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THE SYNTHESIS AND PROPERTIES OF ANTIMONY-SULPHUR AND ANTIMONY-OXYGEN LIGANDS

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Summary

The synthesis and properties of a series of potentially bi-, tri- and tetra-dentate ligands containing various combinations of antimony and sulphur and antimony and oxygen donors, is described. Included are $SbPh_n(o\text{-}C_6H_4OMe)_{3-n}$ (n = 0, 1, 2); $SbMe_2(o\text{-}C_6H_4OMe)$; $SbPh_n(o\text{-}C_6H_4SMe_3)_{3-n}$ (n = 0, 1, 2); $SbMe_2(o\text{-}C_6H_4SMe)$; $MeS(CH_2)_3SbR_2$ (R = Me, Ph) and $S(CH_2CH_2CH_2SbPh_2)_2$. Attempts to prepare ligands with dimethylene backbones including $(R_2SbCH_2CH_2)_2S$ (R = Me, Ph) failed. The ligands were characterised by analysis, ^1H NMR and mass spectra, and by the preparation of quaternary derivatives.

Introduction

Bi- and multidentate ligands containing one or more antimony donor atoms have been studied only relatively recently [1,2]. To some extent this neglect reflects the relatively poor σ donor properties of antimony, but is mainly due to the considerably greater difficulties involved in preparing the ligands [1]. As an extension of recent work on ditertiary stibines, we have prepared a range of hybrid ligands containing various combinations of antimony with oxygen, nitrogen or sulphur donors. The metal complexes of PN and PO donor analogues have attracted some attention as potential catalysts in view of the ease with which the hard donor is displaced from soft metal ions by substrates such as CO [3,4]. A few examples of hybrid stibines have been reported previously [5—7].

Results and discussion

Antimony-oxygen donors. Three *o*-methoxyphenylstibines $(o\text{-}MeOC_6H_4)SbPh_2$ (I), $(o\text{-}MeOC_6H_4)_2SbPh$ (II), and $(o\text{-}MeOC_6H_4)_3Sb$ (III) are easily prepared from the Grignard of *o*-bromoanisole and the appropriate chlorostibine

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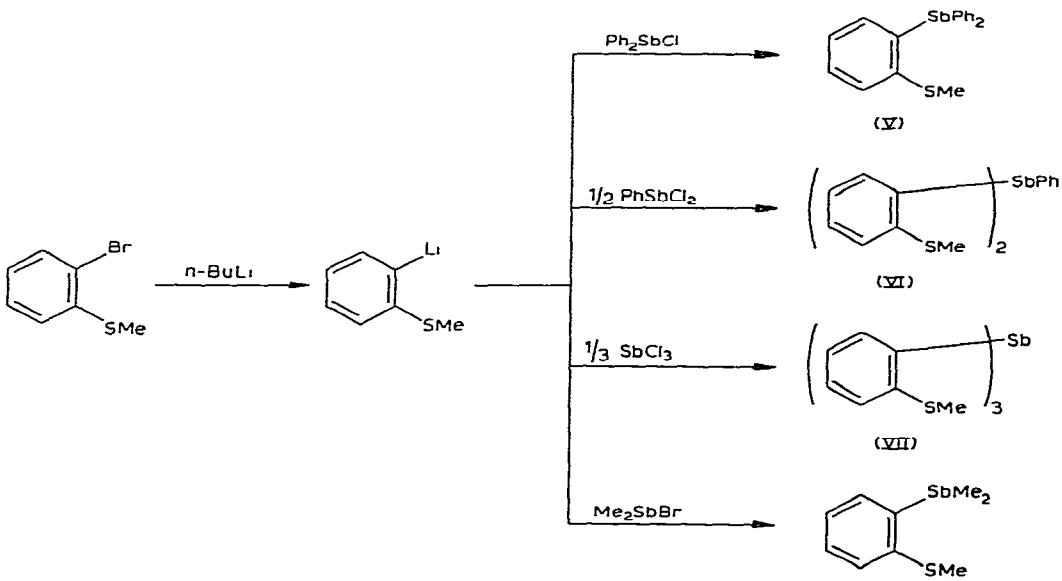
$Ph_{3-n}SbCl_n$ (n = 1, 2, 3). In the case of III it was necessary to use excess Grignard and reflux the mixture to produce complete replacement of chlorine. Even then the ^1H NMR spectra of crude samples showed the presence of varying amounts of another o-$MeOC_6H_4$ species, which was removed on recrystallisation from ethanol. The impurity was not isolated but in the light of Harris et al.'s results [7] was probably $(o\text{-}MeOC_6H_4)_2SbCl$. The three ligands are air-stable white crystalline solids, readily soluble in organic solvents. (o-methoxyphenyl)dimethylstibine (IV) was similarly prepared from o-$MeOC_6H_4MgBr$ and Me_2SbBr as a colourless, air-sensitive liquid. It was readily converted into the crystalline stibonium salt $(o\text{-}MeOC_6H_4)SbMe_3^+I^-$ by iodomethane. The ^1H NMR spectra (Table 1) of I—IV show sharp singlets at τ 6.0—6.5 due to the OMe groups. The mass spectra of the ligands are straightforward, the major fragment ions resulting from successive Sb—C cleavage (see Experimental). For I and II the base peaks are $PhSb^+$, whilst for III the observed base is C_7H_7O (m/e 107), but when ^{123}Sb fragments are also considered, the actual base is $C_7H_7OSb^+$ (m/e 228, 230) as expected (total I = 131% of observed base). The fragmentation pattern of IV is very different, and is reminiscent of those of o-$C_6H_4(EMe_2)_2$ [6,8] having $(P - Me)^+$ as the base peak and showing successive loss of methyl groups from the parent.

