

Coordination Chemistry of Organostibines

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Received July 19, 1977

The study of the coordination chemistry of heavy group 5B (P, As, Sb, Bi) donor ligands commenced with the preparation of two isomers of $[\text{Pt}(\text{PEt}_3)_2\text{Cl}_2]$ over 100 years ago.¹ Trimethylstibine complexes of palladium(II) and platinum(II) were reported in 1925,² but the interest in this general area dates from the work of Mann and Jensen in the 1930s. This interest has developed very rapidly in the last 25 years through the work of a large number of chemists, of whom Chatt and Nyholm are preeminent. During this period the field diversified to include the study of hydrogenation and polymerization catalysts and the spectroscopic and magnetic properties of transition metal ions in unusual environments.

Interest has always centered upon the phosphorus and arsenic ligands, with stibines remaining relatively neglected. Early studies established that even with "soft" metals the stibine complexes were the least stable of the three, while stibines appeared to have little affinity at all for 3d metal ions, except in low oxidation states. Stibines were further neglected in the rapid development of bi- and multidentate ligands since incorporation of antimony proved difficult, and 10 years ago neither chelating stibines nor antimony-containing multidentates had been prepared.

In this Account we are concerned mainly with our own studies on the synthesis and complexation of antimony ligands. We have tried to show that stibines exhibit considerable similarities to phosphines and arsines, but also significant differences. Review articles providing comprehensive coverage of the field up to the beginning of 1977 are available.^{3,4}

Trends in the Chemistry of Phosphorus, Arsenic, Antimony, and Bismuth Ligands

The first problem encountered in attempting to rationalize trends within group 5B donor coordination chemistry is the vast size and scope of the field, and it is hardly to be expected that "hard and fast" rules applicable to all cases can be stated. Here we have attempted the more modest task of delineating certain

observed trends, correlating them where possible with the electronic or steric properties of the ligands.

Since steric and electronic properties are interrelated, separation in an absolute sense is impossible. Nonetheless, the establishment of the properties of stibines relative to other common ligands is clearly important. The interpretation of electronic effects brings one into the contentious and confused area of " σ " vs. " $\sigma + \pi$ " bonding models. When disagreement about the significance of π bonding in phosphine complexes is widespread, it is hardly likely that the picture will be clearer for heavier donor atoms like antimony, where the experimental data is much less complete. At the present time consensus of opinion⁵ seems to be that in normal or higher oxidation state complexes the group 5B donors are predominantly or exclusively σ donors.

Relative electronic effects can be estimated from the spectrochemical series and study of the trans influence. Steric effects due to the donor atom itself will clearly increase in the order $\text{P} < \text{As} < \text{Sb} < \text{Bi}$, while the effects caused by substituents on the group 5B atom can be treated in a semiquantitative way using the cone angle concept of Tolman.⁶

Looking first at predominantly electronic effects, it is apparent that σ donation increases $\text{R}_3\text{P} > \text{R}_3\text{As} > \text{R}_3\text{Sb} (> \text{R}_3\text{Bi})$.⁵ Numerous electronic spectral studies⁷⁻⁹ have established that the position of group 5B donors in the spectrochemical series is $(\text{RO})_3\text{P} > \text{R}_3\text{P} > \text{NH}_3 \sim \text{R}_3\text{As} > \text{H}_2\text{O} > \text{R}_2\text{S} > \text{R}_3\text{Sb} > \text{Cl}$, with the effect of changes in the R group being alkyl > cycloalkyl > aryl. Our own studies¹⁰⁻¹² of complexes of the bidentates $o\text{-C}_6\text{H}_4(\text{EPh}_2)(\text{E}'\text{Ph}_2)$ (E, E' = P, As, Sb) have shown that the expected spectrochemical series for E, E' is observed, viz. $\text{P,P} > \text{P,As} > \text{As,As} \sim \text{P,Sb} > \text{As,Sb} > \text{Sb,Sb}$. The anomalous spectrochemical series observed for the apical donor in complexes of some tripodal tetradentates $\text{E}(o\text{-C}_6\text{H}_4\text{E}'\text{R}_2)_3$ ($\text{P} > \text{As} < \text{Sb}$) is due to steric influences—either compression of the apical

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(4) "Phosphine, Arsine and Stibine Complexes of the Transition Elements", W. Levason and C. A. McAuliffe, Elsevier, Amsterdam, in press.

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donor upon the metal, which results in an enhanced spectrochemical effect, or distortion of the trigonal bipyramidal geometry.¹³⁻¹⁵

Trans influence, defined as a trans bond weakening effect, has been correlated with the rehybridization of the metal orbitals in response to the form of the donor σ orbital.⁵ The order derived from various physical measurements, including $\nu(\text{M}-\text{Cl})$ (IR), $d(\text{M}-\text{X})$ (X-ray), and $^1J(\text{Pt}-\text{H})$ and $^2J(\text{Pt}-\text{H})$ (NMR), is (alkyl)₃P > Ph₃P ~ (PhO)₃P > R₃As > amines > halides, with R₃Sb very similar to R₃As. Clearly some deviation from this order may be expected with different metal ions, and one should bear in mind that other factors may influence individual cases, e.g., coupling of $\nu(\text{M}-\text{X})$ with other vibrations, or intermolecular steric effects in the case of $d(\text{M}-\text{X})$. The trans influence in stibine complexes is apparent in the ¹²¹Sb Mössbauer spectra (see below).

