Journal of Organometallic Chemistry, 209 (1981) 161—168
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE SYNTHESIS AND PROPERTIES OF ANTIMONY-NITROGEN DONOR LIGANDS

WILLIAM LEVASON * and BAHARUDDIN SHEIKH

Department of Chemistry, The University, Southampton SO9 5NH (Great Britain)

(Received October 6th, 1980)

Summary

The synthesis of the hybrid ligands $SbPh_n(o\text{-}C_6H_4NMe_2)_{3-n}$ (n = 0, 2), $Me_2N(CH_2)_3SbR_2$, $MeN(CH_2CH_2SbR_2)_2$ and $N(CH_2CH_2CH_2SbR_2)_3$ (R = Me, Ph), are described.

The ligands were characterised by ^1H NMR and mass spectra, and by the preparation of quaternary derivatives and stibine-sulphides. Attempts to prepare $Me_2NCH_2CH_2SbPh_2$ and $N(CH_2CH_2SbPh_2)_3$ were unsuccessful.

Introduction

We have previously [1] described the synthesis of ligands containing various combinations of antimony and sulphur (—SR) or oxygen (—OR) donor groups. The present paper describes antimony-nitrogen (—NR_2) analogues. Since these donors reflect the extremes of hard and soft behaviour in Group VB ligands, their coordination chemistry should be particularly interesting. The synthesis of (*o*-dimethylaminophenyl)dimethylstibine $o\text{-}C_6H_4(SbMe_2)(NMe_2)$ (I) has been described previously [2,3].

Results

The Grignard reagent prepared from (*o*-bromophenyl)dimethylamine reacts with dimethylbromostibine, Me_2SbBr, to form I, [2,3] and with diphenylchlorostibine, Ph_2SbCl, to produce the new ligand (*o*-dimethylaminophenyl)diphenylstibine, $o\text{-}C_6H_4(NMe_2)(SbPh_2)$ II. The tripodal, tetradentate tris(*o*-dimethylaminophenyl)stibine, $(o\text{-}Me_2NC_6H_4)_3Sb$ III, was prepared from $o\text{-}Me_2NC_6H_4MgBr$ and antimony trichloride, or in rather higher yield using the *o*-lithio derivative $o\text{-}Me_2NC_6H_4Li$. Ligands II and III are air-stable solids. Their mass spectra show ions due to successive Sb—C cleavage, with Ph—Ph^+ as the base peak for II (cf. the distibine $o\text{-}C_6H_4(SbPh_2)_2$ [4]), and $C_6H_4NMe_2^+$ (m/e = 121)

0022—328X/81/0000—0000/$02.50,

for III. The fragmentation of the methyl analogue I is as usual very different showing stepwise loss of Me groups [3,5].

Several attempts to prepare (2-dimethylaminoethyl)diphenylstibine, $Me_2NCH_2CH_2SbPh_2$, from $NaSbPh_2$ and (2-chloroethyl)dimethylamine, $ClCH_2CH_2NMe_2$, in liquid ammonia were unsuccessful. The product of these reactions was a brownish oil, the ^1H NMR spectrum of which revealed the complete absence of methylene groups and the Me_2N-unit. Air oxidation of this oil slowly produced a white solid identified as diphenylstibinic acid [1].

However, (3-dimethylaminopropyl)diphenylstibine, $Me_2NCH_2CH_2CH_2SbPh_2$ IV, was readily obtained from $NaSbPh_2$ and $Me_2NCH_2CH_2CH_2Cl$, as a fawn oil which appears to be air-stable. On heating with MeI in ethanol, IV produces a white monomethiodide, the ^1H NMR spectrum confirming the nitrogen as the alkylated heteroatom (Table 1), as expected since Ph_2SbR groups do not quaternise under these conditions [1,6]. The corresponding reaction of $Me_2NCH_2CH_2CH_2Cl$ and $NaSbMe_2$ produced (3-dimethylaminopropyl)dimethylstibine, $Me_2NCH_2CH_2CH_2SbMe_2$ V, as a colourless, distillable oil. This is air-sensitive, depositing a white material on exposure to air, but is markedly less air-sensitive than the structurally similar distibine $Me_2SbCH_2CH_2CH_2SbMe_2$ [7] which is spontaneously inflammable at temperatures $>\simeq 80°C$. Ligand V gave a diquaternary derivative on reaction with MeI.