Antimony-sulphur ligands. Four o-methylthiophenylstibines (V, VI, VII and VIII) were prepared from (o-bromophenyl)methylsulphide, n-butyllithium and the chlorostibine (Scheme 1). (o-methylthiophenyl)diphenylstibine (V), bis-(o-methylthiophenyl)phenylstibine (VI) and tris(o-methylthiophenyl)stibine (VII) are air-stable, microcrystalline solids. (o-Methylthiophenyl)dimethylstibine (VIII) is an air-sensitive oil which readily gave a monomethiodide on treatment with iodomethane in acetone. A comparison of the ^1H NMR spectra



SCHEME 1

TABLE 1

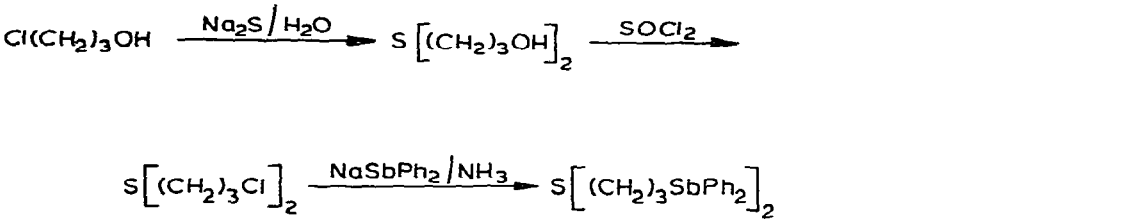
^{1}H NMR DATA ON THE LIGANDS

		Chemical shift (τ) and assignment [a]
I	$(MeOC_6H_4)SbPh_2$	2.6—3.0(m)C_6H_5 + C_6H_4, 6.5(s)OMe
II	$(MeOC_6H_4)_2SbPh$	2.5—3.2(m)C_6H_5 + C_6H_4, 6.2(s)OMe
III	$(MeOC_6H_4)_3Sb$	2.5—3.2(m)C_6H_4, 6.2(s)OMe
IV	$(MeOC_6H_4)SbMe_2$	2.6—3.2(m)C_6H_4, 6.25(s)OMe, 9.05(s)$SbMe_2$
V	$(MeSC_6H_4)SbPh_2$	2.6—3.0(m)C_6H_4 + C_6H_5, 7.55(s)SMe
VI	$(MeSC_6H_4)_2SbPh$	2.5—3.2(m)C_6H_4 + C_6H_5, 7.6(s)SMe
VII	$(MeSC_6H_4)_3Sb$	2.4—3.0(m)C_6H_4, 7.5(s)SMe
VIII	$(MeSC_6H_4)SbMe_2$	2.7—3.1(m)C_6H_4, 7.55(s)SMe, 9.2(s)$SbMe_2$
IX	$MeSCH_2CH_2CH_2CH_2SbPh_2$	2.5—2.9(m)C_6H_5, 8.2(s)SMe, 7.5, 8.1(m) [d] CH_2
X	$MeSCH_2CH_2CH_2SbMe_2$	7.95(s)SMe, 9.25(s)$SbMe_2$, 7.5, 8.2(m) [d] CH_2
XI	$S(CH_2CH_2CH_2SbPh_2)_2$	2.5—3.1(m)C_6H_5, 7.6, 8.1(m) CH_2
IV	MeI [b]	2.3—3.2(m)C_6H_4, 6.15(s)OMe, 7.75(s)$SbMe_3^+$
VIII	MeI [b]	2.5—3.2(m)C_6H_4, 7.6(s)SMe, 8.0(s)$SbMe_3^+$
IX	MeI [c]	2.4—3.0(m)C_6H_5, 7.5(s)SMe_2^+, 7.2, 8.0(m) [d] CH_2
X	MeI [c,e]	7.2(s)SMe_2^+, 7.2—7.8(m)(CH_2) [d], 8.5(s)$SbMe_3^+$

[a] $CDCl_3$ relative TMS except [b] $(CD_3)_2CO$ or [c] $(CD_3)_2SO$. [d] Complex multiplets. [e] Very slightly soluble.

of VIII and the methiodide shows that quaternisation occurs at antimony since the $SbMe_2$ resonance at τ 9.2 in the free ligand shifts to τ 8.0 in the derivative (with the expected increase in relative intensity) whilst the SMe signal at ca. τ 7.5 is unshifted.