Some examples of steric effects are the tendency of ligands of the type Ph₂ECH₂EPh₂ to chelate to a metal ion and the influence of group 5B ligands upon the linkage isomerism in palladium(II) and platinum(II) thiocyanate complexes.

The diphosphine Ph₂PCH₂PPh₂ functions either as a chelating or as a monodentate ligand depending upon the conditions and metal ion involved.¹⁶ The corresponding diarsine exhibits a preference for monodentate behavior,¹⁷ while the distibine chelates very infrequently.^{18,19} Clearly the strain within the four-membered rings increases with size of the group 5B element and tends to favor monodentate behavior. The decreased σ donor power (i.e., an electronic effect) would also operate in the same order; hence the energy released upon forming two bonds, which would tend to compensate for the strain, also decreases P > As > Sb.

Steric effects of the substituents are expected to decrease P > As > Sb for constant substituent. Examples of this effect may be the decreased tendency for cyclometalation P > As⁴ and the effect of other ligands upon the -SCN/-NCS isomerism in palladium(II) and platinum(II) complexes.²⁰ In planar complexes [M(bidentate)(CNS)₂] (CNS does not imply any particular mode of bonding) the bidentate exerts a marked effect upon whether the thiocyanate group is N- or S-bonded. The M-NCS linkage is linear, the $\angle\text{M}-\text{SCN}$ is 120°; hence ligands whose substituents (usually phenyl groups) would interact with the more sterically demanding M-SCN linkage would favor isothiocyanato (M-NCS) coordination. Thus, the tendency to S-bonding increases as the bidentate donors change P < As < Sb, since the larger group 5B atom moves the substituents further from the metal. However this is not the whole story; if the palladium(II) and platinum(II) series with *o*-C₆H₄(EPh₂)(E'Ph₂) are compared, the tendency to S-bonding does increase as E,E' changes from P,P → Sb,Sb, but the change from N,S found with

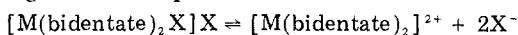
o-C₆H₄(PPh₂)₂ to S,S found with *o*-C₆H₄(SbPh₂)₂ occurs at different ligands for the two metals, viz., [Pd(*o*-C₆H₄(PPh₂)(SbPh₂))(NCS)(SCN)] and [Pd(*o*-C₆H₄(AsPh₂)₂)(NCS)(SCN)], while both of these ligands give [Pt(L-L)(SCN)₂]. Since the covalent radii (1.21 Å) of both metals are the same, clearly electronic effects are involved.^{12,21-23}

Both Nyholm's and Venanzi's groups have studied the tendency for pentacoordinate complexes to form with phosphine and arsine ligands,^{3,4} P < As, and have established for the metal ion involved the trend to pentacoordination Ni(II) > Pd(II) > Pt(II). The tendency of antimony donors to promote five-coordination in nickel(II) is even more pronounced, and is demonstrated by the following facts: (a) with diphosphines and diarsines the diperchlorate complexes are the tetracoordinate [Ni(L-L)₂](ClO₄)₂, while the antimony-containing *o*-C₆H₄(PPh₂)(SbPh₂) and Me₂Sb(CH₂)₃SbMe₂ complexes are five-coordinate [Ni(L-L)₂(H₂O)](ClO₄)₂; and (b) in contrast to the phosphorus and arsine analogues, stibine ligands do not readily yield planar [Ni(L-L)X₂] compounds; they either form only a [Ni(L-L)₂X]⁺ or achieve a higher coordination number by halogen bridging e.g., as in the hexacoordinate [Ni(*o*-C₆H₄(PPh₂)(SbPh₂))₂]_n.^{10,24,25}

For palladium(II) and platinum(II) the case is more complicated. A spectroscopic and conductimetric study of M(bidentate)₂X₂ (X = Cl, Br, I, CNS) complexes shows that the tendency to exist in solution as the five-coordinate [M(bidentate)₂X]X increases Pd > Pt and with the bidentate *o*-C₆H₄(PPh₂)₂ < *o*-C₆H₄(PPh₂)(AsPh₂) < *o*-C₆H₄(AsPh₂)₂ ~ *o*-C₆H₄(PPh₂)(SbPh₂). However, with *o*-C₆H₄(AsPh₂)(SbPh₂) and *o*-C₆H₄(SbPh₂)₂, the competing reaction

$$\text{M}(\text{bidentate})_2\text{X}_2 \rightleftharpoons \text{M}(\text{bidentate})\text{X}_2 + \text{bidentate}$$

also occurs. We thus believe that the failure to isolate pentacoordinate complexes with aryldistibines is due to a greater tendency to lose one bidentate ligand and not to a decreased tendency to pentacoordination, which would have been demonstrated by a shift to the right of the equilibrium.^{11,12,26}



Surprisingly, especially in view of its behavior toward nickel(II), the stronger donor Me₂Sb(CH₂)₃SbMe₂ also fails to yield bis(ligand) complexes,²⁴ and we can offer no explanation for this phenomena at the moment.

