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Platinum Metal Complexes of the Methoxyphenylstibines $Ph_{3-n}Sb(o\text{-}MeOC_6H_4)_n$ (n = 1, 2, 3), $o\text{-}Me_2SbC_6H_4OMe$ and of $Me_2Sb(CH_2)_2O(CH_2)_2O(CH_2)_2SbMe_2$

SIMON J. HIGGINS, WILLIAM LEVASON*, FRANCIS P. McCULLOUGH** and BAHARUDDIN SHEIKH

Department of Chemistry, The University, Southampton SO9 5NH, U.K.

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The stibine-ether $Me_2Sb(o\text{-}C_6H_4OMe)$ (L) forms cis-*$[PdL_2Cl_2]$,* cis-*$[PtL_2Cl_2]$,* fac-*$[RhL_3Cl_3]$ and* mer-*$[IrL_3Cl_3]$ which contain the ligand bonded only through antimony, and $[RhL_2Cl_3]$ which contains one monodentate (Sb-coord) and one chelating (Sb–O) ligand. The latter complex reacts with CO to give $[RhL_2(CO)Cl_3]$. The $Ph_{3-n}Sb(o\text{-}C_6H_4OMe)_n$ (n = 1, 2, 3) form only* mer-*$[RhL_3Cl_3]$ and* mer-*$[IrL_3Cl_3]$. For Pd(II) and Pt(II) the $[ML_2Cl_2]$ complexes are* trans *when L = $Sb(o\text{-}C_6H_4OMe)_3$, but* cis *with L = $Ph_2Sb(o\text{-}C_6H_4OMe)$. The potentially tetradentate $Me_2Sb(CH_2)_2O(CH_2)_2O(CH_2)_2SbMe_2$ (L′), behaves as a* trans *chelating bidentate in $[PdL'Cl_2]$, and coordinates only via the antimony. The preparations of $RhL'Cl_3$, $IrL'Cl_3$, $RuL'Cl_3$, $RuL'(CO)Cl_2$ and $(OsCl_4)_2L'\cdot H_2O$ are described. Infrared, electronic and ^1H NMR spectra are reported for all the complexes.*

Introduction

There has been considerable recent interest in the platinum metal complexes of ligands containing both hard (typically $-NR_2$ or -OR) and soft ($-PR_2$, AsR_2) donor groups [1–9]. The hard donor often binds relatively weakly to these soft metal ions, and dissociates readily, or is easily displaced often reversibly by incoming soft substrates such as carbon monoxide. These reactions are clearly very relevant to homogeneous catalytic systems. Phosphine-ether ligands bond only through the phosphorus to Pd(II), Pt(II), Rh(I) or Ir(I) [1, 2, 4–6, 9], but behave as P, O donors to Ru(II) [12]. In the cases where the -OR group is not directly bound to the metal it can still exert a profound effect on the chemistry, *e.g. trans*-$[IrL_2(CO)Cl]$ (L = $Me_2P(o\text{-}C_6H_4OMe)$) undergoes much faster oxidative addition than the analogues with L = PMe_2Ph or $PMe_2(p\text{-}C_6H_4OMe)$, due to direct O → Ir interaction in the former case increasing the nucleophilicity [4]. Ligands containing bulky substituents at phosphorus have also been shown to undergo O or C metallation at Pt(II), and with Rh and Ir can generate rare examples of the M(II) oxidation states [6, 9]. The arsine-ether $Me_2As(o\text{-}C_6H_4OMe)$ was investigated some years ago [10, 11], but the only work on stibine-ether complexes is some preliminary data on $Me_2Sb(o\text{-}C_6H_4OMe)$ by Volponi *et al.* [12–14]. Here we describe some systematic studies of platinum metal complexes of four *o*-methoxyphenylstibines. A preliminary account of aspects of this work has been communicated [15].

Experimental

Physical measurements were made as described previously [16]. The syntheses of the *o*-methoxyphenylstibines [17] and $Me_2Sb(CH_2)_2O(CH_2)_2O(CH_2)_2SbMe_2$ [18] have been described elsewhere.

The complexes were prepared by similar routes, representative examples of which are described. Complexes of $Me_2SbC_6H_4OMe$ and $Me_2Sb(CH_2)_2O(CH_2)_2O(CH_2)_2SbMe_2$ were made under a dinitrogen atmosphere.

Dichlorodi(o-methoxyphenyldimethylstibine)palladium(II)

A solution of sodium tetrachloropalladate(II) (0.3 g 1 mmol) in ethanol (10 cm^3) was treated with the ligand (0.51 g 2 mmol) in CH_2Cl_2 (10 cm^3) and the mixture warmed gently (<40 °C) for 2 hours. The yellow solution was filtered, and diethyl ether added slowly to the filtrate to precipitate the complex, which was filtered off and dried *in vacuo* 65%.

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*Author to whom correspondence should be addressed.