The reaction of sodium diphenylstibide in liquid ammonia with 3-chloropropylmethyl sulphide produced 3-methylthiopropyldiphenylstibine, $MeS(CH_2)_3SbPh_2$ (IX) as a viscous oil. This could not be distilled, but after removal of volatile impurities at 50°C (0.1 Torr) the ^{1}H NMR spectrum indicated the absence of significant impurities. Attempts to selectively brominate the antimony (to $-SbPh_2Br_2$) or oxidise the sulphur (to the sulphone) did not yield pure derivatives, probably due to some attack at the other heteroatom, but a monomethiodide was prepared from MeI in refluxing acetone. The ^{1}H NMR spectrum of this derivative (Table 1) showed no peak due to $Sb—Me^+$, but the SMe resonance at τ 8.1 in the free ligand had disappeared and a new signal at τ 7.5 had appeared which we assign to S^+Me_2. Thus in the case of ligand IX, quaternisation occurred at sulphur. This was not unexpected since diarylalkylstibines are not quaternised by MeI [9]. The completely aliphatic analogue $MeS(CH_2)_3SbMe_2$ (X) was prepared using $NaSbMe_2$ in liquid ammonia. It is a colourless, air-sensitive liquid which was converted to the diquaternary derivative $Me_2S^+(CH_2)_3Sb^+Me_3(I^-)_2$ on treatment with excess MeI.



SCHEME 2

The tridentate bis(3-diphenylstibinopropyl) sulphide $[Ph_2Sb(CH_2)_3]_2S$ (XI), was prepared by the sequence of reactions in Scheme 2 is a viscous oil. The required bis(3-chloropropyl) sulphide was readily obtained from thionyl chloride and the corresponding alcohol, contrary to the literature report [10]. Treatment of XI with MeI gave a white powder, analytically corresponding to a monomethiodide, but this was insufficiently soluble for the ^1H NMR spectrum to be obtained. Presumably quaternisation occurs at the sulphur. All of the thiopropylstibines have a repulsive persistant odour, considerably more unpleasant than either alkyl sulphides or alkylstibines in isolation.