In view of the failure to prepare the dimethylene-backboned bidentate (above) we were surprised to observe that reaction of bis(2-chloroethyl)methylamine, $MeN(CH_2CH_2Cl)_2$, with $NaSbPh_2$ in liquid ammonia produced the tridentate bis(2-diphenylstibinoethyl)methylamine, $MeN(CH_2CH_2SbPh_2)_2$ VI. The ligand could also be prepared using $LiSbPh_2$ in THF [8] in place of the $NaSbPh_2$/liquid ammonia. The cleavage of Ph_3Sb by lithium is slower than by Na/NH_3, but providing the THF is rigorously dry and the reaction conducted at 0°C under oxygen free conditions the yields are good (after destruction of PhLi by ^{t}BuCl, ca. 80% as measured by the amount of chloro compound required to completely discharge the red stibide colour). The ligand VI gave a mono-

TABLE 1

^1H NMR SPECTRA

Ligand		Chemical shift and assignment [a] (τ)
I	o-$C_6H_4(SbMe_2)(NMe_2)$	2.3—3.0(m) C_6H_4, 7.4(s) NMe_2, 9.2(s) $SbMe_2$
II	o-$C_6H_4(SbPh_2)(NMe_2)$	2.5—2.9(m) C_6H_5 + C_6H_4, 7.45(s) NMe_2
III	$(o\text{-}C_6H_4NMe_2)_3Sb$	2.6—3.2(m) C_6H_4, 7.35(s) NMe_2
IV	$Ph_2Sb(CH_2)_3NMe_2$	2.4—3.0(m) C_6H_5, 7.7—8.3(m) CH_2 [c], 8.1(s) NMe_2
V	$Me_2Sb(CH_2)_3NMe_2$	7.8(m) NCH_2, 7.9(s) NMe_2, 8.3—8.7(m) [c] CH_2, 9.4(s) $SbMe_2$
VI	$MeN[CH_2CH_2SbPh_2]_2$	2.4—2.8(m) C_6H_5, 7.4(m) +7.9(m) CH_2 [c], 7.95(s) NMe
VII	$MeN[CH_2CH_2SbMe_2]_2$	7.4(t) NCH_2, 7.8(s) NMe, 8.4(t) $SbCH_2$, 9.25(s) $SbMe_2$
VIII	$N[CH_2CH_2CH_2SbPh_2]_3$	2.5—2.9(m) C_6H_5, 7.3—7.8(m) 8.3(m) [c] CH_2
IX	$N[CH_2CH_2CH_2SbMe_2]_3$	7.55(m) NCH_2, 8.5—8.8(m) CH_2, 9.3(s) $SbBe_2$
I	MeI [b]	2.3—3.2(m) C_6H_4, 7.3(s) NMe_2, 8.2(s) Sb^+Me_3
IV	MeI [b]	2.2—2.8(m) C_6H_5, 6.8(m) NCH_2, 6.9(s) N^+Me_3, 7.5—8.3(m) CH_2 [c]
V	MeI [b]	6.85(m) NCH_2, 6.9(s) NMe_3^+, 7.9(m) CH_2, 8.35(s) Sb^+Me_3
VI	MeI [b]	2.0—2.7(m) C_6H_5, 6.8, 7.7(m) CH_2 [c], 7.1(s) N^+Me_2
	$MeN[CH_2CH_2Sb(S)Me_2]_2$	7.15(t) NCH_2, 7.65(t) $SbCH_2$, 7.7(s) NMe, 8.45(s) $Sb(S)Me_2$
	$N[CH_2CH_2CH_2Sb(S)Me_2]_3$	7.4(m) NCH_2, 7.8—8.3(m) CH_2Sb + CH_2CH_2Sb [c], 8.45(s) $Sb(S)Me_2$