**Present address: Dow Chemicals (Texas Division), I + MR Freeport, Tex., U.S.A.

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The other Pd(II) complexes were prepared similarly and recrystallised by extraction with warm CH_2Cl_2, and concentration of the extract under reduced pressure, followed by precipitation with diethyl ether. 50–60% yields.

Dichlorodi(o-methoxyphenyldiphenylstibine)platinum(II)

Potassium tetrachloroplatinate(II) (0.41 g 1 mmol) dissolved in a 1:1 mixture of water and ethanol (20 cm^3), was added to the ligand (0.77 g, 2 mmol) in dichloromethane (30 cm^3), and the mixture refluxed for 2 hours. The yellow solution was concentrated to *ca.* 15 cm^3 under reduced pressure, and diethyl ether added dropwise to precipitate the complex (78%). The product was recrystallised from CH_2Cl_2/Et_2O.

Trichlorotris(o-methoxyphenyldiphenylstibine)rhodium(III)

To a solution of the ligand (1.14 g 3 mmol) in CH_2Cl_2 (10 cm^3) a warm ethanol (10 cm^3) solution of $RhCl_3 \cdot 3H_2O$ (0.26 g 1 mmol) was added, and the mixture refluxed gently for 2 hours, and cooled. Diethyl ether (10 cm^3) was added slowly, and the red-brown solid which separated on standing filtered off, rinsed with diethyl ether and dried (48%).

Trichlorotris(o-methoxyphenyldimethylstibine)rhodium(III)

A solution of rhodium(III) chloride hydrate (0.26 g 1 mmol) in ethanol (10 cm^3) was treated with the ligand (0.9 g 3.5 mmol) in ethanol (10 cm^3) and the mixture gently refluxed for 3 hours. The solution was filtered, cooled, and the yellow crystals which separated on standing filtered off and dried (*ca.* 50%).

Trichlorobis(o-methoxyphenyldimethylstibine)rhodium(III)

Was prepared in an essentially similar manner to the tris complex using a 1:1.5 Rh:L ratio (70%).

Trichlorobis(o-methoxyphenyldimethylstibine)carbonylrhodium(III)

A solution of $[Rh(Me_2SbC_6H_4OMe)_2Cl_3]$ (1 mmol) in $CH_2Cl_2/CHCl_3$ [1:1 20 cm^3] was stirred under carbon monoxide for 24 hours, and then the solvent was removed *in vacuo*. Yield quantitative.

Trichlorotris(o-methoxyphenyldiphenylstibine)iridium(III)

A hot solution of the ligand (1.14 g 3 mmol) in n-butanol (25 cm^3) was added to a solution of iridium trichloride hydrate (0.35 g 1 mmol) in a 1:1 ethanol/H_2O mixture (30 cm^3), and the solution refluxed for 4 hours. The solution was rotatory evaporated to *ca.* 10 cm^3, and the solid precipitated by dropwise addition of diethyl ether (75%).

[Pd(dsde)Cl₂]

A cold solution of Na_2PdCl_4 (0.3 g 1 mmol) in ethanol 10 cm^3, was stirred whilst the ligand (0.42 g 1 mmol) in CH_2Cl_2 (10 cm^3) was added. After 1 hour, the solution was filtered from some black material, and the solvent removed *in vacuo*. The oil produced was extracted with $CHCl_3$ (10 cm^3) and the extract concentrated to *ca.* 2 cm^3, when dry hexane (10 cm^3) was added with vigorous stirring. The solid which separated was filtered off and dried (~50%).

[Rh(dsde)Cl₃]

A solution of $RhCl_3 \cdot 3H_2O$ (0.26 g 1 mmol) in ethanol (10 cm^3) was refluxed with dsde (0.42 g 1 mmol) for 1 hour, and the solution cooled. The red solid which separated was filtered off, rinsed with diethyl ether and dried *in vacuo* (70%).

$Ir(dsde)Cl_3$ and $Ru(dsde)Cl_3$ were prepared similarly from $IrCl_3 \cdot 3H_2O$ and $RuCl_3 \cdot 3H_2O$ respectively, and $Ru(dsde)(CO)Cl_2$ and $(OsCl_4)_2dsde \cdot H_2O$ were prepared in 2-ethoxyethanol.

Results and Discussion

Palladium(II) and Platinum(II)