It is apparent that the ability of group 5B ligands to complex with higher oxidation states of the transition metals decreases rapidly: P > As > Sb. As an example, a surprisingly wide range of alkyl- and aryldiphosphine and -diarsine complexes of nickel(II) can be oxidized by bromine to nickel(III), but all stibine analogues tried so far decompose.²⁷ Similarly, the harder 3d M(II)

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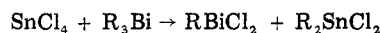
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form numerous phosphine complexes and a number of arsine complexes, but rarely bond to stibines.^{3,4} Even the few known complexes are decomposed by oxygen or nitrogen donor solvents, which of course means that they must be prepared in weakly or noncoordinating solvents such as ethers or halocarbons. For both of these situations, it is probable that an important factor in instability is that the metal ion (either because it is a 3d ion or because of its higher formal charge) is less well matched in terms of orbital size and energy with antimony than with phosphorus or arsenic.

The same decreased ability to bond, $P > As > Sb$, appears to exist for the early transition-metal halides, but here the data are much less complete, due both to experimental difficulties and, until fairly recently, to lack of effort. Although a few cases of SbR_3 coordination to early transition have been described, e.g., $WOCl_3\{o-C_6H_4(AsMe_2)(SbMe_2)\}$,²⁸ it is evident that they are much less stable than phosphorus or arsenic analogues.

Fragmentation reactions of group 5B ligands are considerably more common than was supposed a few years ago.⁴ Since group 5B bonds to carbon become weaker on descending the group, these reactions are likely to be of importance for antimony and bismuth. In fact, very few reactions involving $Sb-C$ and $Bi-C$ bond fission have been studied in detail. No doubt in many reactions described in which stibines and metal halides produce tars or other uncharacterized black solids $Sb-C$ fission is a possibility. Scrambling of substituents on reaction of main group halides with stibines and bismuthines, e.g.



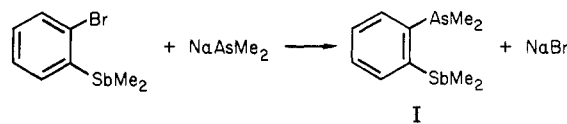
has been known for over 60 years, but has not attracted much recent work. The same type of reaction can be envisaged for transition-metal halides, but since transition-metal alkyls are reactive, only their decomposition products may be detected.

We have said very little about bismuth ligands. The donor power of bismuth is very weak indeed, and the weak $C-Bi$ bond means that fragmentation of the ligand may be a facile alternative reaction, suggesting that the number of complexes of bismuthines will remain relatively small. Nonetheless, as the final members of the group, bismuthines are of interest for comparison purposes. Much remains to be done in stibine chemistry, and some ideas for future work are mentioned below. It is hoped that this Account may demonstrate that stibines are not merely "poorly coordinating phosphines and arsines", but have significant and interesting differences.

Antimony and Bismuth Ligands

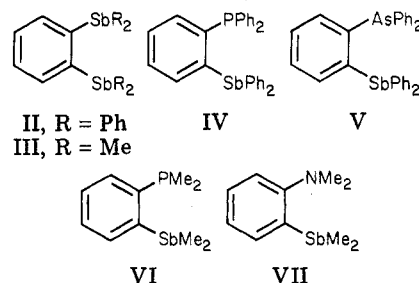
Tertiary stibines $R_{3-n}R'_nSb$ are readily prepared either from the metal stibides R_2SbM ($M = Li, Na$) and $R'X$ or from $R_{3-n}SbCl_n$ and $R'Li$ or $R'MgX$,²⁹ similar to the preparation of the phosphorus or arsenic analogues. Ditertiary stibines and antimony-containing multidentate ligands are obtained with some difficulty, attributable mainly to the consequences of the weakness of the $C-Sb$ bond. This weakness means that in the stepwise syntheses used to prepare such ligands $C-Sb$

bond fission may be a competing reaction; organolithium and Grignard reagents used to form $C-E$ ($E = P, As, Sb$) bonds can also cleave $C-Sb$ bonds under various conditions. In the synthesis³⁰ of (*o*-(dimethylarsino)phenyl)dimethylstibine (I), if the nu-