[a] $CDCl_3$ relative internal TMS, except [b] $(CD_3)_2SO$. [c] Complex or unresolved multiplets.

methiodide with MeI, quaternisation occurring at the nitrogen (Table 1). The corresponding methylstibine, $MeN(CH_2CH_2SbMe_2)_2$ VII, was also readily prepared. This was an air-sensitive fawn oil which could not be distilled *, but which showed no evidence of decomposition on heating to 50°C/0.1 torr to remove volatile impurities. Quaternisation gave a white microcrystalline solid, poorly soluble in organic solvents, for which both the analytical data and ^1H NMR spectrum indicated that a mixture of quaternary derivatives had been obtained. These could not be separated due to poor solubility. The stibine sulphide derivative $MeN(CH_2CH_2Sb(S)Me_2)_2$ was easily prepared from the ligand and two equivalents of sulphur in refluxing toluene. It is a fawn, air-stable solid, readily soluble in toluene, and $CHCl_3$. The ^1H NMR spectrum has a single -Sb(S)(Me_2) resonance at 8.45 τ.

Attempts to synthesise the tripod tetradentate $N(CH_2CH_2SbPh_2)_3$ from $N(CH_2CH_2Cl)_3$ and either $NaSbPh_2$/liquid NH_3 or $LiSbPh_2$/THF failed, the major product being diphenylstibinic acid.

The propane-backboned analogue, tris(3-diphenylstibinopropyl)amine VIII presented no problems (Scheme 1).

SCHEME 1

$$2\ Cl(CH_2)_3OH + H_2N(CH_2)_3OH \xrightarrow[EtOH]{K_2CO_3} N(CH_2CH_2CH_2OH)_3$$

$$\downarrow \text{(i) } SOCl_2 \text{ (ii) NaOH}$$

$$N(CH_2CH_2CH_2SbPh_2)_3 \xleftarrow[THF]{LiSbPh_2} N(CH_2CH_2CH_2Cl)_3$$

(VIII)

Ligand VIII was obtained as a brownish viscous oil which resisted all attempts to crystallise it. The reaction of $NaSbMe_2$ with $N(CH_2CH_2CH_2Cl)_3$ in liquid ammonia gave the alkyl analogue tris(3-dimethylstibinopropyl)amine IX, as a mobile, yellowish, air-sensitive liquid. The proton NMR spectrum revealed the presence of a small amount of tetramethyldistibane impurity, which was largely but not completely, removed by pumping at ca. 50°C/0.01 torr. Attempts to produce a quaternary derivative of this ligand gave a sticky white solid which decomposed in air. The sulphide $N(CH_2CH_2CH_2Sb(S)Me_2)_3$ was readily prepared as a brown oil which solidifies ca. 10°C. The $^nPr_3Sb{=}S$ is also a low melting solid (35°C) [11].

The ^1H NMR spectra of the tridentates $MeN(CH_2CH_2SbR_2)_2$ (Table 1) showed the expected triplets for NCH_2 and CH_2Sb signals, but for the propane-backboned ligands the backbone protons produced poorly resolved multiplets at ca. 7.5 τ NCH_2 and ca. 8.3—8.7 τ CH_2Sb + CH_2CH_2Sb. The quaternary derivatives also gave complex multiplet resonances for the backbone protons.

