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SYNTHESIS OF *o*-PHENYLENEBIS(DIMETHYLSTIBINE) AND SOME DERIVATIVES OF DIVALENT NICKEL, PALLADIUM, AND PLATINUM AND OF ZEROVALENT CHROMIUM, MOLYBDENUM, AND TUNGSTEN

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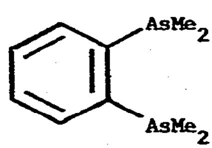
Summary

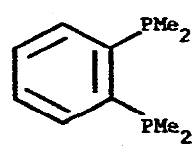
The ditertiary distibine *o*-phenylenebis(dimethylstibine) *(distib)* has been prepared in 9% yield from the reaction between sodium dimethylstibide and *o*-bromoiodobenzene in liquid ammonia. The distibine readily forms the square-planar complexes $[MX_2(distib)]$ (where M = Pd or Pt and X = Cl,Br,I, or SCN) and the five co-ordinate diamagnetic complex $[NiCl(distib)_2]Cl$. UV irradiation of solutions of chromium, molybdenum, and tungsten hexacarbonyls in tetrahydrofuran with the ligand affords the expected octahedral complexes $[M(CO)_4(distib)]$ (where M = Cr,Mo, or W). A weaker ligand field strength of the ditertiary distibine compared with the analogous ditertiary diarsine is indicated by a comparison of the electronic spectra of the Pd^{II} and Ni^{II} complexes of both ligands.

Introduction

Since the preparation of *o*-phenylenebis(dimethylarsine) by Chatt and Mann [1] in 1939 there has been much interest in preparing similar chelating agents [2]. The corresponding ditertiary diphosphine has been synthesised [3] and some of its metal complexes described [4]-[6]. In addition the mixed Group VB donor atom bidentates, for example, the amino- [7] and phosphino-arsines [8](IV), the amino- [9] and arsino-stibines [10](V) and the phosphino- and arsino-stibines [11](VI) have been prepared. We report here full details [12] of the synthesis of the antimony analogue of the ditertiary diarsine (I) and diphosphine (II), namely *o*-phenylenebis(dimethylstibine) (III) and some of its metal chelates.



(I)



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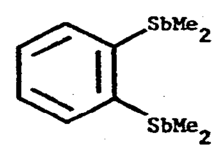
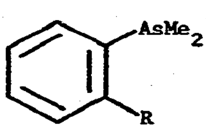
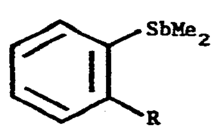


(III)



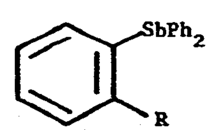
(IV)

(where R = NMe_2 or PEt_2)



(V)

(where R = NMe_2 or $AsMe_2$)



(VI)

(where R = PPh_2 or $AsPh_2$)

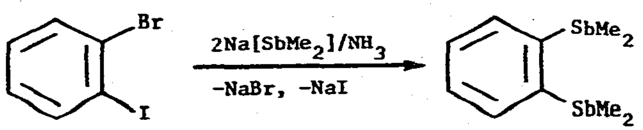
Results and discussion

Preparation of *o*-phenylenebis(dimethylstibine)(III)

The following series of reactions were used to synthesise (III):

$$SbCl_3 \xrightarrow[-3MgClI]{3MeMgI} SbMe_3 \xrightarrow{Br_2} Me_3SbBr_2 \qquad (1)$$

$$Me_3SbBr_2 \xrightarrow[-MeBr]{\Delta} Me_2SbBr \xrightarrow[-NaBr]{2Na/NH_3} Na[SbMe_2] \qquad (2)$$



(3)

The ditertiary distibine(III) is a yellow air-sensitive liquid b.p. 124 - 125° C/0.5 mm, which could only be obtained in small quantities because of the low yield (9%) in the last step (eq. 3). The major product of the reaction was tetramethyldistibine b.p. 46 - 47° C/0.5 mm which was readily separated by fractional distillation, however, and which apparently arose from an oxidative coupling of the anion (eq. 5) and not from its incomplete formation in the first place (eq. 4) since in the case of reaction 3 the deep-red colour persisted until almost all of the *o*-bromoiodobenzene had been added.

