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SYNTHESIS AND PROPERTIES OF TETRADENTATE DISTIBINE-DIAMINE, DISTIBINE-DITHIOETHER AND DISTIBINE-DIETHER LIGANDS

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Summary

The preparation and properties of five open chain tetradentate ligands with SbNNSb, SbSSSb and SbOOSb donor sequences, specifically $R_2Sb(CH_2)_3N(Me)(CH_2)_2N(Me)(CH_2)_3SbR_2$, $R_2Sb(CH_2)_3S(CH_2)_2S(CH_2)_3SbR_2$ (R = Me, Ph) and $Me_2Sb(CH_2)_2O(CH_2)_2O(CH_2)_2SbMe_2$ are described.

Introduction

Open-chain (facultative) tetradentate ligands have been studied in considerable detail in recent years [1]. Examples with P_4 [2], As_4 [3], S_4 [4] and Se_4 [4] donor sets have been prepared in addition to the long known tetramines (N_4) [6]. Mixed donor tetradentates have a particularly complex coordination chemistry, and examples of relevance to the present work include: $Ph_2P(CH_2)_2N(Me)(CH_2)_2N(Me)(CH_2)_2PPh_2$ (PNNP donor sequence) [7]; $Ph_2As(CH_2)_2N(Me)(CH_2)_2N(Me)(CH_2)_2AsPh_2$ (AsNNAs) [8]; $Ph_2P(CH_2)_3S(CH_2)_3S(CH_2)_3PPh_2$ (PSSP) [9] $Me_2As(CH_2)_3S(CH_2)_3S(CH_2)_3AsMe_2$ (AsSSAs) [10]; $Ph_2P(CH_2)_2O(CH_2)_2O(CH_2)_2PPh_2$ (POOP) [11], and $Ph_2As(CH_2)_2O(CH_2)_2O(CH_2)_2AsPh_2$ (AsOOAs) [8]. Tetradentate stibines (Sb_4) have yet to be prepared, but here we report some hybrid tetradentates with SbOOSb, SbNNSb, SbSSSb donor sequence.

Results

The synthetic route to the distibine-diamines is shown in Scheme 1, starting with 1,2-*N*,*N*′-dimethylethylenediamine. The ligand (R = Me), *N*,*N*′-bis-

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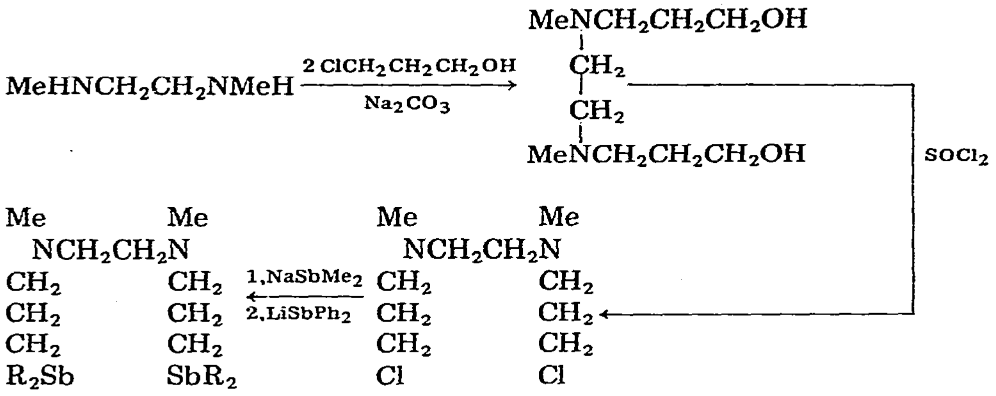
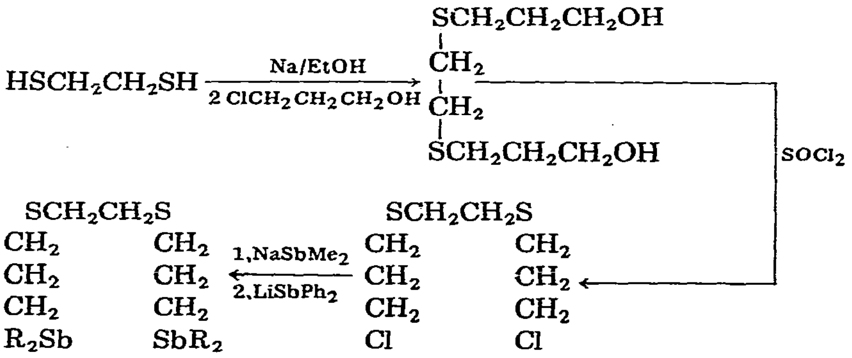