The reaction of the four methoxyphenylstibine ligands (L) with Na_2PdCl_4 in a 2:1 mol ratio in ethanol/dichloromethane produced yellow $[PdL_2Cl_2]$ complexes, and the $[PtL_2Cl_2]$ analogues were obtained similarly using K_2PtCl_4 in $H_2O/EtOH/CH_2Cl_2$ (1:2:1). The $[M(Me_2Sb(o\text{-}C_6H_4OMe))_2Cl_2]$ (M = Pd, Pt) have been reported previously [12, 13], and our results are in good agreement (Table I) and lead to the assignment of *cis* square planar geometry to both complexes. The six $[ML_2Cl_2]$ [L = $Ph_{3-n}Sb(o\text{-}C_6H_4OMe)_n$ (n = 1, 2, 3)] have similar electronic spectra characteristic of planar complexes with Sb_2Cl_2 donor sets [19, 20]. The far IR spectra of stibine complexes generally contain strong ligand absorptions which may make assignments of structures based upon identification of the ν(M–Cl) difficult. The ν(M–Cl) vibrations identified (Table I) are consistent with the assignment of *cis* planar [20] structures to $[Pd(Ph_2Sb(o\text{-}C_6H_4OMe))_2Cl_2]$ and $[Pt(L)_2Cl_2]$ (L = $Ph_2Sb(o\text{-}C_6H_4OMe)$, $PhSb(o\text{-}C_6H_4OMe)_2$) in the solid state. The $[M(Sb(o\text{-}C_6H_4OMe)_3)_2Cl_2]$ however contain only one moderately strong ν(M–Cl) vibration at 340 (Pt) and 350 (Pd) cm^{-1} consistent with a *trans* structure. The yellow $[Pd(PhSb(o\text{-}C_6H_4OMe)_2)_2Cl_2]$ is unusual in that three bands at 360, 330, 300 cm^{-1} assignable as ν(Pd–Cl) were observed, which are probably due to both *cis* and *trans* isomers present in the solid. Several samples of this material

TABLE I. Methoxyphenylstibine Complexes.

Complex	Colour	C%	H%	IR (cm^{-1})		$E_{max} \times 10^{-3}$ cm^{-1} (ϵ_{mol})[a]	^1H NMR (δ)[b]	
				ν(Aryl–OMe)	ν(M–Cl)		Me–Sb	Me–O
PdL_2Cl_2								
L = $Me_2SbC_6H_4OMe$	yellow	31.1(31.0)	3.5(3.7)	1250	314, 300	25.8(4960), 32.3sh(12500)	1.45	3.7
$Ph_2SbC_6H_4OMe$	yellow	47.9(48.3)	3.8(3.8)	1250	310sh	24.6sh(5300), 32.2(20000)		3.8, 3.4[3:1]
$PhSb(C_6H_4OMe)_2$	yellow	48.2(47.8)	3.8(3.8)	1250	360, 330, 300	24.8(6200), 30.5(16500)		3.8, 3.3[5:1]
$Sb(C_6H_4OMe)_3$	deep yellow-green	47.2(47.5)	3.5(4.0)	1250	350	25.5(6020), 30.5(14000)		3.75
PtL_2Cl_2								
L = $Me_2SbC_6H_4OMe$	pale yellow	28.0(27.8)	3.1(3.3)	1250	310, 285	26.5sh(450), 32.0(2500)	1.5	3.75
$Ph_2SbC_6H_4OMe$	pale yellow	44.3(44.2)	3.4(3.3)	1248	320	24.6sh, 26.45(1650), 30.75(7570)		3.4
$PhSb(C_6H_4OMe)_2$	pale yellow	43.9(44.0)	3.6(3.5)	1250	325, 290	25.0(1900), 31.2(9030)		3.4
$Sb(C_6H_4OMe)_3$	pale green-yellow	43.0(43.6)	3.4(3.6)	1250	340	31.4sh(5400)		INSOL
RhL_3Cl_3								
L = $Me_2SbC_6H_4OMe$	yellow	33.3(32.9)	3.3(3.5)	1250	310	25.5(4460)sh, 33.33(29800)	1.4	3.7
$Ph_2SbC_6H_4OMe$	orange-red	50.0(50.6)	3.6(3.8)	1250	340	21.8(1640)sh, 33.3(20350)		3.7, 3.4[2:1]
$PhSb(C_6H_4OMe)_2$	dull-orange	49.7(49.7)	4.0(3.9)	1250	345, 305sh	20.6(1070)sh, 33.8(20600)		3.7-3.4(br)
$Sb(C_6H_4OMe)_3$	dull-orange	49.4(49.25)	4.1(4.1)	1250, 1240	330, 275sh	20.9(1730)sh, 34.25(50700)sh		3.7-3.2(*mult*)
RhL_2Cl_3								
L = $Me_2SbC_6H_4OMe$	red-brown	30.2(29.8)	3.4(3.6)	1250, 1223	335, 280	22.2(2315)sh, 30.1(11100), 37.9(31000)	1.3, 1.6	3.2, 3.8 [1.1, 1.3, 3.7, 3.85[c]
$[Rh(Me_2SbC_6H_4OMe)_2(CO)Cl_3]$	pale brown	29.7(30.2)	3.3(3.4)	1255, 1250sh	310, 283	25.0(940)sh, 35.5(10760)sh	1.3	3.8[c]
				ν(C≡O) = 2072 (CH_2Cl_2), 2065 (solid)				
IrL_3Cl_3								
L = $Me_2SbC_6H_4OMe$	yellow	30.3(30.3)	3.1(3.3)	1248	315, 290sh	32.0(11500), 34.9(11700)	1.4, 1.7	3.8, 3.6
$Ph_2SbC_6H_4OMe$	pale yellow	45.8(45.5)	3.3(3.5)	1248	320	32.5(10200)sh, 34.9(18700)sh		3.7, 3.5[2:1]
$PhSb(C_6H_4OMe)_2$	yellow	46.2(46.8)	3.6(3.7)	1250	315sh	32.3(12200)sh, 36.2(21300)sh	–	3.8, 3.2(br)
$Sb(C_6H_4OMe)_3$	pale yellow	46.4(46.5)	3.9(3.9)	1245	310, 285	30.7(5220)sh, 34.5(58200)sh	–	3.7(br)