The mass spectra of the two bidentates $Me_2NCH_2CH_2CH_2SbR_2$ did not exhibit a parent ion, the highest *m/e* observed corresponding to the cleavage of a terminal group from the antimony. This is reasonable in the light of the results

* Decomposition has also been observed on attempting to distill the aminearsine analogues [9], and small amounts of decomposition occur even with the α,ω-bis(dimethylstibino)alkanes [10].

from the corresponding distibines: for $Me_2Sb(CH_2)_3SbMe_2$ the ion of highest *m/e* is also $P - Me^+$, whilst for $Ph_2Sb(CH_2)_3SbPh_2$, $P - Ph^+$ is the first major peak ($I = 10\%$), although a weak parent ion ($I = 1\%$) was detectable [12]. The main fragment ions in the case of ligand IV are $P - Ph^+$, Ph_2Sb^+, $PhSb^+$, $Ph{-}Ph^+$ with the ion at *m/e* = 58 as base peak. This is [13] the immonium ion $(CH_3)_2N{=}CH_2^+$ produced by cleavage β to the nitrogen. For ligand V nitrogen-containing fragments are rather more prominent, (Experimental section) and again the base is the ion of *m/e* = 58.

The tridentate $MeN(CH_2CH_2SbMe_2)_2$ did not exhibit a parent ion but $P - Me^+$ was intense (*m/e* = 371/373/375 $\Sigma I = 132\%$ of observed base). The observed base was again the immonium ion at *m/e* = 58. The mass spectra of $MeN(CH_2CH_2SbPh_2)_2$ and the two tetradentates were less informative due to extensive decomposition, not unexpected in view of the masses and the presence of several relatively weak C—Sb bonds. All the expected nitrogen and monoantimony fragments were found, but no peaks corresponding to diantimony species were found. The spectra charged with time, probably due to thermal decomposition on the probe.

Discussion

The most unexpected result was the successful synthesis of the dimethylene-backboned bidentates $MeN(CH_2CH_2SbR_2)_2$, which contrasts with the failure to obtain either the bi- or tetradentate analogues $Me_2NCH_2CH_2SbPh_2$ and $N(CH_2CH_2SbPh_2)_3$. Elimination also occurs on reaction of stibide nucleophiles with 1,2-dichloroethane [14], *cis* and *trans* 1,2-dichloroethylene [15] and bis-(2-chloroethyl)sulphide, $S(CH_2CH_2Cl)_2$ [1], but normal substitution reactions occur with phosphorus and arsenic nucleophiles. The phosphorus and arsenic analogues of the amine-stibines are also known, viz. $Me_2NCH_2CH_2PPh_2$ [16], $Me_2NCH_2CH_2AsPh_2$ [9], $N(CH_2CH_2PPh_2)_3$ [17], and $N(CH_2CH_2AsPh_2)_3$ [18].

Clearly in the reactions of 2-chloroethyl compounds with antimony nucleophiles there is a subtle balance between elimination and substitution. A somewhat similar anomaly occurs in the reactions of $LiAsPh_2$ with 1,2-dichloroethane which gives $Ph_2AsCH_2CH_2AsPh_2$, whilst 1,2-dibromoethane gives tetraphenyldiarsine Ph_4As_2 [19]. In the cases where elimination occurred the antimony-containing product was diphenylstibinic acid, Ph_2SbO_2H, no doubt the air-oxidation product of Ph_2SbH (or Ph_4Sb_2?) initially formed *. The other product of elimination will be the appropriate enamine [20,21], which under the conditions of the reaction and workup will be hydrolysed to amine and aldehyde, accounting for our failure to isolate any nitrogen-containing products.

Experimental

Physical measurements and the antimony starting materials were obtained as before [1]. The preparation of (*o*-dimethylaminophenyl)dimethylstibine, I, has been described elsewhere [3]. The chloroalkylamines $Me_2N(CH_2)_2Cl$ and

* In a previous study [15] oxidation of Ph_4Sb_2 under certain conditions was found to give $Ph_2SbOSbPh_2$. It is not certain whether the production of Ph_2SbO_2H in the present case reflects different conditions or a different starting material, Ph_2SbH.