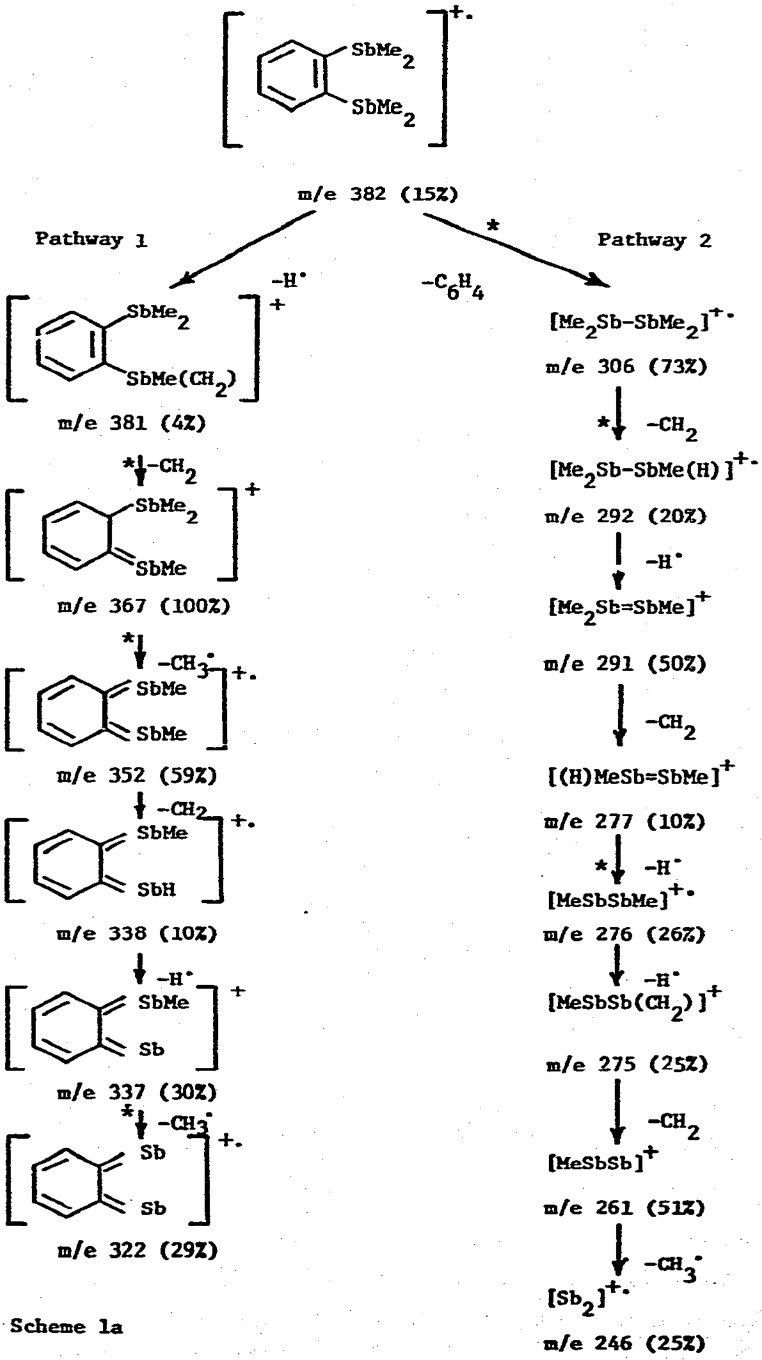
$$2Me_2SbBr \xrightarrow[-2NaBr]{2Na/NH_3} 2[Me_2Sb\cdot] \longrightarrow Me_2SbSbMe_2 \qquad (4)$$

$$Me_2SbSbMe_2 \underset{Oxidation(-2Na^+,-2e)}{\overset{2Na}{\rightleftharpoons}} 2[Me_2Sb]Na \qquad (5)$$