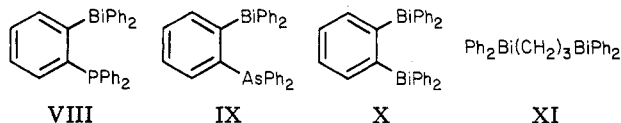
cleophile ($AsMe_2^-$) is added dropwise to the (*o*-bromophenyl)dimethylstibine, and is thus never in excess, the yield is 64%; inverse addition gives only 23% yield and much decomposition is caused by the excess nucleophile. The weak $C-Sb$ bond (some bond-dissociation energies: $P-C$, 70–75 kcal mol⁻¹ (PPh_3); $P-C$, 65.0 (PMe_3); $As-C$, 54.8 ($AsMe_3$); $As-C$, 63.8 ($AsPh_3$); $Sb-C$, 51.5 ($SbMe_3$); $Sb-C$, 58.3 ($SbPh_3$); $Bi-C$, 34.1 ($BiMe_3$); $Bi-C$, 42.2 ($BiPh_3$)) is probably also responsible for the reaction of Me_2Sb^- or Ph_2Sb^- with $ClCH_2CH_2Cl$ to yield C_2H_4 and R_2SbSbR_2 , instead of the formation of the appropriate bidentate ligand as occurs with $AsPh_2^-$, PPh_2^- , or PMe_2^- .³¹ Elimination also occurs in attempts³¹ to prepare *cis*- or *trans*- $Ph_2SbCHCHSbPh_2$ from $NaSbPh_2$ and the appropriate dichloroethylene. However, the use of $NaSbR_2$ and dichloroalkanes, $Cl(CH_2)_nCl$ ($n = 1, 3, \dots$), does produce ditertiary stibines in good yield, e.g., $Me_2Sb(CH_2)_nSbMe$, 45%.²⁴

o-Phenylenedistibines have proved to be considerably more difficult to obtain. *o*-Phenylenebis(diphenylstibine) (II) is not formed by reaction of *o*-dichloro-



benzene with $NaSbPh_2$, and the methyl analogue, III, is formed only in traces using $NaSbMe_2$.^{26,32} Successful syntheses utilize^{26,33} *o*- $C_6H_4Br(SbCl_2)$, itself obtained only in poor yield, ~15%.^{30,34} Using the appropriate *o*-bromophenyl derivative ligands (I), IV–VII have been prepared by analogous reactions.^{10,30,32}

More recently we have synthesized the bismuth-containing ligands VIII and IX from *o*- $C_6H_4Br(PPh_2)$



or *o*- $C_6H_4Br(AsPh_2)$, *n*- $BuLi$, and Ph_2BiCl .³⁵ However, we have been unable to obtain ditertiary bismuthines such as X or XI by extensions of this procedure.³³

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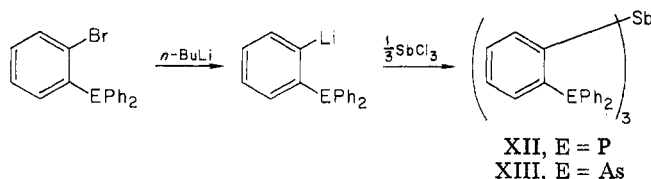
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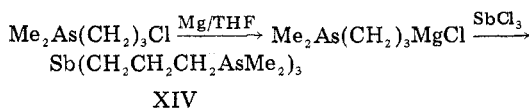
(28) W. Levason, C. A. McAuliffe, and F. P. McCullough, *Inorg. Chem.*, **16**, 2911 (1977).

(29) Reference 4, Chapter 1.

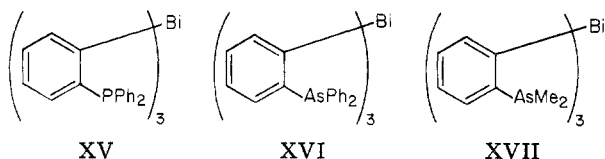
Chelating ligands containing more than two antimony donors are unknown; attempts to prepare them³⁴ have foundered upon the problem of sequentially introducing $-SbR_2$ groups. The obvious route to $Sb(o-C_6H_4SbPh_2)_3$ from $o-C_6H_4Br(SbPh_2)$, $n-BuLi$, and $SbCl_3$ fails since the $n-BuLi$ attacks the C-Sb bond²⁶ rather than cleanly removing the bromine atom as happens with the phosphine and arsine analogues. An apical antimony donor can be incorporated into a tetradentate fairly easily. Tridentate $RSb(\sim ER_2)_2$ ($E = P, As$) are unknown but can doubtless be prepared. Treatment of $SbCl_3$ with (*o*-lithiophenyl)diphenylphosphine or -arsine yields tripod tetradentates XII and XIII.^{13,36} Tri-



methylene interdonor linkages can also be incorporated.³⁷



A logical extension of this work has resulted in the preparation of three tripod tetradentate bismuthines, XV–XVII.^{14,34,38} It is possible¹⁴ to prepare Bi-



$(CH_2CH_2CH_2AsMe_2)_3$ (XVIII) in poor yield by addition of $Me_2As(CH_2)_3MgCl$ to $BiCl_3$ in THF at $-30^\circ C$. Inverse addition or reaction at room temperature yields only trace amounts of the ligand both due to the weakness of the Bi-C(alkyl) bonds and probably because the ligand is destroyed by excess Grignard.