SCHEME 1. (I, R = Me; II, R = Ph)

(3-dimethylstibinopropyl)-*N*,*N'*-dimethylethylenediamine * is a yellow, air-sensitive oil. Since it cannot be distilled without decomposition, and is too air-sensitive for chromatographic purification, great care is necessary in the synthesis if a reasonably pure product is to be obtained. Most of the remaining impurities in the crude ligand can be removed by prolonged pumping at 50°C/0.01 Torr. The ligand (R = Ph), *N*,*N'*-bis(3-diphenylstibinopropyl)-*N*,*N'*-dimethylethylenediamine was obtained in a very impure form by this route, as judged by the ^1H NMR spectrum which showed the presence of substantial amounts of aromatic impurities. Various modification to the reaction conditions did not improve the purity significantly. The whole sample of crude ligand was therefore treated with nickel(II) bromide in n-butanol, and the n-butanol removed in vacuo to leave a pink-purple oil. This was extracted repeatedly with diethyl ether, and petroleum ether (60—80°), which leached out the organic impurities, whilst the nickel(II) complex of the ligand remained behind. This was then decomposed by refluxing with concentrated aqueous ammonia, and the free ligand extracted into diethyl ether. Evaporation of the ether produced the pure ligand as a white waxy solid, which melted around room temperature.



SCHEME 2. (III, R = Me; IV, R = Ph)

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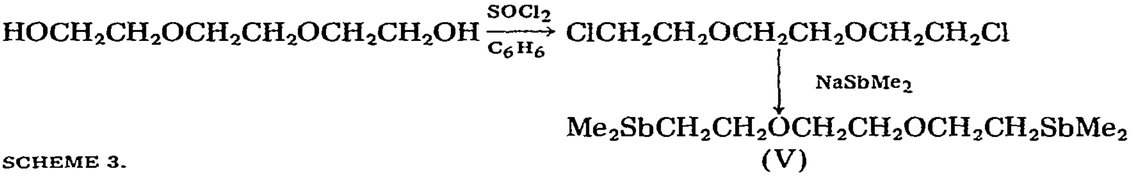
* A more systematic name would be 2,6,9,13-tetramethyl-2,13-distiba-6,9-diazatetradecane.

Two distibine-dithioethers were obtained by essentially similar routes (Scheme 2). Removal of all volatile material in high vacuum was successful in producing the methylstibine III, 1,2-bis(3-dimethylstibinopropylthio)ethane * in reasonable purity, but the phenyl analogue IV was only obtained very impure, and was purified via its nickel(II) complex.

The distibine diether, 2,11-dimethyl-2,11-distiba-5,8-dioxadodecane (V, $Me_2Sb(CH_2)_2O(CH_2)_2O(CH_2)_2SbMe_2$) was readily prepared from triethyleneglycol (Scheme 3).



$$HOCH_2CH_2OCH_2CH_2OCH_2CH_2OH \xrightarrow[C_6H_6]{SOCl_2} ClCH_2CH_2OCH_2CH_2OCH_2CH_2Cl \xrightarrow{NaSbMe_2} \underset{(V)}{Me_2SbCH_2CH_2OCH_2CH_2OCH_2CH_2SbMe_2}$$

SCHEME 3.