$Me_2N(CH_2)_3Cl$ were obtained from their hydrochlorides (Aldrich) by treatment with aqueous NaOH, followed by ether extraction and drying (Na_2SO_4). $MeN(CH_2CH_2Cl)_2$ and $N(CH_2CH_2Cl)_3$ were prepared by literature methods [22,23] from the corresponding alcohols (Aldrich). The preparation of $N(CH_2CH_2CH_2Cl)_3$ is described below. In general all the chloroalkylamines were prepared freshly when required, and the crude oils obtained by evaporation of the organic extractant (usually ether or $CHCl_3$) used directly. Caution: Chloroethylamines are nitrogen mustards and should be treated with due care.

All ligand preparations were conducted under a dry dinitrogen atmosphere.

(o-Dimethylaminophenyl)diphenylstibine, o-$C_6H_4(SbPh_2)(NMe_2)$ (II)

The Grignard reagent was prepared from *o*-bromophenyldimethylamine [3] (11.5 g 0.056 mol) and magnesium (1.5 g 0.06 mol) in dry diethylether (100 cm^3), and chlorodiphenylstibine (17.6 g 0.056 mol) in tetrahydrofuran (100 cm^3) added. The mixture was refluxed for 1 hour, cooled, hydrolysed and separated. The organic layer was dried (Na_2SO_4), evaporated, and the resulting oil crystallised from ethanol; 9 g, 33%. Found: C, 60.3; H, 4.8; N, 3.4. $C_{20}H_{20}NSb$ calcd.: C, 60.6; H, 5.0; N, 3.5%. M.P. 76—78°C. Mass spectrum *: 395(1.5) $C_{20}H_{20}NSb$; 318(15) $C_{14}H_{15}NSb$; 275(9) $C_{12}H_{10}Sb$; 198(43) C_6H_5Sb; 154(100) $C_{12}H_{10}$.

Tris(o-dimethylaminophenyl)stibine, $Sb(o\text{-}C_6H_4NMe_2)_3$ (III)

Method 1: This was using a similar preparation to II from *o*-$C_6H_4Br(NMe_2)$ (30.9 g 0.15 mol), magnesium (3.9 g 0.16 mol) and $SbCl_3$ (12.2 g 0.05 mol) in THF; 12 g 47%.

Method 2: A solution of *o*-$C_6H_4Br(NMe_2)$ (40 g 0.2 mol) in diethyl ether (100 cm^3) was added dropwise to n-butyllithium (1.6 *M*, 125 cm^3) in hexane at 0°C. After 1 hour a solution of antimony trichloride (15.2 g 0.065 mol) in THF (100 cm^3) was added and the mixture refluxed for 30 minutes. After hydrolysis the organic layer was separated, dried and evaporated. The resulting oil was recrystallised from ethanol and acetone; 18 g, 57%, M.P. 145°C. Found: C, 59.4; H, 6.1; N, 8.6. $C_{24}H_{30}N_3Sb$ calcd.: C, 59.8; H, 6.2; N, 8.7%. Mass spectrum: 481(4) $C_{24}H_{30}N_3Sb$; 361(15) $C_{16}H_{20}N_2Sb$; 240(4) $C_8H_{10}NSb$; 121(100) $C_8H_{10}N$.

(3-Dimethylaminopropyl)diphenylstibine, $Me_2N(CH_2)_3SbPh_2$ (IV)

A solution of sodium (4 g, 0.17 mol) in liquid ammonia (350 cm^3) was treated with powdered triphenylantimony (30 g, 0.085 mol) and the mixture stirred for 4 hours. Dry ammonium chloride (4.6 g, 0.087 mol) added, and after a further 1/2 hour, (3-chloropropyl)dimethylamine (10 g 0.08 mol) added dropwise until the red colour was discharged. The ammonia was boiled off, water (200 cm^3) and diethylether (200 cm^3) added, and the organic layer was separated, and dried (Na_2SO_4). Evaporation left a fawn oil which was pumped on at ambient temperature/0.5 torr for 3 hours; 20 g, 66%. Mass spectrum: 284(53)

* Expressed as *m/e*, (% intensity relative to base) ion. Masses refer to ^{121}Sb and intensities are uncorrected.