The mass specra of the ligands were generally as expected. For the series $Ph_nSb(o\text{-}C_6H_4SMe)_{3-n}$ the major fragments were derived from C—Sb cleavage, although in contrast the oxygen analogues: (a) the base is $(P - C_6H_4X)^+$ (X = H or SMe) rather than $(SbC_6H_4X')^+$ (X' = H or OMe) and (b) cleavage of phenyl groups is preferred to C_6H_4X in the unsymmetrical ligands. The fragmentation pattern of $(o\text{-}MeSC_6H_4)SbMe_2$ is again characteristic of an $o\text{-}C_6H_4(EMe_n)_2$ type molecule [6,8], exhibiting stepwise loss of Me groups.

For the aliphatic backboned $MeS(CH_2)_3SbR_2$ the fragmentation patterns are more complicated, but generally similar to the distibine [11] and dithioether [12] analogues. Thus ligand IX produced prominent ions corresponding to $P - Ph^+$, Ph_2Sb^+, $C_{12}H_{10}^+$, $C_3H_7S^+$, $C_3H_6S^+$ with $PhSb^+$ as the base peak.

Attempted preparation of $(R_2SbCH_2CH_2)_2S$ (R = Me, Ph)

The reaction of $S(CH_2CH_2Cl)_2$ with $NaSbMe_2$ and $NaSbPh_2$ was investigated in attempts to prepare tridentate ligands with 2-carbon backbones. Further interest lay in the known elimination reaction of 1,2-dihaloethanes with alkali stibides [13,14]. From the $NaSbMe_2$ a pyrophoric yellowish oil with a highly persistent repulsive odour was produced. The ^1H NMR spectrum of this oil showed that CH_2 groups were absent, the main feature being a broad singlet at ca. τ 8.9 which we assign to Me_4Sb_2. On cooling in liquid nitrogen this oil became a dark-red solid which returned to a yellow oil on melting, a highly characteristic reaction of tetramethyldistibane, Me_4Sb_2 [15]. The reaction of this oil with excess iodomethane produced a white solid, identified by analysis and ^1H NMR spectroscopy as $Me_4Sb^+I^-$, which is consistent with the reaction:

$$Me_4Sb_2 + 2\ MeI \rightarrow Me_4Sb^+I^- + Me_2SbI \quad \text{(cf. ref 16).}$$

The ^1H NMR spectrum of the crude product also showed the multiplet structure characteristic [17] of a $H_2C{=}CHS$- group (3.6 d, d, J 18,10 Hz, 4.6 d, J 18 Hz). In the case of the $NaSbPh_2 + S(CH_2CH_2Cl)_2$ reaction the crude product was a brownish oil which again showed the $H_2C{=}CHS$- resonances in the ^1H NMR spectrum, a large aromatic signal, and the absence of any methylene groups. The oil slowly deposited on white solid on exposure to air in ethanol solution. This solid had an analysis consistent with diphenylstibinic acid Ph_2SbO_2H; it did not have a sharp melting point transforming into a glass at ca. 165—175°C *. Since Ph_2SbO_2H is known [18] to result from the air-oxidation of

* Ph_2SbO_2H has been variously reported to melt at 178°C [19], 285°C [20], >250°C [18].

diphenylstibine Ph_2SbH, it is probable that the reaction of $NaSbPh_2$ and $S(CH_2CH_2Cl)_2$ produces divinyl sulphide and Ph_2SbH.

An attempt to prepare $PhSCH_2CH_2SbPh_2$ was similarly unsuccessful. We conclude that the inability to prepare 1,2-distibinoethanes by nucleophilic substitution reactions extends to stibine-thioethers with dimethylene backbones. It is noteworthy that the corresponding phosphine of arsine-thioether ligands are readily made from $RSCH_2CH_2Cl$ or $S(CH_2CH_2Cl)_2$ and $Li(Na)AsR_2$ or $Li(Na)PR_2$ in liquid ammonia or THF, e.g. $Ph_2PCH_2CH_2SR$ (R = Me, Et, Ph) [20,21], $S(CH_2CH_2PPh_2)_2$ [22] and $S(CH_2CH_2AsPh_2)_2$ [23].