The product is a colourless, very air-sensitive oil. Our attempts to isolate the phenyl analogue $Ph_2Sb(CH_2)_2O(CH_2)_2O(CH_2)_2SbPh_2$ have been unsuccessful. The reaction in Scheme 3, using $LiSbPh_2$ in THF gave a fawn oil, which on the basis of its ^1H NMR spectrum contained the desired product and much aromatic impurity (as estimated by integration ca. 10% of the distibine diether). This ligand does not complex with nickel(II) precluding a purification route as used for the N or S analogues. Attempts to separate the ligand and impurities via the formation of palladium(II) complexes, and fractional crystallisation, or by chromatography have been successful.

The preparation of air-stable derivatives of these ligands presented some problems. Alkylation with iodomethane does not yield single species but mixtures of quaternary salts (cf. ref. 12). However the reaction of ligands I and III with sulphur in toluene, gave the corresponding stibine sulphides as foul-smelling brown oils, which were characterised by analysis and ^1H NMR spectra. Halogenation of antimony is not a clean reaction for I or III due to attack at the other heteroatom, but for V this is not a problem, and the white bromide, $Me_2Sb(Br_2)CH_2CH_2OCH_2CH_2OCH_2CH_2Sb(Br_2)Me_2$ was readily prepared. The phenyl-substituted stibine ligands were air-stable oils at room temperature, which were most conveniently characterised via their palladium(II) complexes. Details of the latter will be reported elsewhere.

Experimental

Physical measurements and the synthesis of the antimony starting materials have been discussed elsewhere [12,13]. All ligand preparations were conducted under an atmosphere of dry nitrogen.

N,N'-Bis(3-dimethylstibinopropyl)-N,N'-dimethylethylenediamine (I)

N,N'-Dimethylethylenediamine (30 g, 0.35 mol) and 3-chloropropanol (66 g, 0.7 mol) were mixed in ethanol (200 cm^3), finely powdered sodium carbonate (40 g) added, and the mixture refluxed for 24 h. The clear solution was diluted with diethyl ether (500 cm^3) and the solid removed by filtration.

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* Systematic name 2,13-dimethyl-2,13-distiba-6,9-dithiatetradecane.

TABLE 1

^{1}H NMR DATA [a]