$C_{11}H_{17}SbN$; 275(12) $C_{12}H_{10}Sb$; 198(35) C_6H_5Sb; 154(57) $C_{12}H_{10}$; 84(12) $C_5H_{10}N$; 77(21) C_6H_5; 58(100) C_3H_8N.

A quaternary derivative was prepared by refluxing IV with excess MeI in ethanol, and recrystallised from ethanol; M.P. 218°C dec. Found: C, 42.5; H, 4.9; N 2.7. $C_{18}H_{25}NSbI$ calcd.: C, 42.7; H, 4.8%; N, 2.8%.

(3-Dimethylaminopropyl)dimethylstibine, $Me_2N(CH_2)_3SbMe_2$ (V)

Sodium (5 g, 0.2 mol) and Me_3SbBr_2 (18 g, 0.05 mol) were added in succession to liquid ammonia (400 cm^3) at −78°C, and the mixture stirred for 3 hours. A solution of (3-chloropropyl)dimethylamine (6.5 g, 0.05 mol) in diethyl ether (25 cm^3) added dropwise. The ammonia was evaporated, water (200 cm^3) and dichloromethane (200 cm^3) added, the organic layer separated, dried (Na_2SO_4), and distilled. The residue was fractionated in vacuo to give the ligand as a clear liquid; B.P. 40°C/0.5 torr, 7 g, 60%. Mass spectrum: 222(41) $C_6H_{15}NSb$; 207(5) $C_5H_{12}NSb$; 151(7) C_2H_6Sb; 85(13) $C_5H_{11}N$, 84(27) $C_5H_{10}N$, 58(100) C_3H_8N.

A methiodide was prepared by adding the ligand to excess MeI in refluxing ethanol. The white product which separated was washed with ethanol and ether and dried; M.P. 188°C. Found: C, 22.2; H, 4.6; N, 2.7. $C_9H_{24}NSbI_2$ calcd.: C, 21.9; H, 4.5; N, 2.8%.

Bis(2-diphenylstibinoethyl)methylamine, $MeN(CH_2CH_2SbPh_2)_2$ (VI)

Method 1: A solution of sodium diphenylstibide in liquid ammonia was prepared as in IV. This was treated dropwise with bis(2-chloroethyl)methylamine $MeN(CH_2CH_2Cl)_2$ (6.6 g, 0.04 mol) in THF (100 cm^3). A greyish suspension was produced. The ammonia was boiled off, water (250 cm^3) and CH_2Cl_2 (200 cm^3) added, the organic layer separated, dried (Na_2SO_4) and rotatory evaporated. The product was a fawn oil, 15 g, 55%, which was maintained at 50°C/0.1 torr for 3 hours to remove volatile impurities.

Method 2: Tetrahydrofuran (400 cm^3) freshly distilled from sodium wire, was cooled to 0°C. Clean lithium (1.6 g, 0.23 mol) cut into small pieces under nitrogen was added, followed by Ph_3Sb (30 g, 0.085 mol). After about 15 minutes a deep red colour developed. The mixture was stirred at 0°C for 6 hours. It was then filtered under nitrogen to remove excess lithium, and t-butylchloride (6.2 g, 0.068 mol) added dropwise. After a further $\frac{1}{2}$ hour, $MeN(CH_2CH_2Cl)_2$ (5.2 g, 0.035 mol) was added dropwise until the red colour was discharged. Work up in the usual way yielded an oil; 15 g, 67%.

A quaternary derivative was prepared from MeI in ethanol. The product was poorly soluble in most solvents. M.P. 150°C dec. Found: C, 46.6; H, 4.5%; N, 1.7. $C_{30}H_{34}Sb_2NI$ calcd.: C, 46.2; H, 4.3; N, 1.8%.