Complexes of these ligands will be reported in subsequent papers.

Experimental

Analyses (C, H, N) were performed on an F&M Analyser. ^1H NMR spectra were measured in $CDCl_3$, $(CD_3)_2CO$ or $(CD_3)_2SO$ solutions relative in internal TMS on a Perkin—Elmer R12 spectrometer. Mass spectra were recorded at 70 eV on an AEI MS12. All ligand preparations were conducted under a dry dinitrogen atmosphere. Triphenylstibine (ALFA) and antimony trichloride (BDH) were used as received. Diethyl ether and tetrahydrofuran were dried by distillation from sodium wire. Dibromotrimethylantimony [24], bromodimethylstibine [24], dichlorophenylstibine [25] and chlorodiphenylstibine [14] were prepared by literature routes.

(o-Methoxyphenyl)diphenylstibine, $(o\text{-}MeOC_6H_4)SbPh_2$ (I)

The Grignard reagent prepared from magnesium (1.6 g, 0.06 mol) *o*-bromoanisole (12.3 g, 0.06 mol) and diethyl ether (200 cm^3) was treated dropwise with chlorodiphenylstibine (20.5 g, 0.06 mol) in tetrahydrofuran (100 cm^3), and the resulting white suspension refluxed for 1 h. It was hydrolysed with aqueous ammonium chloride solution, the organic layer separated, dried (Na_2SO_4) and evaporated. The resulting oil was dissolved in ethanol (50 cm^3). and deposited white crystals on standing. Yield: 8.0 g, 65%. Analysis: Found: C, 59.8; H, 4.5. $C_{19}H_{17}SbO$ calcd.: C, 59.53; H, 4.44%. M.p. 89—90°C. Mass spectrum *: 382(41) $C_{19}H_{17}SbO$; 275(10) $C_{12}H_{10}Sb$; 228(19) C_7H_7SbO; 198(100) C_6H_5Sb; 154(82) $C_{12}H_{10}$.

Phenylbis(o-methoxyphenyl)stibine, $(o\text{-}MeOC_6H_4)_2SbPh$ (II)

This was prepared similarly from $PhSbCl_2$ (8.0 g, 0.03 mol) in place of Ph_2SbCl, and recrystallised from ethanol. Yield: 14.3 g, 80%. Analysis: Found: C, 58.4; H, 4.6. $C_{20}H_{19}SbO_2$ calcd.: C, 58.1; H, 4.6%. M.p. 124°C. Mass spectrum: 412(17) $C_{20}H_{19}SbO_2$; 305(15) $C_{13}H_{12}SbO$; 228(67) C_7H_7SbO; 198(100) C_6H_5Sb.

Tris(o-methoxyphenyl)stibine, $(o\text{-}MeOC_6H_4)_3Sb$ (III)

III was prepared in a similar manner to I using $SbCl_3$ with an $SbCl_3$/RMgX ratio of ca. 1/3.5. The mixture was refluxed for 1 h, then worked up as before.

* Mass spectra are given as ion mass (intensity % base peak). Peaks refer to ^{121}Sb and intensities are uncorrected.

Two recrystallisation from ethanol gave white crystals. Analysis: Found: C, 56.9; H, 4.5. $C_{21}H_{21}SbO_3$ calcd.: C, 56.9; H, 4.7%. M.p. 191°C. Mass spectrum: 442(53) $C_{21}H_{21}SbO_3$; 335(71) $C_{14}H_{14}SbO_2$; 228(92) C_7H_7OSb; 107(100) C_7H_7O.