[a] CH_2Cl_2 solution. [b] $CDCl_3$ shifts relative internal TMS (δ scale). [c] $(CD_3)_2SO$ solution.

were prepared, and all had the same far IR spectrum. The presence of both *cis* and *trans* forms in the solid probably results from similar solubilities of the two isomers. All these complexes contain a medium intensity vibration at *ca.* 1250 cm^{-1} also present in the free ligands attributable to an aryl–OMe stretch, which confirms the -OMe group is not coordinated to the metal [1, 2].

In $CDCl_3$ solution the ^1H NMR spectra (Table I) indicate that only one isomer of $[Pd(Sb(o\text{-}C_6H_4\text{-}OMe)_3)_2Cl_2]$ is present since only a single sharp -OMe resonance is seen at 3.75(δ), but the $[Pd(PhSb(o\text{-}C_6H_4OMe)_2)_2Cl_2]$ and $[Pd(Ph_2Sb(o\text{-}C_6H_4\text{-}OMe))_2Cl_2]$ spectra show two OMe resonances *ca.* 3.8, 3.4 (δ), which are not affected by addition of free ligand suggesting that these are due to *trans* and *cis* isomers respectively, and that exchange with free ligand is slow on the NMR time scale. In more polar solvents, *e.g.* $(CD_3)_2SO$ the two -OMe resonances are still present but change in relative intensity in favour of the *ca.* 3.4 δ signal. The increased proportion of the polar *cis* isomer would be expected in a more polar solvent. The ^1H NMR spectra of the platinum complexes are straightforward suggesting the presence of only *cis* isomers with L = $Ph_2Sb(o\text{-}C_6H_4OMe)$ and $PhSb(o\text{-}C_6H_4\text{-}OMe)_2$, whilst $[Pt(Sb(o\text{-}C_6H_4OMe)_3)_2Cl_2]$ was insufficiently soluble for the ^1H NMR spectrum to be obtained. The change from *cis* → *trans* structures for these $[ML_2Cl_2]$ complexes along the series L = $Ph_2Sb(o\text{-}C_6H_4OMe)$, $PhSb(o\text{-}C_6H_4OMe)_2$, $Sb(o\text{-}C_6\text{-}H_4OMe)_3$ is most probably due to the increasing steric demands; stibine ligands without bulky substituents generally seem to give *cis* isomers [20]. The greater tendency to form *cis* isomers Pt > Pd observed is also a general trend with group VB donors [21], although the occurrence of *cis* isomers for Pd(II) at least in solution is much more common than once thought [22].

The reaction of Na_2PdCl_4 with the stibines in a 1:1 mol ratio was also studied. The low affinity of Pd(II) for oxygen donors suggested that Sb, O chelation was unlikely, but the formation of halide bridged dimers $Pd_2L_2Cl_4$ was expected. Dimers of this type are known with $SbPr_3^n$ [23], $SbEt_3$ [24], Sb-$(t\text{-butyl})_3$ [25], and most significantly with (*o*, *m*- and *p*-tolyl)$_3$Sb [26], and are described as dark-red solids, which decompose readily in the cases of the alkyl stibines. In the present case all attempts to react a 1:1 ratio of Pd(II) salt:methoxyphenylstibine, or react $[PdL_2Cl_2]$ with $PdCl_4^{2-}$, resulted in rapid darkening of the solution and precipitation of black solids, often accompanied by the formation of a metallic mirror. Similar decomposition occurred with platinum(II), although the reaction is slower. In neither case were we able to obtain any evidence for the formation of $M_2L_2X_4$ complexes. Decomposition of stibine complexes to black materials has been observed previously [23, 25], but appears to be much more marked with these (*o*-methoxyphenyl) stibines than with Ph_3Sb or the (tolyl)$_3$Sb [26].