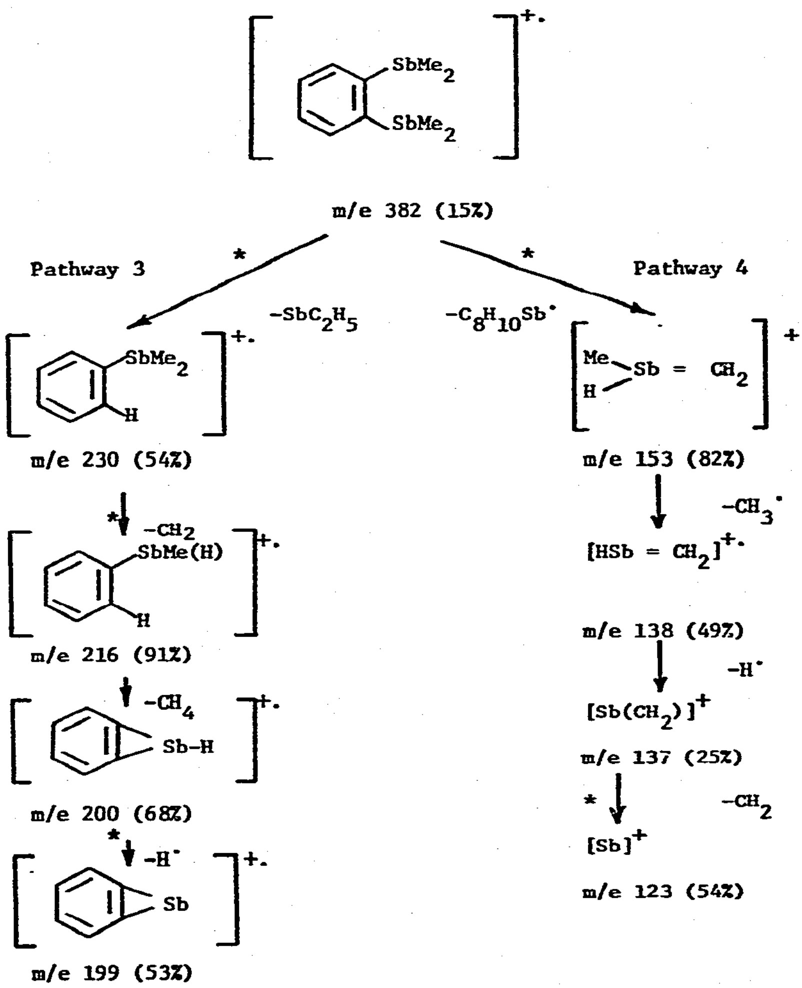
Accordingly the yield of (III) was not improved by increasing the reaction time. When *o*-dibromobenzene was used as the aromatic substrate the yield of (III) was further reduced (2-5%) and when a reaction between the anion and *o*-dichlorobenzene in liquid ammonia was attempted none of the desired product was obtained although the same reaction with the corresponding arsenide ion in tetrahydrofuran as solvent affords the diarsine(I) in 44.5% yield [13].

<u>Physical properties of *distib*</u>

In addition to a correct elemental analysis the ^1H n.m.r. spectrum of (III) in $CDCl_3$ showed a sharp singlet at δ 0.98 and a multiplet at δ 7.08 - 7.62 with an intensity ratio corresponding to the methyl and


SbMe2
SbMe2
m/e 382 (15%)
Pathway 1
Pathway 2
-H·
-C6H4
*
SbMe2
SbMe(CH2)
m/e 381 (4%)
-CH2
SbMe2
SbMe
m/e 367 (100%)
-CH3·
SbMe
SbMe
m/e 352 (59%)
-CH2
SbMe
SbH
m/e 338 (10%)
-H·
SbMe
Sb
m/e 337 (30%)
-CH3·
Sb
Sb
m/e 322 (29%)
[Me2Sb-SbMe2]+·
m/e 306 (73%)
-CH2
[Me2Sb-SbMe(H)]+·
m/e 292 (20%)
-H·
[Me2Sb=SbMe]+
m/e 291 (50%)
-CH2
[(H)MeSb=SbMe]+
m/e 277 (10%)
-H·
[MeSbSbMe]+·
m/e 276 (26%)
-H·
[MeSbSb(CH2)]+
m/e 275 (25%)
-CH2
[MeSbSb]+
m/e 261 (51%)
-CH3·
[Sb2]+·
m/e 246 (25%)

Scheme 1a



Scheme 1b

Observed metastable peaks are indicated by an asterisk.

aromatic protons, respectively. A sample of (III) exhibited a molecular ion at $^{m}/_{e}$ 382 (15%) in its mass spectrum at 70 eV. Because of the importance of the basic structure the whole spectrum is reproduced in Figure 1 and details of the four different fragmentation pathways observed are summarised in Scheme 1. For simplicity only the mass values for the Sb 123 isotope are quoted in Scheme 1.