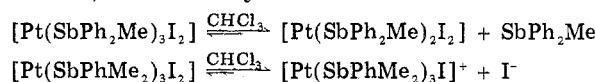
Summarizing, it is clear that a considerable number of bi- and multidentate antimony-containing ligands are known, and various analogues can probably be obtained, e.g., $Me_2As(CH_2)_3SbMe_2$ and $Sb(CH_2CH_2PPh_2)_3$. The challenge which remains is to incorporate three or more antimony donors into one ligand.

The spectroscopic properties, including the mass spectra,^{26,35,39–42} of many of the above ligands are well documented.

Coordination Chemistry

A study of the reactions of monodentate tertiary stibines $SbPh_3$, $SbPh_2Me$, $SbPhMe_2$, $SbCy_3$ ($Cy =$ cyclohexyl), $SbEt_3$, $Sb(o-tolyl)_3$, $Sb(m-tolyl)_3$, $Sb(p-tolyl)_3$ with palladium(II) and platinum(II) salts re-

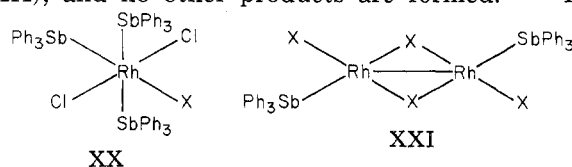
sulted in the formation of ML_2X_2 ($X = Cl, Br, I, NO_2$) complexes, although some of the PdL_2Cl_2 could not be obtained pure. On the basis of vibrational spectra and ¹²¹Sb Mössbauer studies (see below) the complexes of the bulky $SbCy_3$ and $Sb(o-tolyl)_3$ ligands are assigned trans planar structures, while the less sterically demanding ligands generally yield cis complexes.^{43,44} The thiocyanate analogues $ML_2(SCN)_2$ are S-bonded, except for $[Pd\{Sb(o-tolyl)_3\}_2(NCS)(SCN)]$ which is the only example of an $-NCS$ linkage in a stibine complex.⁴⁴ The $PtL_2(SCN)_2$ appear to be cis planar and the $PdL_2(SCN)_2$ are trans in the solid state, but complex equilibria involving $-SCN$, $-NCS$, and bridging $-NCS$ -linkages occur in solution.⁴⁴ Only bis ligand complexes form with palladium(II), but platinum(II) yields the $Pt(SbPh_2Me)_3I_2$ and $Pt(SbPhMe_2)_3I_2$ in the presence of excess ligand.⁴³ These purple solids are five-coordinate in the solid state but are extensively dissociated in solution to planar species, the former by loss of stibine, the latter by ionization:



An unusual $Pt(SbPhMe_2)_4Cl_2$ species has also been isolated;^{21,43} this is largely dissociated in solution and exhibits fast ligand exchange (on the NMR time scale): $Pt(SbPhMe_2)_4Cl_2 \rightleftharpoons [Pt(SbPhMe_2)_2Cl_2] + 2SbPhMe_2$

The corresponding $[Pt(SbPhMe_2)_4](ClO_4)_2$ can be obtained from $[Pt(SbPhMe_2)_2Cl_2]$, $AgClO_4$, and $SbPhMe_2$.²¹

The *mer*- $[Rh(SbPh_3)_3Cl_3]$ undergoes metathesis to yield *mer*- $[Rh(SbPh_3)_3Cl_2X]$ ($X = Br, I, NCS, SnCl_3$) (XX), and no other products are formed.⁴⁵ This



contrasts with the phosphine and arsine analogues which yield $[RhL_3X_2Cl]$ and then $[RhL_3X_3]$. Tri(*o*-tolyl)stibine also reacts in an anomalous manner with $RhCl_3 \cdot 3H_2O$, yielding a diamagnetic dimeric rhodium(II) species, XXI.⁴⁶ Triphenylstibine is chlorinated by iron(III) chloride⁴⁷ and manganese(III)⁴⁸ chloride to Ph_3SbCl_2 (cf. Ph_3P which yields $Fe(PPh_3)_2Cl_3$ and $Mn(OPPh_3)_2Cl_2$, respectively).