Rhodium(III)

Volponi *et al.* [14] reported a yellow-brown $[Rh(Me_2Sb(o\text{-}C_6H_4OMe))_2Cl_3]$ complex formed from $RhCl_3\cdot 3H_2O$ and the ligand in a 1:2 ratio. We find that $RhCl_3\cdot 3H_2O$ and $Me_2Sb(o\text{-}C_6H_4\text{-}OMe)$ in ethanol in a Rh:L ratio 1:3.5 produces bright yellow $[RhL_3Cl_3]$, whilst a 1:2 or preferably 1:1.5 ratio gives the red-brown $[RhL_2Cl_3]$. These two complexes can be interconverted by boiling

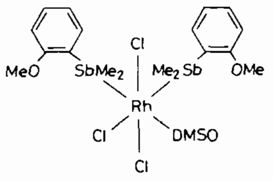
$$\underset{\text{red-brown}}{RhL_2Cl_3} \quad \underset{RhCl_3\cdot 3H_2O}{\overset{L}{\rightleftarrows}} \quad \underset{\text{yellow}}{RhL_3Cl_3}$$

the appropriate mixture in n-propanol.

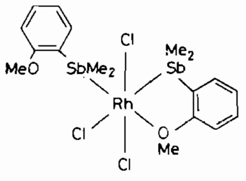
The other (*o*-methoxyphenyl) stibines gave red-orange $[RhL_3Cl_3]$ (Table I) when either a 1:2 or 1:3 Rh:ligand ratio was used.

The yellow $[Rh(Me_2Sb(o\text{-}C_6H_4OMe))_3Cl_3]$ contains single sharp Sb-Me (δ = 1.4) and O-Me (δ = 3.7) resonances indicating only one antimony environment and hence the *fac* isomer. The yellow colour is also consistent with this isomer (*cf.* yellow *fac*-$[RhL_3Cl_3]$ with L = PR_3, AsR_3 [27]). Only one ν(Rh–Cl) vibration could be clearly identified to high frequency of the stibine ligand absorption, at 310 cm^{-1}, which is also in the range expected [28] for *fac*-$[RhL_3Cl_3]$, and the second band expected is probably hidden by the ligand absorption. (Theory *fac* isomer = A_1 + E). The orange $[RhL_3Cl_3]$ L = $Ph_{3-n}Sb(o\text{-}C_6H_4OMe)_n$ (n = 1, 2, 3) have similar far IR spectra consisting of one strong ν(Rh–Cl) band at *ca.* 330–345 cm^{-1} and in some cases a second band is discernable as a shoulder on the ligand absorption at lower frequency. The presence of a band at *ca.* 330 cm^{-1} assigned as B_1 (Rh–Cl) is consistent with a *mer* structure [28], and two A_1(Rh–Cl) vibrations are expected to lower frequency but are obscured by ligand absorption. The IR band at *ca.* 1250 cm^{-1} characteristic of the aryl-OMe group vibration is unshifted in all these complexes showing the methoxy-group is uncoordinated. The ^1H NMR spectra are less useful in assignment of structures to these $[RhL_3Cl_3]$ complexes. In *mer*-$[Rh(Ph_2Sb(o\text{-}C_6H_4OMe))_3Cl_3]$ there is a sharp signal at 3.7 δ and a broad one at 3.4 (2:1 relative intensity) consistent with the structure proposed, but for the complexes of $PhSb(o\text{-}C_6H_4OMe)_2$ and $Sb(o\text{-}C_6H_4OMe)_3$ the ^1H NMR spectra in the 3–4 δ region contain broad signals in which several lines can be partially distinguished. These complexes are very crowded, and models suggest considerable interaction between the -OMe groups and neighbouring ligands, and this would produce slightly different electronic environments for the methyl groups.

The only 1:2 complex prepared [$Rh(Me_2Sb(o\text{-}C_6H_4OMe))_2Cl_3$] has two ν(Rh–Cl) vibrations in the far IR spectrum at 335, 280 cm^{-1} which are frequencies characteristic of a *mer* arrangement of the chlorines. The 'aryl-OMe' frequency in the free ligand 1250 cm^{-1} corresponds to one band at 1250 cm^{-1} in the complex but there is a new absorption at 1223 cm^{-1}. The latter is absent in the free ligand and in *mer*-[RhL_3Cl_3], and can be assigned to a coordinated methoxy group [1, 2]. Hence the IR data suggests an Sb_2OCl_3 donor set. In $CDCl_3$ solution the ^1H NMR spectrum consists of broad absorptions at 1.3, 1.6 δ (Sb–Me) and 3.2, 3.8 δ (OMe). The spectrum in $(CD_3)_2SO$ contains sharp signals at 1.1, 1.3 and 3.7, 3.85 δ which suggests that the DMSO has displaced the coordinated methoxy group, and that structure A should be assigned to this complex. On the basis of the IR data on the solid and the ^1H NMR spectrum in $CDCl_3$, the structure of [RhL_2Cl_3] is proposed to be [B], which is analogous to that established for the *o*-methoxyphenyldimethylarsine analogue, [$Rh(Me_2As(o\text{-}C_6H_4OMe))_2Cl_3$] by an X-ray study [11]. The rather broad NMR spectrum of complex [B] in $CDCl_3$, compared with the sharp absorptions of complex [A] and of the [RhL_3Cl_3] analogue, suggest that exchange between the coordinated and uncoordinated -OMe groups may be occurring. A rather similar exchange process has been proposed for [$Ru(Ph_2P(o\text{-}C_6H_4OMe))_2(CO)Cl_2$] [2]. Variable temperature ^1H NMR spectra of complex [B] in $CDCl_3$ were recorded over the range +40 to –40 °C, but little change was observed. Attempts to reach lower temperatures were frustrated by poor solubility of the complex, which crystallised out as the temperature was lowered. The reaction of this complex with CO is discussed below.