The mass spectrum of (III) showed some similarities to the spectrum

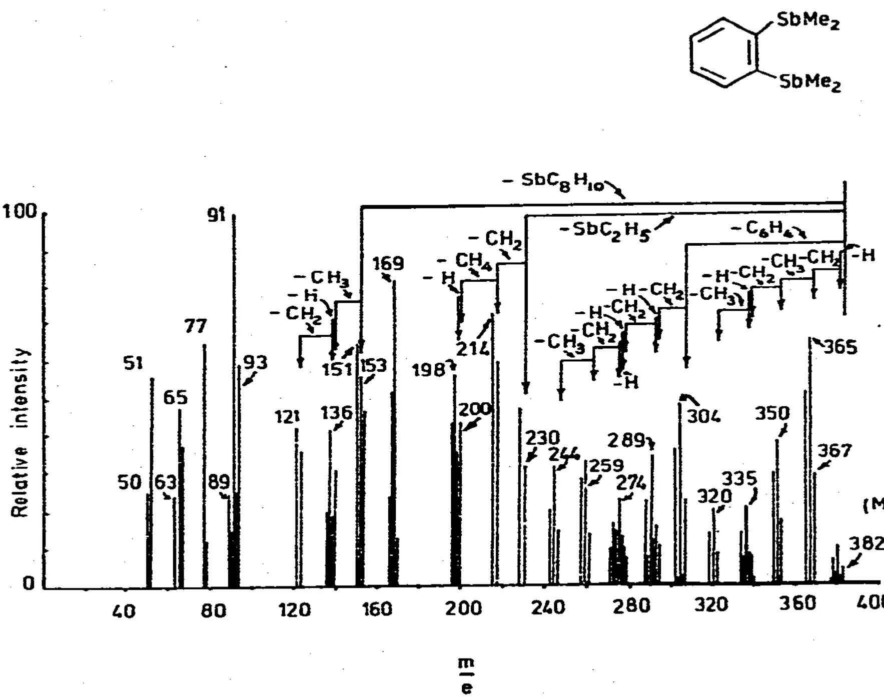


Figure 1. Diagram of mass spectrum of *o*-phenylenebis (dimethylstibine). E. Shewchuk and S.B. Wild, Synthesis of *o*-phenylenebis(dimethylstibine) and some derivatives of divalent nickel, palladium, and platinum and of zerovalent chromium, molybdenum and tungsten.

of the arsenic analogue (I)[14]. The salient features arising from a comparison of the fragmentation patterns of the two ligands are (i), the most abundant ion containing a Group VB atom is in both cases $[M-CH_3]^+$ (ii), the distibine fragments to a greater degree than the diarsine and (iii) the distibine affords ions containing the Sb-Sb linkage (Pathway 2) which are absent from the spectrum of the diarsine.

<u>Complexes of Pd^{II} and Pt^{II}</u>

The distibine(III) readily forms complexes of the type $[MX_2(distib)]$

(where M = Pd or Pt and X = Cl,Br,I, or SCN). The bright yellow complex $[PdCl_2(distib)]$ was prepared by adding one equivalent of the bidentate to a solution of $PdCl_2$ dissolved in concentrated hydrochloric acid and diluted with methanol. The other derivatives were simply prepared by metatheses with the appropriate salts using a two-phase CH_2Cl_2/H_2O solvent system. The divalent platinum complexes were obtained similarly from the pale yellow $[PtCl_2(distib)]$ complex which readily precipitated from an aqueous solution of $K_2[PtCl_4]$ when a solution of the distibine in ethanol was added.

The diamagnetic complexes $[MX_2(distib)]$ vary in colour from pale yellow to orange-red and are non-electrolytes in nitrobenzene solution. The square-planar complexes are moderately soluble in organic solvents and details of their physical properties and elemental analyses are summarised in Table 1. The position of the sharp singlet resonance for the equivalent Sb-Me groups in each of the complexes occurs 0.64 – 0.90 p.p.m. downfield from the same resonance in the free ligand and clearly depends on the electronegativity of the group X and its effect on the strength of the σ-bond between the antimony atoms and the platinum metals.

The infrared spectra of the compounds $[M(SCN)_2(distib)]$ show a sharp singlet ν(CN) vibration at 2102 and 2100 cm^{-1} for the Pd^{II} and Pt^{II} compounds respectively, which is clearly diagnostic of S-bonded thiocyanato ligands. Unfortunately, however, the ν(CS) absorption could not be observed in these complexes because of the strong distibine vibrations in the same region although our assignment is consistent with that proposed [15] for the bonding in $[Pd(SCN)_2(diars)]$ (where diars = I).