(o-Methoxyphenyl)dimethylstibine, (o-MeOC$_6$H$_4$)SbMe$_2$ (IV)

The Grignard reagent from *o*-bromoanisole (0.1 mol) was treated with bromodimethylstibine (23.0 g, 0.1 mol) in THF (100 cm^3), and the mixture refluxed for 1 h. The mixture was hydrolysed, the organic layer separated and dried. Distillation of the solvent, followed by fractionation in vacuo gave the ligand as a colourless oil. B.p. 86°C/1 Torr. Yield: 14 g, 58%. Mass spectrum: 258(50) $C_9H_{13}SbO$; 243(100) $C_8H_{10}SbO$; 228(23) C_7H_7SbO; 213(23) C_6H_4SbO; 197(21) C_6H_4Sb; 107(30) C_7H_7O.

A sample was quaternised with iodomethane in ethanol, and the product recrystallised from acetone. Analysis: Found: C, 29.2; H, 3.8%. $C_{10}H_{16}SbOI$ calcd.: C, 28.85; H, 3.85%. M.p. 198—200°C dec.

(o-Methylthiophenyl)diphenylstibine, (o-MeSC$_6$H$_4$)SbPh$_2$ (V)

o-Bromothioanisole [26] (20 g, ~0.1 mol) in dry diethyl ether (100 cm^3) was treated with n-butyllithium (60 cm^3, 1.6 *M*) at 0°C and stirred for 1 h. The resulting solution was treated with diphenylchlorostibine (30.8 g, 0.1 mol) in THF (80 cm^3), and stirred for a further hour. The mixture was hydrolysed with ammonium chloride solution, the organic layer separated and dried. After removal of the solvent, the residue was recrystallised from ethanol to give a white crystalline solid. Yield: 16 g, 40%. Analysis: Found: C, 56.6; H, 4.2. $C_{19}H_{17}SbS$ calcd.: C, 57.1; H, 4.3%. M.p. 96°C. Mass spectrum: 398(20) $C_{19}H_{17}SbS$; 321(100) $C_{13}H_{12}SbS$; 275(32) $C_{12}H_{10}Sb$; 198(64) C_6H_5Sb; 154(85) $C_{12}H_{10}$.

Phenylbis(o-methylthiophenyl)stibine, (o-MeSC$_6$H$_4$)$_2$SbPh (VI)

VI was prepared in an essentially similar manner from $PhSbCl_2$, *o*-$MeSC_6H_4$-Br and n-BuLi in a 1/2/2 mol ratio, and recrystallised from n-butanol 30%. Analysis: Found: C, 54.1; H, 4.4. $C_{20}H_{19}SbS_2$ calcd.: C, 53.9; H, 4.3%. M.p. 120°C. Mass spectrum: 444(32) $C_{20}H_{19}SbS_2$, 367(100) $C_{14}H_{14}SbS_2$, 321(40) $C_{13}H_{12}SbS$; 244(11) C_7H_7SbS; 198(26) C_6H_5Sb.

Tris(o-methylthiophenyl)stibine, (o-MeSC$_6$H$_4$)$_3$Sb (VII)

Was prepared as for V using $SbCl_3$, *o*-$MeSC_6H_4Br$ and n-BuLi in a 1/3/3 mol ratio, and recrystallised from acetone. Yield: 38%. Analysis: Found: C, 51.8; H, 4.7. $C_{21}H_{21}SbS_3$ calcd.: C, 51.3; H, 4.2%. M.p. 149°C. Mass spectrum: 490(15) $C_{21}H_{21}SbS_3$; 367(100) $C_{14}H_{14}SbS_2$; 244(14) C_7H_7SbS; 123(15) C_7H_7S.

(o-Methylthiophenyl)dimethylstibine, (o-MeSC$_6$H$_4$)SbMe$_2$ (VIII)

o-Bromothioanisole [26] (18 g, 0.088 mol) in dry ether (150 cm^3) was cooled to 0°C, and treated dropwise with n-butyllithium (44 cm^3, 2 *M*) in hexane. The mixture was stirred at 0°C for 1 h, and then dimethylbromostibine (20.4 g, 0.088 mol) in THF (100 cm^3) added. The mixture was stirred for 1 h, hydrolysed with deoxygenated water, the organic layer separated and dried

over Na_2SO_4. The ether was distilled off, and the residue fractionated in vacuo. The fraction b.p. 110—132°C/6 Torr was redistilled. B.p. 94—96°C/0.5 Torr. Yield: 14 g, 58%. Mass spectrum: 274(11) $C_9H_{13}SbS$; 259(100) $C_8H_{10}SbS$; 244(54) C_7H_7SbS; 229(47) C_6H_4SbS; 197(29) C_6H_4Sb.