The first examples of stable nickel(II)-stibine complexes were obtained²⁴ with $Me_2Sb(CH_2)_3SbMe_2$ and are the pentacoordinate square-pyramidal $[NiL_2X]ClO_4$ ($X = Cl, Br, I$) and $[NiL_2(H_2O)](ClO_4)_2$; no planar $[NiLX_2]$ appear to form.⁴⁹ Diteriary arylstibines, $Ph_2Sb(CH_2)_3SbPh_2$ or $o-C_6H_4(SbPh_2)_2$, failed to complex with nickel(II), but with incorporation

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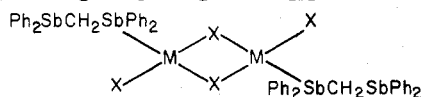
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of a phosphorus or arsenic donor, e.g., ligands IV and V, complexes $[\text{Ni}(\text{IV})_2\text{X}]\text{ClO}_4$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}$) and $[\text{Ni}(\text{V})_2\text{I}]_2[\text{NiI}_4]$ can be isolated.¹⁰ The stibine-phosphine (IV) differs from other members of this series in that it forms 1:1 complexes $[\text{Ni}(\text{IV})\text{X}_2]_n$ ($\text{X} = \text{Br}, \text{I}$) which are polymeric and pseudo-octahedral,²⁵ whereas the analogous diphosphine or diarsine species are planar. Ligand I yields planar $[\text{Ni}(\text{I})_2](\text{ClO}_4)_2$ and square-pyramidal $[\text{Ni}(\text{I})_2\text{X}]^+$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}$), which are very similar to the complexes of *o*-phenylenebis(dimethylarsine).³⁰

Bis(diphenylstibino)methane, $\text{Ph}_2\text{SbCH}_2\text{SbPh}_2$, would form a very strained four-membered ring if it behaved as a chelate, and thus it is not unexpected that it bonds as a monodentate ligand to palladium(II) and platinum(II) to give $[\text{M}(\text{ligand})\text{X}_2]_2$ (XXII) and $[\text{M}$



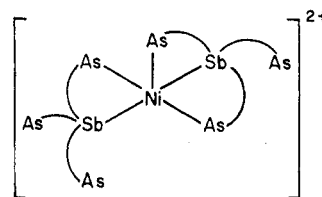
XXII

$(\text{ligand})_2\text{X}_2]$.¹⁸ The ligands with the trimethylene linkages, $\text{Ph}_2\text{Sb}(\text{CH}_2)_3\text{SbPh}_2$ ⁵⁰ and $\text{Me}_2\text{Sb}(\text{CH}_2)_3\text{SbMe}_2$,²⁴ can chelate, and planar $[\text{M}(\text{ligand})\text{X}_2]$ are formed with both metals. Both monoligand, $[\text{M}(\text{L-L})\text{X}_2]$, and bisligand, $\text{M}(\text{L-L})_2\text{X}_2$, complexes form with ligand IV; the latter are five-coordinate in solution but may be six-coordinate in the solid state. The replacement of P by As (ligand V) produces different behavior in that bis ligand $[\text{M}(\text{L-L})_2\text{X}]^+$ species can only be obtained with ClO_4^- counterions; in the presence of excess halide ions only planar $[\text{M}(\text{L-L})\text{X}_2]$ can be obtained, clearly suggesting that halide ions successfully compete with the second L-L for coordination to the metal.¹¹ This trend is even more apparent with the distibine analogue II which affords⁵¹ only planar $[\text{M}(\text{L-L})\text{X}_2]$ even in the presence of excess L-L and large counterions such as ClO_4^- or BPh_4^- , although a bis ligand compound can be obtained in the presence of weakly coordinated nitrate ions in $\text{Pd}(\text{L-L})_2(\text{NO}_3)_2$.⁵¹ The ready formation of $[\text{Rh}(\text{L-L})\text{X}_3]_2$ as well as, or instead of, $[\text{Rh}(\text{L-L})_2\text{X}_2]^+$ when L-L is IV or V may also be attributable to the relative ease with which L-L is displaced by X^- .¹¹

Phenyl-substituted stibine ligands fail to complex with harder metal ions such as cobalt(II)⁵² or iron(III),⁴⁷ while with early transition-metal systems ill-defined reduction reactions occur.^{28,53} Alkyl substitution produces ligands of considerably greater σ -donor power. Taking *o*- $\text{C}_6\text{H}_4(\text{SbMe}_2)(\text{AsMe}_2)$ (I) as an example we have been able to isolate complexes of manganese(II), the "hardest" of the divalent 3d metal ions, of type $[\text{Mn}(\text{L-L})_2\text{X}_2]$.⁵⁴ These complexes are, however, exceedingly moisture sensitive and even under rigorously dry conditions we could not isolate distibine analogues.⁵⁴ Interestingly, ligand I seems to be considerably less reducing than $\text{Me}_2\text{Sb}(\text{CH}_2)_3\text{SbMe}_2$, since iron(III) ($[\text{Fe}(\text{I})_2\text{Cl}_2]\text{FeCl}_4$),⁴⁷ oxomolybdenum(V) ($[\text{MoO}(\text{I})\text{Cl}_3]$),⁵⁵ and oxotungsten(V) ($[\text{WO}(\text{I})\text{Cl}_3]$)²⁸ complexes

can be isolated with the former, whereas the latter is chlorinated by iron(III) to $\text{Me}_2\text{Sb}(\text{Cl}_2)(\text{CH}_2)_3\text{Sb}(\text{Cl}_2)\text{Me}_2$,⁴⁷ and yields tars with molybdenum(V) or tungsten(V) compounds.