The visible absorption spectrum of a solution of $[PdCl_2(distib)]$ in dimethylformamide solution shows three absorption bands which are centred at 25090 (ε = 2020), 39500 (ε > 10000), and 36200 cm^{-1} (ε > 5000). The intense bands are change transfer bands but the weak absorption band may be assigned to the transition $^1A_1 \longrightarrow {}^1E$ in accordance with the analysis of the spectra of complexes of this type made by Ho *et al.*[16] which is based on absorption and circular-dichroism studies. For the compound $[PdCl_2(diars)]$ (where diars = I) in the same solvent this transition is observed

TABLE 1

DETAILS OF PHYSICAL PROPERTIES AND ELEMENTAL ANALYSES OF THE COMPOUNDS [MX_2(distib)]

Compound	Colour	M.p. (^{o}C)	Yield (%)	Analyses: Found(Calcd.)(%) C	H	δ(Sb-Me)/p.p.m. ($CDCl_3$)
[$PdCl_2$(distib)]	Yellow	147-148	81	21.2 (21.6)	2.6 (2.9)	1.62(s)
[$PdBr_2$(distib)]	Orange	105-106 (decomp.)	86	18.8 (18.6)	2.4 (2.5)	1.78(s)
[PdI_2(distib)]	Orange-red	102-103 (decomp.)	80	16.5 (16.2)	2.1 (2.2)	1.84(s)
[$Pd(SCN)_2$(distib)]	Yellow-orange	177-179 (decomp.)	82	23.8 (23.9)	2.6 (2.7)	1.88(s)
[$PtCl_2$(distib)]	Pale yellow	163-164	52	18.7 (18.6)	2.3 (2.5)	1.67(s)
[$PtBr_2$(distib)]	Yellow	195-196 (decomp.)	80	16.2 (16.4)	2.3 (2.2)	1.71(s)
[PtI_2(distib)]	Deep yellow	213-214 (decomp.)	85	14.4 (14.5)	2.1 (2.0)	1.74(s)
[$Pt(SCN)_2$(distib)]	Yellow	205-207	80	20.7 (20.9)	2.4 (2.3)	1.82(s)

at 27630 cm^{-1} (ϵ = 1830) which indicates that the diarsine has the stronger ligand field strength of the two.

Complexes of Ni^{II}

When a solution containing two mole equivalents of *distib* in ethanol was treated with $[Ni(H_2O)_6]Cl_2$ in the same solvent a deep red solution resulted from which red $[NiCl(distib)_2]Cl$ could be precipitated by the addition of cyclohexane. The salt is diamagnetic and is a uni-univalent electrolyte in nitrobenzene solution and is therefore apparently five co-ordinate in this solvent. The electronic spectrum in ethanol or nitrobenzene solutions at 300° K shows absorptions at 18300 (ϵ = 700) and 23000 cm^{-1} (ϵ = 200) which may be assigned to d-d transitions in the low-spin complex and a strong absorption above 29500 cm^{-1} (ϵ > 5000) which is due to charge transfer transitions. The spectrum of the distibine complex is very similar to those reported by Preer and Gray[17] for the complexes $[NiX(diars)_2]X$ (where diars = I and X = Cl,Br, or I) at 300 and 77° K. They observed d-d transitions at 21285 (ϵ = 1060) and 25895 cm^{-1} (ϵ = 170) at 300° K for the complex $[NiCl(diars)_2]Cl$ which were assigned to the transitions $^1A_1 \longrightarrow {}^1E$ and $^1A_1 \longrightarrow {}^1A_2$, respectively, of a low-spin square pyramidal structure.

The electronic spectrum of $[NiCl(distib)_2]Cl$ is also similar to the one obtained for $[NiCl(SP)_2]Cl$ [where SP = (*o*-methylthiophenyl) diphenylphosphine][18]. A square pyramidal structure was also suggested for $[NiCl(Sb\text{-}As)_2]Cl$ (where Sb-As = *o*-dimethylarsinophenyldimethylstibine [10] or *o*-diphenylarsinophenyldiphenylstibine[11]) using similar arguments. Again, as found in the case of square-planar Pd^{II} complexes, the ligand field strength of (III) is weaker than that of (I).