(A)



(B)

The [$Rh(Sb(o\text{-}C_6H_4OMe)_3)_3Cl_3$] complex was heated with $RhCl_3 \cdot 3H_2O$ in ethanol in an attempt to produce a [RhL_2Cl_3] complex. Several attempts at this preparation gave products of somewhat variable composition intermediate between RhL_3Cl_3 and 'RhL_2Cl_3', but none of the materials showed any evidence for the presence of coordinated methoxy-groups in their IR spectra.The failure to produce Rh–OMe coordination with the $Ph_{3-n}Sb(o\text{-}C_6H_4OMe)_n$ ligands is surprising in view of the behaviour of $Me_2Sb(o\text{-}C_6H_4OMe)$, and is particularly so when the large size of the ligands is considered. Coordination of one -OMe group in place of the third stibine would be expected to reduce the crowding about the metal (models and the complex NMR spectra seem to indicate considerable crowding in [RhL_3Cl_3] for $PhSb(o\text{-}C_6H_4OMe)_2$ and $Sb(o\text{-}C_6H_4OMe)_3$). Since this Rh–OMe coordination does not take place, it is presumably electronically unfavourable. It is notable that the X-ray studies of [$Rh(Me_2As(o\text{-}C_6H_4OMe))_2Cl_3$] [11] and [$Ru(Ph_2P(o\text{-}C_6H_4OMe))_2Cl_2$] [2] show that the M–OMe bonds are very long (2.24 Å in the Rh, and 2.299(3) and 2.257(3) Å in the Ru) compared to the sum of the covalent radii [29] *ca.* 2.0 Å. It is possible that with the weaker donor aryl stibines, the Rh(III) prefers to bind an extra stibine donor rather than interact weakly with an -OMe group.

Iridium(III)

The only complexes isolated of iridium(III) with the *o*-methoxyphenylstibines were the yellow [IrL_3Cl_3]. Even with $Me_2Sb(o\text{-}C_6H_4OMe)$ attempts to produce an [IrL_2Cl_3] complex failed, consistent with a lower affinity of Ir(III) than Rh(III) for O-donor ligands. The far IR spectra of the [IrL_3Cl_3] (Table I) contain one strong ν(Ir–Cl) vibration in the region 310–320 cm^{-1}, and sometimes a weaker band at *ca.* 290 cm^{-1} is just discernable on the stibine absorptions. These vibration frequencies are consistent with a meridional arrangement of the chloride ligands [30], rather than a facial one when ν(Ir–Cl) occur at lower frequencies [31]. More prolonged heating of the reaction mixture used to obtain these materials, gave products contaminated with small amounts of other complexes which had weak IR bands at 2000–2100 cm^{-1}, probably [$Ir(CO)L_2Cl_3$] complexes. Once produced these constitute a persistent impurity in the [IrL_3Cl_3] and are very difficult to remove by recrystallisation.

Other Metals

None of the stibine ligands reacted with nickel(II) or cobalt(II) salts. The reaction of excess stibine with copper(II) chloride in ethanol, gave cream CuLCl complexes, whilst reaction with AgI dissolved in an aqueous solution of KI gave cream AgLI.The IR (4000–200 cm^{-1}) and NMR spectra of the Cu(I) and Ag(I) complexes were almost identical with those of the free ligands, as expected with d^{10} ions. These complexes are probably tetramers [21], but this cannot be established without an X-ray study. The complex behaviour towards Ru(II), Ru(III) and Os(IV) is currently under examination.

TABLE II. Complexes of $Me_2Sb(CH_2)_2O(CH_2)_2O(CH_2)_2SbMe_2$ (dsde).

Complex	Colour	C%[a]	H%	IR ν(M–Cl) cm^{-1}
$[Pd(dsde)Cl_2]$	yellow-green	20.8(20.1)	4.3(4.0)	345(s)
$Rh(dsde)Cl_3$	red	19.0(19.1)	3.7(3.8)	340(s), 280(m)
$Ir(dsde)Cl_3$	yellow-green	16.2(16.7)	3.5(3.3)	315(s), 290sh
$Ru(dsde)Cl_3$[e]	black	19.8(19.2)	3.6(3.8)	320(sh), 280(s)
$Ru(dsde)(CO)Cl_2$[f]	fawn-yellow	21.5(21.3)	3.5(3.9)	–
$Os_2(dsde)Cl_8 \cdot H_2O$[g]	green	10.8(10.8)	2.6(2.4)	320(sh), 302, 294(sh)