Bis(2-dimethylstibinoethyl)methylamine, $MeN(CH_2CH_2SbMe_2)_2$ (VII)

Sodium (8.5 g, 0.36 mol) and Me_3SbBr_2 (30 g, 0.09 mol) were added in succession to liquid ammonia and the mixture stirred for 3 hours at −78°C. A solution of bis(2-chloroethyl)methylamine (7.1 g, 0.046 mol) in THF (100 cm^3) was added very slowly until the red colouration was discharged. The ammonia was evaporated, diethylether (200 cm^3) and water (200 cm^3) added, the organic layer separated and dried. The solvent was distilled off at atmospheric pressure and the other volatiles removed at 50°C/0.1 torr. The residue was a fawn oil

which appeared essentially pure (^{1}H NMR). 12 g, 67%. Mass spectrum: 371(41) $C_8H_{20}NSb_2$; 287(15) $C_3H_9Sb_2$; 194(38) $C_4H_{11}NSb$; 192(28) C_4H_9NSb; 178(14) C_4H_9Sb; 151(77) C_2H_6Sb; 136(27) CH_3Sb; 121(15) Sb; 84(13) $C_5H_{10}N$; 58(100) C_3H_8N.

Sulphide derivative. Recrystallised sulphur (0.1 g, 0.3 mmol) was dissolved in boiling toluene (25 cm^3) and the ligand (0.5 g, 0.13 mmol) added. The mixture was refluxed for 1 hour, cooled and decanted from a small amount of solid material. Diethyl ether (25 cm^3) was added slowly, and the fawn solid separated on standing. Found: C, 23.4; H, 4.6; N, 2.8. $C_9H_{23}NSb_2S_2$ calcd.: C, 23.8; H, 5.1; N, 3.1. M.P. 151°C dec.

Tris(3-diphenylstibinopropyl)amine, $N(CH_2CH_2CH_2SbPh_2)_3$ (VIII)

A mixture of 3-hydroxypropylamine (15 g, 0.2 mol) and 3-chloropropanol (38 g, 0.4 mol) were added to ethanol (300 cm^3) containing potassium carbonate (40 g, ca. 0.3 mol) and the mixture refluxed for 12 hours. The colourless mixture was filtered, and the filtrate evaporated to leave a viscous oil (32 g) which was shown by ^{1}H NMR to be the crude tris(3-hydroxypropyl)amine $N(CH_2CH_2CH_2OH)_3$; 5.6(s) OH, 6.4(t) OCH_2, 7.3(m) NCH_2, 8.2(m) τ CH_2CH_2.

The crude oil was dissolved in $CHCl_3$ (200 cm^3) and treated dropwise at 0°C with thionyl chloride (70 g, 0.58 mol) and stirred for 1 hour. The mixture was then refluxed for 3 hours, cooled and poured into 40% aqueous potassium hydroxide. The mixture was stirred vigorously, then the organic layer separated, dried (Na_2SO_4), and the solvent distilled off. A brown oil remained; 15 g, 36%. ^{1}H NMR: 6.4(t) $ClCH_2$, 7.6(t) NCH_2, 8.1 τ(m) $CH_2CH_2CH_2$, $N(CH_2CH_2CH_2Cl)_3$.

A solution of $LiSbPh_2$ prepared as in VI (Method 2) was treated dropwise with a solution of $N(CH_2CH_2CH_2Cl)_3$ (5.75 g, 0.023 mol) in THF (30 cm^3) until the red stibide colour was discharged. The mixture was hydrolysed and worked up in the usual way. Removal of the solvent, and prolonged pumping at 0.1 torr produced a viscous oil. Attempts to crystallise this from ethanol, or ethanol/dichloromethane failed to produce a solid; 22 g, 79%. Found: C, 54.8; H, 4.3; N, 1.2. $C_{45}H_{42}NSb$ calcd.: 56.1; H, 4.7; N, 1.5%.

We obtained small amounts of an insoluble white material which appeared to be an impure monomethiodide. The trisulphide derivative was not prepared in a pure form.