$\mathrm{[CH_2N(CH_3)CH_2CH_2CH_2OH]_2}$	5.1(s) OH; 6.35(t) $\mathrm{O}CH_2$; 7.5(m) $\mathrm{N}CH_2$; 7.8(s) $\mathrm{NCH_3}$: 8.3m $\mathrm{CH_2CH_2CH_2}$
$\mathrm{[CH_2N(CH_3)CH_2CH_2CH_2Cl]_2}$	6.4(t) $\mathrm{CH_2Cl}$; 7.4—7.6(m) $\mathrm{N}CH_2$, 7.7(s) $\mathrm{NCH_3}$; 8.05(m) $\mathrm{CH_2}CH_2\mathrm{CH_2}$
$\mathrm{[CH_2N(CH_3)CH_2CH_2CH_2SbMe_2]_2}$	7.5(m) $\mathrm{N}CH_2$; 7.85(s) $\mathrm{NCH_3}$; 8.0—8.7m $\mathrm{Sb}CH_2$ + $\mathrm{CH_2}CH_2\mathrm{CH_2}$; 9.4(s) $\mathrm{SbCH_3}$
$\mathrm{[CH_2N(CH_3)CH_2CH_2CH_2Sb(S)Me_2]_2}$	7.4(m) $\mathrm{N}CH_2$; 7.8(s) $\mathrm{NCH_3}$; 7.9—8.3m $\mathrm{Sb}CH_2$ + $\mathrm{CH_2}CH_2\mathrm{CH_2}$; 8.45(s) $\mathrm{Sb(S)CH_3}$
$\mathrm{[CH_2N(CH_3)CH_2CH_2CH_2SbPh_2]_2}$	2.4—2.8(m) $\mathrm{C_6H_5}$; 7.7(m) $\mathrm{N}CH_2$; 7.9(s) $\mathrm{NCH_3}$; 8.1—8.3 $\mathrm{Sb}CH_2$ + $\mathrm{CH_2}CH_2\mathrm{CH_2}$
$\mathrm{[CH_2SCH_2CH_2CH_2OH]_2}$	5.5(s) OH; 6.35(t) $\mathrm{O}CH_2$; 7.2—7.4(m) $\mathrm{S}CH_2$; 8.2(m) $\mathrm{CH_2}CH_2\mathrm{CH_2}$
$\mathrm{[CH_2SCH_2CH_2CH_2Cl]_2}$	6.4(t) $CH_2\mathrm{Cl}$; 7.2—7.5(m) $\mathrm{S}CH_2$; 8.2(m) $\mathrm{CH_2}CH_2\mathrm{CH_2}$
$\mathrm{[CH_2SCH_2CH_2CH_2SbMe_2]_2}$	7.3—7.6(m) $\mathrm{S}CH_2$; 8.2—8.6(m) $\mathrm{Sb}CH_2$ + $\mathrm{CH_2}CH_2\mathrm{CH_2}$; 9.3(s) $\mathrm{SbCH_3}$
$\mathrm{[CH_2SCH_2CH_2CH_2Sb(S)Me_2]_2}$	7.2—7.5(m) $\mathrm{S}CH_2$; 7.8—8.1(m) $\mathrm{Sb}CH_2$ + $\mathrm{CH_2}CH_2\mathrm{CH_2}$; 8.5(s) $\mathrm{Sb(S)CH_3}$
$\mathrm{[CH_2SCH_2CH_2CH_2SbPh_2]_2}$	2.4—2.8(m) $\mathrm{C_6H_5}$; 7.3—7.6(m) $\mathrm{S}CH_2$; 8.2—8.4 $\mathrm{Sb}CH_2$ + $\mathrm{CH_2}CH_2\mathrm{CH_2}$
$\mathrm{[CH_2OCH_2CH_2OH]_2}$ [b]	5.8(s) OH: 6.4(m) $\mathrm{O}CH_2$
$\mathrm{[CH_2OCH_2CH_2Cl]_2}$	6.3(m) $\mathrm{CH_2}$
$\mathrm{[CH_2OCH_2CH_2SbMe_2]_2}$	6.5(m) $\mathrm{O}CH_2$; 8.35(t) $CH_2\mathrm{Sb}$; 9.3(s) $\mathrm{SbCH_3}$
$\mathrm{[CH_2OCH_2CH_2Sb(Br_2)Me_2]_2}$	6.3(m) $\mathrm{O}CH_2$; 7.9(m) $\mathrm{Sb}CH_2$; 8.35(s) $\mathrm{Sb(Br_2)}CH_3$
$\mathrm{[CH_2OCH_2CH_2SbPh_2]_2}$	2.4—2.9(m) $\mathrm{C_6H_5}$; 6.35(m) $\mathrm{O}CH_2$; 8.3(t) $CH_2\mathrm{Sb}$

[a] In $\mathrm{CDCl_3}$ relative to internal TMS. Intensities as expected. $J(\mathrm{CH_2—CH_2})$ = 6 Hz. In the cases of the propane backbones the $CH_2\mathrm{Sb}$ + $CH_2\mathrm{CH_2}$ resonances usually overlap to give poorly resolved multiplets.

[b] Commercial sample.