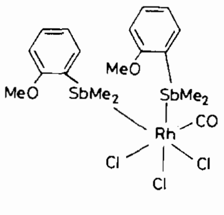
Complex	$E_{max} \times 10^{-3}$ cm^{-1} [b] (ϵ_{mol})	^1H NMR (δ)[d]
$[Pd(dsde)Cl_2]$	34.5(12800), 26.8(3560)	1.35(s)Sb-Me, 2.3(t) Sb-CH_2, 3.7(m)OCH_2, ($CDCl_3$)
$Rh(dsde)Cl_3$	33.3(22400), 24.1(1230)sh[c]	1.4(s)Sb-Me, 2.3(m)SbCH_2, 3.6(m)OCH_2, (d^6-dmso)
$Ir(dsde)Cl_3$	34.0(9400), 26.2sh(1040)[c]	1.3-1.4Sb-Me, 2.3(m)SbCH_2, 3.4-3.6(m)OCH_2, (d^6-dmso)
$Ru(dsde)Cl_3$[e]	30.1(4100), 18.75(1240)[c]	–
$Ru(dsde)(CO)Cl_2$[f]	30.7sh(750) 25.6(sh)(400)[c]	1.2-1.3SbMe, 2.4(m)SbCH_2, 3.4-3.6(m)OCH_2, (d^6-dmso)
$Os_2(dsde)Cl_8 \cdot H_2O$[g]	29.4(9520), 27.0(7360)	–
	24.5(sh)(2350), 16.4(sh)(515)[c]	–

[a] Fd (calc). [b] Solution spectrum in CH_2Cl_2. [c] In dmso. [d] Free ligand 3.5(m) OCH_2, 1.75(t) CH_2Sb, 0.7(s) Sb-Me (δ). [e] μ_{eff} = 2.25 BM, Λ_M = 10 $ohms^{-1}$ cm^2 M^{-1} (DMSO). [f] μ_{eff} = 0 BM. [g] μ_{eff} = 1.3 BM/Os atom.

Reactions with Carbon Monoxide

Dichloromethane solutions of the $[PdL_2Cl_2]$, $[PtL_2Cl_2]$ (excepting L = $Sb(o\text{-}C_6H_4OMe)_3$ which was very slightly soluble), $[RhL_3Cl_3]$ and $[IrL_3Cl_3]$ were saturated with CO at room temperature, and the IR spectra of these solutions recorded immediately. Free CO in CH_2Cl_2 absorbs at 2135 cm^{-1}, and with one exception (below) this was the only new band observed in any of the spectra. The exception was $[Pd(Sb(o\text{-}C_6H_4OMe)_3)_2Cl_2]$ where the yellow solution turned greenish yellow, and a new IR band appeared at 2080 cm^{-1} attributable to coordinated CO. On warming the solution and purging with nitrogen the intensity of this band decreased but a metallic mirror was also produced. Decomposition also occurred on evaporation, and the carbonyl species has not been isolated.

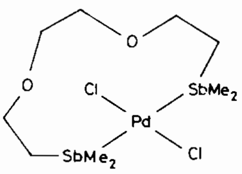
The red-brown $[Rh(Me_2Sb(o\text{-}C_6H_4OMe))_2Cl_3]$ in CH_2Cl_2 rapidly took up CO, and on evaporation a brown solid $[RhL_2(CO)Cl_3]$ with ν(CO) = 2065 cm^{-1} was obtained. The CO could be completely removed by warming the CH_2Cl_2 solution and sweeping it with N_2, and the uptake and removal of CO could be cycled several times without any decomposition being apparent. The ν(CO) value is similar to those reported for other $[Rh(PR_3)_2(CO)Cl_3]$ and $[Rh(AsR_3)_2(CO)Cl_3]$ [32] which have *trans* group VB ligands, *mer* chlorines (and hence CO *trans* Cl). The far IR spectrum of the stibine complex however has ν(Rh–Cl) at 310, 283 cm^{-1} more consistent with a *fac* arrangement of chlorines (*cf.* $Rh(Me_2Sb(o\text{-}C_6H_4OMe))_3Cl_3$) and clearly lacks the band at *ca.* 340 cm^{-1} expected for a *trans* Cl–Rh–Cl unit. The ^1H NMR spectra in $CDCl_3$ or $(CD_3)_2SO$ are similar and contain single Me–Sb and Me–O resonances, which indicates structure [C].