A monomethiodide was prepared in the usual way, and recrystallised from acetone. M.p. 190°C dec. Analysis: Found: C, 29.2; H, 3.6. $C_{10}H_{16}SbSI$ calcd.: C, 28.8; H, 3.8%.

3-Methylthiopropyldiphenylstibine, $MeS(CH_2)_3SbPh_2$ (IX)

Sodium (4.3 g, 0.18 mol) was dissolved in liquid ammonia (400 cm^3) and triphenylstibine (30 g, 0.085 mol) added. The solution was stirred for 3 h, and then treated with ammonium chloride (4 g, 0.08 mol). A solution of 3-chloropropylmethylsulphide [27] (9.9 g, 0.08 mol) in THF (30 cm^3) added, when the red colour was discharged. The ammonia was boiled off, water (100 cm^3) and methylene chloride (150 cm^3) added. The organic layer was separated, dried (Na_2SO_4) and evaporated. Volatile impurities were removed at 50°C (0.1 Torr). Yield 19 g, 65%. Mass spectrum: 364(5) $C_{16}H_{19}SbS$; 287(48) $C_{10}H_{14}SbS$; 275(29) $C_{12}H_{10}Sb$; 245(15) C_7H_8SbS; 198(100) C_6H_5Sb; 154(46) $C_{12}H_{10}$; 75(46) C_3H_7S; 74(60) C_3H_6S.

Treatment of the oil with MeI in refluxing acetone gave a white powder. M.p. 168°C dec. Analysis: Found: C, 39.8; H, 4.2. $C_{17}H_{22}SSbI$ calcd.: C, 40.2; H, 4.3%.

3-Methylthiopropyldimethylstibine, $MeS(CH_2)_3SbMe_2$ (X)

Sodium (5 g, 0.2 mmol) was dissolved in liquid ammonia (400 cm^3) and Me_3SbBr_2 (18 g, 0.05 mol) added. The mixture was stirred for 3 h at —78°C, and then 3-chloropropyl methyl sulphide (6.5 g, 0.05 mmol) in diethyl ether (25 cm^3) added dropwise, when rapid discharge of the red colour occurred. The ammonia was evaporated, deoxygenated water (200 cm^3) and dichloromethane (200 cm^3) added, and the organic layer separated and dried. The solvent was distilled off, and distillation of the residual oil gave the ligand. B.p. 60°C/0.5 Torr. Yield: 10 g, 75%. Mass spectrum: 225(100) $C_5H_{13}SbS$; 210(6) $C_4H_{10}SbS$; 195(11) C_3H_6SbS; 151(10) C_2H_6Sb; 136(14) CH_3Sb; 75(13) C_3H_7S; 74(31) C_3H_6S.

Treatment of the ligand with MeI in ethanol gave a white solid. M.p. ≈250°C dec. Analysis: Found: C, 18.7; H, 3.9. $C_8H_{21}SbSI_2$ calcd.: C, 18.3; H, 4.0%.

Bis(3-diphenylstibinopropyl)sulphide, $S(CH_2CH_2CH_2SbPh_2)_2$ (XI)

Hydrated sodium sulphide ($Na_2S \cdot 9\ H_2O$) (38 g, 0.16 mol), 3-chloro-1-hydroxypropane (30 g, 0.32 mol) and water (300 cm^3) were refluxed together for 3 h. The cooled black mixture was repeatedly extracted with diethyl ether (10 X 25 cm^3), and the combined extracts dried (Na_2SO_4). Distillation of the solvent left a colourless oil (16 g) shown by ^1H NMR spectroscopy to be crude bis(3-hydroxypropyl)sulphide. 5.6 (s) (OH) [H], 6.3 (t) CH_2OH [2 H], 7.3 (t) CH_2S [2 H], 8.1 (m) $CH_2CH_2CH_2$ [2 H].