The tripod ligands XII and XIII form trigonal-bipyramidal nickel(II) complexes, $[\text{NiLX}]\text{BPh}_4$. Comparison of their electronic spectra with those of the complexes of ligands where the apical antimony has been replaced by P or As reveals an anomalous spectrochemical series of the apical donor $\text{P} > \text{As} < \text{Sb}$,¹³ which has been attributed to the compression of the apical donor onto the metal as a result of the steric properties of the ligand. In particular, the short C_2 interdonor linkage is too short to bridge the axial and equatorial positions of a regular trigonal bipyramid; hence the apical donor is "compressed" onto the metal ion, an effect which is increasingly important as the apical atom becomes larger. A similar compression effect is present in the nickel(II) complexes of $\text{Sb}(\text{o-C}_6\text{H}_4\text{AsMe}_2)_3$,¹⁵ but for the $\text{Sb}(\text{CH}_2\text{CH}_2\text{CH}_2\text{AsMe}_2)_3$ ligand the longer interdonor linkage produces apparently undistorted trigonal-bipyramidal $[\text{NiLX}]^+$ complexes, and substitution of the apical Sb donor by P and As results in a normal spectrochemical series $\text{P} > \text{As} > \text{Sb}$.³⁷ The $\text{Sb}(\text{o-C}_6\text{H}_4\text{AsMe}_2)_3$ ligand also forms⁵⁶ an unusual diperchlorate, $[\text{NiL}_2](\text{ClO}_4)_2$, with structure XXIII, whereas the other non-antimony-containing



XXIII

tripod ligands generally produce trigonal-bipyramidal $[\text{NiL}(\text{H}_2\text{O})]^{2+}$ or $[\text{NiL}(\text{OCIO}_3)]^+$; this behavior may again be a result of the strain if the $\text{Sb}(\text{o-C}_6\text{H}_4\text{AsMe}_2)_3$ were to form a trigonal-bipyramidal species; hence the observed structure and stoichiometry are preferred. The three tripods $\text{Sb}(\text{o-C}_6\text{H}_4\text{ER}_2)_3$ ($\text{ER}_2 = \text{PPh}_2, \text{AsPh}_2, \text{AsMe}_2$) also form trigonal-bipyramidal palladium(II) and platinum(II) complexes.^{34,36} Cobalt(II) species, $[\text{CoLX}]\text{BPh}_4$, have been prepared with ligand XII and on the basis of their magnetic moments and electronic spectra have been assigned trigonal-bipyramidal structures distorted by a static Jahn-Teller effect.⁵⁷

Very few examples of tertiary bismuthine coordination complexes are known,³ and prior to the work described below only substituted carbonyl derivatives were completely characterized. It appeared to us that, since incorporation of antimony into a multidentate ligand also containing P or As allowed us to obtain $\text{Ni}^{\text{II}}\text{-Sb}^{\text{III}}$ bonds, a similar approach might be successful with bismuth. The two tripod bismuthines XV and XVI do not act as tetradentate chelates but only as bidentate As_2 or P_2 donors toward palladium(II) and platinum(II), e.g., XXIV. Attempts to force penta-coordination upon the metal in these systems resulted in decomposition.³⁴ Since phenyl-substituted groups

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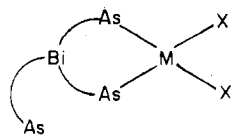
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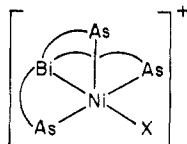
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XXIV

are not very suitable for ^1H NMR studies we subsequently prepared XVII. This ligand gave $[\text{Ni}(\text{XVII})\text{-X}]\text{BPh}_4$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) and $[\text{Ni}_2(\text{XVII})_3](\text{ClO}_4)_4$. The former were assigned five-coordination structures, both the ^1H NMR and electronic spectra suggesting a distorted structure (XXV) nearer to the square pyramid



XXV

than to the trigonal bipyramid.^{14,38} This behavior is best rationalized as due to the inability of the large bismuth atom to occupy the apical position in a trigonal bipyramid when the axial-equatorial linkage is a C_2 backbone. These complexes clearly contain $\text{Ni}^{\text{II}}\text{-Bi}^{\text{III}}$ coordination, and although the steric constraints of the ligand are doubtless responsible for the stabilization of this unique coordination bond, there must be some electronic ability of the bismuthine to form the bond. If this were not so the ligand could easily have behaved as a tridentate, forming tetrahedral complexes as does the ligand $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$.⁵⁸ The related ligand $\text{Bi}(\text{CH}_2\text{CH}_2\text{CH}_2\text{AsMe}_2)_3$ ¹⁴ yields a trigonal-bipyramidal $[\text{Ni}(\text{L})(\text{H}_2\text{O})](\text{ClO}_4)_2$ —here as with $\text{Sb}(\text{CH}_2\text{CH}_2\text{CH}_2\text{AsMe}_2)_3$ the longer trimethylene linkage allows a trigonal-bipyramidal structure without strain. To our surprise, attempts to synthesize nickel(II) halide complexes of $\text{Bi}(\text{CH}_2\text{CH}_2\text{CH}_2\text{AsMe}_2)_3$ resulted in rapid decomposition, although we did obtain some electronic spectral evidence for $[\text{NiLX}]^+$ intermediates.¹⁴