Complexes of Cr^0, Mo^0 and W^0

The UV irradiation of equimolar quantities of (III) with chromium, molybdenum, or tungsten hexacarbonyl affords the octahedral tetracarbonyls $[M(CO)_4(distib)]$ (where M = Cr,Mo, or W) and details of their physical properties are given in Table 2.

TABLE 2

DETAILS OF PHYSICAL PROPERTIES OF THE COMPOUNDS [$M(CO)_4$(distib)]

Compound	Colour	M.p. (°C)	δ(Sb-Me)/p.p.m. ($CDCl_3$)	ν(CO)/cm^{-1} ($CHCl_3$)
[$Cr(CO)_4$(distib)]	White	127-128 (decomp.)	1.38(s)	2010m, 1930s, 1915s, 1852s
[$Mo(CO)_4$(distib)]	White	212-213	1.36(s)	2022m, 1948s, 1918s, 1857s
[$W(CO)_4$(distib)]	White	> 200	1.33(s)	2025m, 1965s, 1930s, 1870s

The ^{1}H n.m.r. spectra of these complexes showed a singlet $Sb-CH_3$ resonance which was indicative of the *distib* behaving as a chelating ligand. The downfield shift of the Sb-Me resonance upon co-ordination of the *distib* to the zerovalent Group VI B metals was considerably less than that observed in the complexes of divalent palladium and platinum. This observation may be rationalised in terms of an increased electron density on the antimony atoms in the zerovalent complexes.

The infrared spectra of the complexes in solution in the ν(CO) region are consistent with octahedral structures of C_{2v} symmetry for which four infrared active stretching vibrations ($2A_1+B_1+B_2$) are expected. The infrared spectra of the complexes are very similar to those observed for $[M(CO)_4(diars)]$ (where M = Cr,Mo, or W)[19].

Experimental

All reactions were carried out in an atmosphere of pure nitrogen using the Schlenk technique. Solvents were dried in the usual way and degassed by distillation through a stream of pure nitrogen.

Microanalyses were carried out by the Australian Microanalytical Service, Melbourne and by Alfred Bernhardt, Max Planck Institute, Mülheim, Germany. The ^{1}H n.m.r. spectra were recorded at 60 MHz (35° C) using a Varian A-60 spectrometer and chemical shifts are quoted relative to tetramethylsilane as internal standard. The electronic spectra were recorded on solutions in matched 1 cm quartz cells at 27° C using Unicam SP700 recording and Hitachi Perkin-Elmer 139 spectrophotometers. The mass spectra were determined at 70 eV using a Varian MAT CH_4 mass spectrometer. The conductivity measurements were made with a Phillips Bridge (PR 9500) and the magnetic susceptibilities were determined at 25°C by the Faraday method using silver shot for calibration.

The method of Morgan and Davies [20] was used to prepare Me_2SbBr although the decomposition of the Me_3SbBr_2 was carried out at 15 mm. Literature methods were also used to prepare *o*-bromoiodobenzene[21] and dichloro[*o*-phenylenebis(dimethylarsine)]palladium(II)[22].

o-Phenylenebis(dimethylstibine),(III). The addition of small sodium pieces (4.27 g, 186 mmol) to a stirred suspension of Me_2SbBr (21.3 g, 93 mmol) in liquid ammonia (400 cm^3, distilled off Na) produced a deep red solution of sodium dimethylstibide. The solution of the anion was stirred for 1 h and then treated dropwise with *o*-bromoiodobenzene (11.55 g, 42.3 mmol) which almost decolourised the solution. The ammonia was allowed to slowly boil off (*ca* 3.5 h) and tetrahydrofuran (400 cm^3) was added to the almost colourless residue. The mixture, which consisted of a yellow solution and a greyish-white solid, was refluxed for 2.5 h and then stirred for 16 h at 25° C. The tetrahydrofuran was removed under reduced pressure and replaced by diethyl ether (400 cm^3) and the reaction mixture cautiously hydrolysed with water (200 cm^3). Separation of the two layers followed by drying of the organic layer ($MgSO_4$), filtration, and removal of the solvent left a yellow liquid which was fractionally distilled to yield a low boiling fraction b.p. 46 – 47° C/0.5 mm (tetramethyldistibine, 8.5 g, 60%) and a viscous yellow residue. The high boiling fraction was distilled twice to give pure *o*-phenylenebis(dimethylstibine) as a yellow air-sensitive liquid b.p. 124-125° C/0.5 mm (1.4 g, 9%) (Found: C, 31.5; H, 4.2; Sb, 64.0. Calcd. for $C_{10}H_{16}Sb_2$: C, 31.6; H, 4.25; Sb, 64.1%).