Rotary evaporation of the filtrate, followed by heating to 50°C/0.1 Torr produced a viscous yellow oil ca. 50 g, 70%. The ^{1}H NMR spectrum (Table 1) showed it to be crude *N,N'*-dimethyl-*N,N'*-bis(3-hydroxypropyl)ethylenediamine. This oil (20 g, 0.1 mol) was dissolved in chloroform (100 cm^3), cooled to 0°C, and thionyl chloride (24 g, 0.2 mol) added slowly. After stirring for 1 h, the mixture was heated to reflux, cooled and poured into aqueous sodium hydroxide. The organic layer was separated, the aqueous layer extracted with diethyl ether (2 × 100 cm^3), and the combined organic layers dried ($\mathrm{Na_2SO_4}$). Evaporation of the solvents left a brownish oil (14 g, 60%) identified as *N,N'*-dimethyl-*N,N'*-bis(3-chloropropyl)ethylenediamine by its ^{1}H NMR spectrum. This oil decomposes in a few days depositing a white solid, thus it was used immediately.

A solution of sodium dimethylstibide [12] was prepared from sodium (8.3 g, 0.36 mol), $\mathrm{Me_3SbBr_2}$ (30 g, 0.09 mol) and liquid ammonia (300 cm^3). The red solution was treated dropwise with the chloroamine (9.4 g, 0.05 mol) in THF (25 cm^3), the ammonia evaporated, water (200 cm^3) and diethyl ether (200 cm^3) added. The ether layer was separated, dried ($\mathrm{Na_2SO_4}$), and the solvent distilled off. The residual yellow oil was heated to 50°C/0.01 Torr for 4 h. Yield 7.5 g, ca. 35%.

N,N'-Bis(3-diphenylstibinopropyl)-N,N'-dimethylethylenediamine (II)

A solution of lithium diphenylstibide was prepared as described [12] from Li (1.7 g, 0.24 mol), Ph_3Sb (30 g, 0.085 mol) and THF (250 cm^3), and treated with the chloroamine (see above) (7 g, 0.03 mol) until the red colour was discharged. The mixture was hydrolysed, the organic layer separated, dried and evaporated to yield the crude ligand 15 g, as a brown oil.

The oil was added to nickel(II) bromide hydrate (5 g) in n-butanol (100 cm^3) the mixture heated for 1 h, and rotatory evaporated to leave a purple oil. This was extracted overnight with diethyl ether (200 cm^3), and then with more ether (2 × 100 cm^3) and petroleum ether (200 cm^3). The washings were discarded, and the residue refluxed with "880" ammonia (100 cm^3) for 4 h, cooled and ether extracted. Evaporation of the dried extract left a fawn oil, 3.5 g, 16% (on chloramine).

1,2-Bis(3-dimethylstibinopropylthio)ethane (III)

Sodium (9.2 g, 0.4 mol) was dissolved in dry ethanol (400 cm^3) and 1,2-ethanedithiol (18.8 g, 0.2 mol) added. The mixture was heated to reflux, and 3-chloropropanol (37.6 g, 0.4 mol) added slowly. After 2 h, the majority of the ethanol was distilled off, the residue cooled, diethyl ether (400 cm^3) added, and the precipitated solid, filtered off and discarded. The filtrate was evaporated to produce a colourless oil, which slowly solidified to a greyish waxy solid, identified by ^1H NMR spectroscopy as 1,2-bis(3-hydroxypropylthio)-ethane (37 g, 88%). The hydroxy compound (31 g, 0.15 mol) was chlorinated with $SOCl_2$ (80 g, 0.3 mol) in $CHCl_3$ in a similar manner to the amine above. The product was a black oil with a pungent odour, which was further purified by shaking with aqueous sodium bicarbonate, ether extraction, drying and evaporation. Yield 13 g, 35% of 1,2-bis(3-chloropropylthio)ethane.

Sodium dimethylstibide [12] (ca. 0.11 mol) in liquid ammonia (400 cm^3) was treated with a solution of $Cl(CH_2)_3S(CH_2)_2S(CH_2)_3Cl$ (11.5 g, 0.045 mol) in THF (20 cm^3) until the red colour was discharged. The ammonia was evaporated, and the residue treated with water (200 cm^3) and ether (200 cm^3). The organic layer was separated, dried, and distilled. The residue was heated to 50°C/0.01 Torr to remove impurities. Yield 7.6 g, 35%.