Tris(3-dimethylstibinopropyl)amine, $N(CH_2CH_2CH_2SbMe_2)_3$ (IX)

This was prepared in a similar manner to VII from sodium (8.2 g, 0.36 mol), Me_3SbBr_2 (30 g, 0.09 mol) and $N(CH_2CH_2CH_2Cl)_3$ (7.3 g, 0.03 mol). Work-up followed by removal of all volatile materials (50°C/0.01 torr) gave a very air-sensitive yellowish oil, 6.5 g, 36%.

A trisulphide was prepared from sulphur (0.07 g, 2 mmol) and the ligand (0.5 g, 0.7 mmol) in toluene, and recrystallised from $CHCl_3$. It melts below room temperature to a brown oil. Found: C, 26.3; H, 5.1; N, 2.3. $C_{15}H_{26}NSb_3S_3$ calcd.: C, 26.1; H, 5.2; N, 2.0%.

Acknowledgements

We thank the British Council (BS) and NATO for support, Dr. J. Evans for obtaining mass spectra, and Dr. P.J. Parsons for discussion.

References

1 W. Levason and B. Sheikh, J. Organometal. Chem. 208 (1981) 1.
2 G. De Paoli, B. Zarli and C. Panattoni, Ric. Sci., 39 (1969) 355.
3 W. Levason, K.G. Smith, C.A. McAuliffe, F.P. McCullough, R.D. Sedgwick and S.G. Murray, J. Chem. Soc. Dalton, (1979) 1718.
4 W. Levason, C.A. McAuliffe and S.G. Murray, J. Organometal. Chem., 88 (1975) 171.
5 K. Henrick, D.L. Kepert, E. Shewchuk, K.R. Trigwell and S.B. Wild, Aust. J. Chem., 27 (1974) 727.
6 G. Gruttner and M. Wiernik, Ber, 48 (1915) 1751.
7 R.J. Dickinson, W. Levason, C.A. McAuliffe and R.V. Parish, J. Chem. Soc. Dalton, (1978) 177.
8 D. Wittenberg and H. Gilman, J. Org. Chem., 23 (1958) 1063.
9 T.L. Morris and R.C. Taylor, J. Chem. Soc. Dalton, (1973) 175.
10 H.A. Meinema, H.F. Martens and J.G. Noltes, J. Organometal. Chem., 110 (1978) 183.
11 R.A. Zingaro and A. Merijanian, J. Organometal. Chem., 1 (1964) 361.
12 (a) W. Levason, C.A. McAuliffe, S.G. Murray and R.D. Sedgwick, J. Organometal. Chem., 105 (1976) 195; (b) W. Levason, C.A. McAuliffe and R.D. Sedgwick, J. Organometal. Chem., 84 (1975) 239.
13 R.S. Gohlke and F.W. McLafferty, Anal. Chem., 34 (1962) 1281.
14 W. Hewertson and H.R. Watson, J. Chem. Soc., (1962) 1490.
15 K.K. Chow, W. Levason and C.A. McAuliffe, J. Chem. Soc. Dalton, (1976) 1429.
16 D.W. Meek, P.E. Nicpon and V.I. Meek, J. Amer. Chem. Soc., 92 (1970) 5351.
17 L. Sacconi and I. Bertini, J. Amer. Chem. Soc., 90 (1968) 5443.
18 L. Sacconi, I. Bertini and F. Mani, Inorg. Chem., 7 (1968) 1417.
19 A. Tzschach and W. Lange, Chem. Ber., 95 (1962) 1360.
20 M. Mioque and J.P. Duclos, Chim. Ther., 4 (1969) 363.
21 J. Szmuszkovicz, Adv. Org. Chem., 4 (1963) 1.
22 W.E. Hanby and H.N. Rydon, J. Chem. Soc., (1947), 513.
23 J.P. Mason and D.J. Gasch, J. Amer. Chem. Soc., 60 (1938) 2816.