Dichloro[*o*-phenylenebis(dimethylstibine)]palladium(II). Palladous chloride (0.07 g, 0.4 mmol) was dissolved in concentrated hydrochloric acid (1 cm^3) and the solution diluted with methanol (10 cm^3); treatment of this solution with *distib* (0.15 g, 0.4 mmol) in ethanol (10 cm^3) resulted in a yellow solution which when concentrated deposited the bright yellow *complex* (0.18 g).

The complexes [PdX_2(distib)] (where X = Br, I, or SCN).

These derivatives were prepared by mixing a solution of [$PdCl_2$(distib)] in dichloromethane with a six fold excess of an aqueous solution of NaBr, NaI, or KSCN, respectively. After shaking the mixture for 10 min the organic layer was separated, dried over $MgSO_4$, filtered and evaporated to dryness to yield the crude crystalline complexes.

Dissolution of these in a small quantity of dichloromethane followed by dropwise addition of cyclohexane afforded the pure complexes as crystalline solids after drying *in vacuo*.

The yields, analytical data, and physical properties of these complexes are summarised in Table 1.

Dichloro[*o*-phenylenebis(dimethylstibine)]platinum(II). A solution of $K_2[PtCl_4]$(0.18 g, 0.45 mmol) in water (10 cm^3) was added dropwise to *distib* (0.17 g. 0.45 mmol) in ethanol causing the precipitation of the pale yellow product which was filtered off and dried *in vacuo* (0.15 g).

The complexes $[PtX_2(distib)]$ (where X = Br,I, or SCN).

These were prepared in the same way as described for their palladium analogues and details of yields and properties are given in Table 1.

Chlorobis[*o*-phenylenebis(dimethylstibine)]nickel (II) chloride.

A deep red solution formed immediately when $[Ni(H_2O)_6]Cl_2$ (0.02 g, 0.1 mmol) in ethanol (10 cm^3) was added to *distib* (0.08 g, 0.21 mmol) in the same solvent (30 cm^3). The reaction mixture was stirred for 10 mins, concentrated to *ca.* 5 cm^3, and carefully diluted with cyclohexane to yield a deep red solid which was collected and then dried *in vacuo* (25° C), m.p. > 250° C (0.04 g, 45%) (Found: C, 26.5, H, 3.7. Calcd. for $C_{20}H_{32}Cl_2Sb_4Ni$; C, 27.0; H, 3.6%). μ_{eff} = 0.0 B.M. (30° C). Conductivity: 25.8 cm^2 ohm^{-1} mol^{-1} (10^{-3}M in $PhNO_2$).

Tetracarbony[*o*-phenylenebis(dimethylstibine)]chromium(0). A solution of $Cr(CO)_6$ (0.05 g, 0.23 mmol) in tetrahydrofuran (30 cm^3) containing *distib* (0.09 g, 0.24 mmol) was irradiated with UV light for 2.5 h by which time the evolution of CO had ceased. The solvent was removed from the yellow solution and the residue recrystallised from dichloromethane by the addition of n-hexane to afford the product (0.04 g, 32%) (Found: C, 30.5; H . 2.7: Calcd. for $C_{14}H_{16}O_4Sb_2Cr$: C, 30.9; H, 3.0%). Physical details are given in Table 2.

Tetracarbonyl[*o*-phenylenebis(dimethylstibine)]molybdenum(0). From $Mo(CO)_6$ (0.05 g, 0.2 mmol) and *distib* (0.08 g, 0.21 mmol) as described above (0.05 g, 43%)' (Found: C, 28.3; H, 2.6. Calcd. for $C_{14}H_{16}O_4Sb_2Mo$: C, 28.6; H, 2.75%).

Tetracarbonyl[*o*-phenylenebis(dimethylstibine)]tungsten (0). In the same $W(CO)_6$ (0.09 g, 0.26 mmol) and *distib* (0.10 g, 0.27 mmol) afforded the *product* (0.06 g, 34%) (Found: C, 24.7; H, 2.3. Calcd. for $C_{14}H_{16}O_4Sb_2W$: C, 24.9; H, 2.4%).

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