1,2-Bis(3-diphenylstibinopropylthio)ethane (IV)

Lithium diphenylstibide (ca. 0.06 mol) in THF was treated with $Cl(CH_2)_3S(CH_2)_2S(CH_2)_3Cl$ (7 g, 0.03 mol) to produce a black solution. Hydrolysis was effected with saturated aqueous ammonium chloride, the organic layer separated, dried, and filtered. Evaporation produced a dark oil, which was treated with nickel(II) bromide (4 g) in n-BuOH (100 cm^3). The khaki solid was extracted with diethyl ether (3 × 150 cm^3) over a 24 h period, and the extracts discarded. The residual solid was heated under reflux with "880" ammonia (150 cm^3) for 12 h when it slowly dissolved to form a bluish solution, and a viscous oil. Ether extraction, and evaporation gave the pure ligand (3 g, 14%).

2,11-Dimethyl-2,11-distiba-5,8-dioxadodecane

$Me_2Sb(CH_2)_2O(CH_2)_2O(CH_2)_2SbMe_2$ (V) was prepared from Na (8.3 g, 0.36 mol), Me_3SbBr_2 (30 g, 0.09 mol) and $Cl(CH_2)_2O(CH_2)_2O(CH_2)_2Cl$ (6.8 g, 0.04 mol) [8] in liquid ammonia in an essentially similar manner to the nitrogen analogue. After removal of the ammonia, and hydrolysis, the ligand was extracted into diethyl ether. The extract was dried, and the ether distilled off under nitrogen, followed by removal of material volatile at 50° C/0.1 Torr. The residue was shown to be the required ligand in an essentially pure state, yield 7.1 g, 43%.

Stibine sulphide derivatives of I and III

Recrystallised sulphur (0.68 g, 2 mmol) was dissolved in refluxing toluene (25 cm^3) and the ligand (0.5 g, 1 mmol) added. After 1 h the toluene was filtered to remove some suspended solid, and the solution concentrated to ca. 5 cm^3. On standing at 0° C, a fawn solid deposited. The supernatent liquid was poured off, and the solid dried in vacuo. Both melt about room temperature.

I. Found: C, 31.2; H, 6.3; N, 5.2. $C_{14}H_{34}N_2S_2Sb_2$ calcd.: C, 31.35; H, 6.3; N, 5.2%.

III. Found: C, 26.0; H, 5.1. $C_{12}H_{28}S_4Sb_2$ calcd.: C, 26.6; H, 5.1%.

Tetrabromide derivative of V

The ligand (0.5 cm^3) was dissolved in CCl_4 (10 cm^3) and bromine diluted with CCl_4 added dropwise until a permanent orange colour was produced. The white solid was filtered off, rinsed with CCl_4 and dried in vacuo. Found: C, 16.6; H, 3.25. $C_{10}H_{24}Br_4O_2Sb_2$ calcd.: C, 16.8; H, 3.1%. M.p. 168° C dec.

Palladium(II) derivative of II and IV

A filtered solution of Na_2PdCl_4 (1.0 mmol) in ethanol (10 cm^3) was treated with the ligand (1.0 mmol) in ethanol. After stirring for 1 h, the solution was concentrated in vacuo, and the solid which separated out, filtered off, and dried.

II. Found: C, 37.6; H, 4.1; N, 2.4. $C_{34}H_{42}N_2Sb_2Pd_2Cl_4$ calcd.: C, 37.9; H, 3.9; N, 2.4%.

IV. Found: C, 42.0; H, 3.6. $C_{32}H_{24}S_2Sb_2PdCl_2$ calcd.: C, 42.0; H, 4.0%.

Acknowledgements

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