This was dissolved in chloroform (100 cm^3) and treated with thionyl chloride (20 cm^3) in $CHCl_3$ (200 cm^3) at 0°C. The resulting mixture was refluxed for 3 h, cooled and treated with excess dilute NaOH with vigorous shaking. The

organic layer was separated, dried (Na_2SO_4) and distilled. A clear oil distilled at 95—108°C/1 mmHg. Yield: 6 g. 30%. ^{1}H NMR 6.3 (t) CH_2Cl [2 H], 7.35 (t) CH_2S [2 H], 7.95 (m) $CH_2CH_2CH_2$ [2 H].

Sodium diphenylstibide in liquid ammonia was prepared as in IX using half the quantities described, and treated dropwise with bis(3-chloropropyl)sulphide (4 g, 0.015 mol) in THF (80 cm^3). The red colour was discharged slowly, and after about 2 h, dry diethyl ether (150 cm^3) was added and the ammonia boiled off. Work up as in IX gave a clear oil which became viscous after removal of volatile impurities, but could not be solidified. Yield: 12 g, ca. 85% (on Ph_3Sb).

The methiodide was prepared from X and excess MeI in acetone. It was obtained as a white powder which could not be recrystallised due to poor solubility in all solvents tried. Analysis: Found: C, 46.6; H, 4.2. $C_{31}H_{35}Sb_2SI$ calcd.: C, 45.9; H, 4.3%. M.p. 274°C dec. Mass spectrum: 351(13) $C_{18}H_{15}Sb$; 275(15) $C_{12}H_{10}Sb$; 273(7) $C_9H_{11}SbS$; 198(100) C_6H_5Sb; 154(80) $C_{12}H_{10}$; 77(30) C_6H_5; 74(3) C_3H_6S.

Attempted preparation of bis(2-diphenylstibinoethyl) sulphide

The preparation was conducted in a similar manner to XI using Ph_3Sb (30 g, 0.085 mol), Na (4 g, 0.17 mol), and bis(2-chloroethyl) sulphide $S(CH_2CH_2Cl)_2$ (*care: vesicant*) (6.75 g, 0.042 mol) in liquid ammonia. Work up of the organic products (after hydrolysis) was conducted as from compound XI. A brownish oil was produced which had a ^{1}H NMR spectrum ($CDCl_3$) 2.3—2.9 m 3.6 d, d, 4.6 d + minor absorptions attributable to THF, H_2O. On standing the solution in ethanol slowly deposited a white powder. This had only a broad Ph multiplet τ 2.4—2.9 in the ^{1}H NMR spectrum. Analysis: Found: C, 46.0; H, 3.7. $C_{12}H_{11}SbO$ calcd.: C, 46.6; H, 3.5%. M.p.: became glass at ca. 165—175°C, became mobile ~250°C.

Attempted preparation of bis(2-dimethylstibinoethyl) sulphide

The preparation was similar to X using Me_3SbBr_2 (30 g, 0.09 mol), Na (8.4 g, 0.36 mol) and $S(CH_2CH_2Cl)_2$ (7.3 g, 0.045 mol) in liquid ammonia. Work up as above produced a pyrophoric yellow oil. ^{1}H NMR spectrum crude oil 8.9 (s) and weak peaks at 3.6 d, d, 4.6 d, 4.7 s.

A sample of the oil was treated with MeI in refluxing methanol. The white product was washed with acetone and diethyl ether and dried. Analysis: Found: C, 15.2; H, 3.6. $C_4H_{12}SbI$ calcd.: C, 15.5; H, 3.8%. M.p. dec ~300°C. Lit. [28] 298—302°C. ^{1}H NMR (D_2O τ 8.25 s), lit. Me_4Sb^+ (with various anions) τ 8.1—8.25 [29].

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