     [86 103, 861]; *Chem. Abstr.*, 106 (1987) 66917t.

92   E.G. Mednikov and N.K. Eremenko, *Koord. Khim.*, 12 (1986) 802; *Chem.
     Abstr.*, 105 (1986) 144957b.

93   A.A. Lamberov, V.K. Polovnyak, D.E. Stepanov, N.F. Alekseeva, and N.S.
     Akhmetov, *Zh. Obshch. Khim.*, 56 (1986) 2809.

94   E.G. Hope, W. Levason, and N.A. Powell, *Inorg. Chim. Acta*, 115 (1986) 187.

95   A.L. Balch, L.A. Fossett, M.M. Olmstead, and P.E. Reedy, Jr., *Organo-
     metallics*, 5 (1986) 1929.

96   G.J. Lamprecht, C.P. van Biljon, and J.G. Leipoldt, *Inorg. Chim. Acta*,
     119 (1986) L1.

97   A. Spencer, *J. Organomet. Chem.*, 294 (1985) 357.

98   S. Töfke, E.T.K. Haupt, and U. Behrens, *Chem. Ber.*, 119 (1986) 96.

99   M.R. Shaffer and J.B. Keister, *Organometallics*, 5 (1986) 561.

100 G.K. Anderson and G.J. Lumetta, *Inorg. Chim. Acta,* 118 (1986) L9.

101 S.B. Mahato, B.C. Pal, and B.K. Ghosh, Indian Pat. IN 156, 909; *Chem. Abstr.,* 106 (1987) 33322s.

102 K. Akiba, H. Ohnari, and K. Ohkata, *Chem. Lett.,* (1985) 1577.

103 Y. Huang, Y. Shen, and C. Chen, *Synthesis,* (1985) 651.

104 P. Raj, R. Rastogi, K. Singhal, and A.K. Saxena, *Polyhedron,* 5 (1986) 1581.

105 R. Rüther, F. Huber, and H. Preut, *Z. Anorg. Allg. Chem.,* 539 (1986) 110.

106 N.K. Jha, A.C. Misra, P.L. Maurya, and P. Bajaj, *Synth. React. Inorg. Met.-Org. Chem.,* 16 (1986) 623.

107 J. Werner, W. Schwarz, and A. Schmidt, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.,* 36B (1981) 556.

108 W.E. De Bock, D.M. Wambeke, D.F. Van de Vondel, and G.P. Van der Kelen, *J. Mol. Struct.,* 140 (1986) 303.

109 M. Yanaga, T. Miura, K. Endo, H. Nakahara, and M. Takeda, *Bull. Chem. Soc. Jpn.,* 59 (1986) 3085.

110 N.K. Jha, P. Bajaj, A.C. Misra, and P.L. Maurya, *J. Appl. Polym. Sci.,* 32 (1986) 4393.

111 N.K. Jha, A.C. Misra, and P. Bajaj, *Polym. Eng. Sci.,* 26 (1986) 332.

112 T. Otsu, K. Endo, K. Hozawa, and M. Komatsu, *Mem. Fac. Eng., Osaka City Univ.,* 26 (1985) 101; *Chem. Abstr.,* 105 (1986) 153604m.

113 V.K. Jain, J. Mason, and R.C. Mehrotra, *J. Organomet. Chem.,* 309 (1986) 45.

114 W. Dorsch and A. Schmidt, *Z. Anorg. Allg. Chem.,* 508 (1984) 149.

115 J. Bordner, G.O. Doak, and T.S. Everett, *J. Am. Chem. Soc.,* 108 (1986) 4206.

116 W.E. McEwen, G.H. Briles, and D.N. Schulz, *Phosphorus,* 2 (1972) 147.

117 R. Nomura, A. Takabe, and H. Matsuda, *Chem. Express,* 1 (1986) 375; *Chem. Abstr.,* 106 (1987) 101439n.

118 H. Preut, R. Rüther, and F. Huber, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.,* C42 (1986) 1154.

119 N. Kuhn and H. Schumann, *J. Organomet. Chem.,* 304 (1986) 181.

120 K. Tanaka and H. Fukumoto, Jpn. Kokai Tokkyo Koho JP 61 258, 266 [86 258, 266]; *Chem. Abstr.,* 106 (1987) 166187y.

121 K. Tanaka and H. Fukumoto, Jpn. Kokai Tokkyo Koho JP 61 258, 264 [86 258, 264]; *Chem. Abstr.,* 106 (1987) 166186x.

122 K. Tanaka, H. Fukumoto, E. Imai, and T. Ikeda, Jpn. Kokai Tokkyo Koho JP 61 120, 165 [86 120, 165]; *Chem. Abstr.,* 106 (1987) 11203b.

123 K. Tanaka and H. Fukumoto, Jpn. Kokai Tokkyo Koho JP 61 236, 556 [86 236, 556]; *Chem. Abstr.,* 106 (1987) 186408z.

124 N.M. Karayannis, H.M. Khelghatian, and S.S. Lee, *Makromol. Chem.,* 187 (1986) 863.

125 G. Tatzel, M. Greune, J. Weidlein, and E. Jacob, *Z. Anorg. Allg. Chem.,* 533 (1986) 83.

126 V.T. Bychkov, V.V. Sharutin, O.P. Bolotova, A.E. Ermoshkin, and T.N. Konkina, *Zh. Obshch. Khim.,* 55 (1985) 2398.

127 A. Haas and T. Maciej, *Z. Anorg. Allg. Chem.,* 524 (1985) 33.

128 J.I. Kim, *Bull. Soc. Chim. Belg.,* 95 (1986) 435.

129 A. Baba, M. Fujiwara, and H. Matsuda, *Tetrahedron Lett.,* 27 (1986) 77.

130 D.G. Klobasa, P.K. Burkert, and G. Müller, *Z. Naturforsch., A: Phys., Phys. Chem., Kosmophys.,* 41A (1986) 330.

131 H. Kisch, R. Millini, and I.-J. Wang, *Chem. Ber.,* 119 (1986) 1090.

132 Y. Kudo, Jpn. Kokai Tokkyo Koho JP 61 31, 294 [86 31,294]; *Chem. Abstr.,* 105 (1986) 105701u.