Reaction of XVII with Na_2PdCl_4 and NaBPh_4 in ethanol again resulted in decomposition, but in addition to black solids (Bi?) we isolated $[\text{Pd}(\text{AsPhMe}_2)_3\text{Cl}]\text{-BPh}_4$, clearly formed by decomposition of the ligand XVIII.⁵⁹

^{121}Sb Mössbauer Spectra

Antimony differs from either phosphorus or arsenic in that it has a naturally occurring isotope (^{121}Sb , 57% abundance) which exhibits the Mössbauer effect. A $7/2 \rightarrow 5/2$ transition arises from absorption of a 37.15-keV γ ray by the ^{121}Sb nucleus, and in noncubic fields ($\eta = 0$) eight-line spectra are expected. The natural line width is large (2.1 mm s^{-1}), and only a broad absorption envelope is observed; in practice it is necessary to cool both source and absorber in liquid helium to obtain good quality spectra. The isomer shifts observed (relative to BaSnO_3) occur at ca. -9 mm s^{-1} for organoantimony(III) compounds and at ca. -5 mm s^{-1} for

organoantimony(V) compounds.

An examination of a series of $[\text{Pd}(\text{SbR}_3)_2\text{X}_2]$ and $[\text{Pt}(\text{SbR}_3)_2\text{X}]$ complexes revealed that the isomer shifts of the coordinated stibines are considerably more positive than those of the free ligands (by 2–3 mm s^{-1}) and that the quadrupole coupling constants are considerably reduced (by 4–6 mm s^{-1} , ~25–35%). Both are expected results of delocalization of the lone pair onto the transition-metal atom, provided that both the 5s and 5p orbitals are significantly involved. The donation of the lone pair $\text{Sb} \rightarrow \text{M}$ resembles an oxidation process in that it leads to a decrease of electron density (specifically in the s orbital which the Mössbauer spectra monitor) at the antimony and hence the change in isomer shift toward the organoantimony(V) range. We will not discuss the numerical results in detail here,^{60,61} merely record some observed trends.

Firstly, the triphenylstibine complexes show isomer shift values for the palladium(II) complexes which are closer to the free ligand values than the isomer shifts of the platinum(II) analogues, consistent with platinum(II) being the better acceptor toward this particular ligand. Secondly, with a series of *cis*- $[\text{Pt}(\text{SbR}_3)_2\text{X}_2]$ the “acceptor power” of the PtX_2 unit, as measured by decreasing values of the isomer shift, is in the order $\text{I}^- > \text{NO}_2^- > \text{Cl}^-$, correlating well with the trans influence of the X group. In certain other series of complexes, e.g., $[\text{Pd}(\text{SbPh}_3)_2\text{X}_2]$, the order found is $\text{Cl}^- > \text{I}^- > \text{NO}_2^-$, which can be rationalized in terms of the different geometries; the chloro complex is *cis*, the others *trans*. Thus, it is possible to infer, albeit tentatively, the configurations of several other series of $[\text{M}(\text{SbR}_3)_2\text{X}_2]$ from these trends in isomer shift values—particularly valuable for stibine complexes where the more usual infrared spectral criteria are often unobtainable due to strong ligand absorptions in the approximate regions.

The ^{121}Sb Mössbauer spectra of the $[\text{PtL}_3\text{I}_2]$ discussed above⁴³ show the presence of only coordinated antimony and confirm the absence of free ligand in the solid state, consistent with the pentacoordinate structures proposed.

However, the distinction between the two different environments for coordinated stibines is not always possible. The spectra of *mer*- $[\text{Rh}(\text{SbPh}_3)_3\text{Cl}_3]$ show only one site, and computer fitting of the spectrum for two sites produces unrealistic⁶⁰ line widths. This suggests that the differences between the two types of SbPh_3 present are too small to be separated. Preliminary results⁶¹ for $[\text{M}(\text{Ph}_2\text{SbCH}_2\text{CH}_2\text{CH}_2\text{SbPh}_2)_2\text{X}_2]$ ($\text{M} = \text{Pd}, \text{Pt}$), which necessarily have a *cis* structure, are in accord with the results obtained for *cis*- $[\text{M}(\text{SbR}_3)_2\text{X}_2]$ above.

The ^{121}Sb Mössbauer results derive from a joint program of research with Dr. R. V. Parish at U.M.I.S.T. We are grateful to the following organizations for partial support of this work: the Science Research Council, the Royal Society, Imperial Cancer Research Fund, North Atlantic Treaty Organization, and Johnson, Matthey Co. Ltd.

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