(C)

$Me_2Sb(CH_2)_2O(CH_2)_2O(CH_2)_2SbMe_2$ Complexes

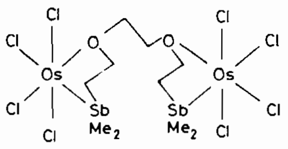
The reaction of this ligand (dsde) with Na_2PdCl_4 or $[Pd(MeCN)_2Cl_2]$ in EtOH/CH_2Cl_2 produced a greenish-yellow solution, from which precipitation with hexane gave $[Pd(dsde)Cl_2]$. The complex is extremely soluble in organic solvents, and the solutions decompose with deposition of black solids, slowly in the cold, rapidly on heating. In $CDCl_3$ the ^1H NMR spectrum is consistent with coordination only via the antimony, (Table II) and in $C_2H_4Cl_2$ the complex is monomeric (mwt found 540, calc 597). The far IR spectrum contains a single medium intensity band at 345 cm^{-1} assignable as the B_{2u}(Pd–Cl) vibration of a *trans* planar Pd(II) complex. The only structure consistent with this data is [D] containing dsde binding as a *trans* chelating bidentate.The complex thus resembles $[Pd(L\text{–}L)Cl_2]$ L–L = $Me_2As(CH_2)_{12}AsMe_2$ [33], $PhS(CH_2)_{12}SPh$ [34], and the solution structure of $[Pd(Me_2As(CH_2)_3S(CH_2)_2S(CH_2)_3AsMe_2)Cl_2]$ [35]. The reaction of dsde with $[Pt(MeCN)_2Cl_2]$ in $CHCl_3$ gave a yellow oil with an essentially similar ^1H NMR spectrum to the Pd(II) complex, but all attempts to isolate the solid Pt(II) complex failed.



(D)

The reaction of dsde with $RhCl_3 \cdot 3H_2O$ or $IrCl_3 \cdot 3H_2O$ in ethanol gave materials of composition $M(dsde)Cl_3$ (Table II). The IR spectra of these complexes (4000–400 cm^{-1}) were very similar to those of $Pd(dsde)Cl_2$ and $Me_2Sb(Br_2)(CH_2)_2O(CH_2)_2O(CH_2)_2Sb(Br_2)Me_2$ [18], and in particular contain broad absorption at *ca.* 1100 cm^{-1} due to the $\text{-}CH_2OCH_2\text{-}$ units, which we interpret tentatively as indicating uncoordinated ether groups in the solid Rh and Ir complexes. The complexes were insufficiently soluble in chlorinated solvents for mwt or ^1H NMR studies, and although the ^1H NMR in d_6-DMSO show no evidence for ether coordination, this is an unreliable guide to the solid structure, since the DMSO may well displace any coordinated ether groups. The structures of these complexes are unclear, but halide-bridged dimers with antimony-coordinated dsde seems likely.

The product of heating dsde with sodium hexachloroosmate(IV) in 2-ethoxyethanol was a deep green solid whose analysis indicated an approximate 'Os_2Cl_8(dsde)' composition. The IR spectrum showed strong bands at ~3500, 1630 cm^{-1} which were attributed to water, strong partially resolved bands at 320–280 cm^{-1} assigned as ν(Os–Cl) and most informative the region 1200–1000 cm^{-1} contains two sharp bands at 1123 and 1050 cm^{-1} indicating coordination of the ether function. The electronic spectrum (Table II) and the magnetic moment μ_{eff} ~ 1.3 BM/Os atom confirm the oxidation state of the metal as Os(IV) [16]. Again poor solubility precluded mwt measurements, but on the basis of the data structure E is proposed for $Os_2Cl_8(dsde) \cdot H_2O$.



(E)

The reactions of dsde with $RuCl_3 \cdot 3H_2O$ are more complex. In refluxing ethanol the product is the black, paramagnetic (μ_{eff} = 2.25 BM) $Ru(dsde)Cl_3$ which is a non-electrolyte in solution and whose IR spectrum contain a sharp band at 1030 cm^{-1} and a broad absorption at *ca.* 1100 cm^{-1}, consistent with ether-oxygen coordination, and an Sb_2Cl_3O donor set is tentatively proposed. Molecular models suggest that dsde could bind as an Sb_2O donor tridentate without severe distortion, and a similar conclusion was reached by other workers for related phosphine-ether ligands [36]. On boiling a mixture of $RuCl_3 \cdot 3H_2O$ and dsde in $2\text{-}EtOC_2H_4OH$ a yellow-fawn material is produced, which is diamagnetic indicating Ru(II) (d^6). However, the IR spectrum showed only the broad bands at *ca.* 1100 cm^{-1} indicating the oxygen donors are not coordinated, ruling out the $Ru(dsde)Cl_2$ with a tetradentate (Sb_2O_2) coordination of the ligand, which was expected by analogy with phosphine-ethers [1, 2]. Moreover the IR spectrum contains a moderately strong band at 1928 cm^{-1}, due to a carbonyl group and hence carbonyl abstraction from the solvent has occurred. Analytically this material corresponds to $Ru(dsde)(CO)Cl_2$, and the low value of the single ν(CO) vibration is not consistent with a *trans* dicarbonyl, but not unreasonable for CO *trans* Cl [37]. The electronic spectrum suggests octahedral Ru(II) rather than five-coordination, and this coupled with the IR and ^1H NMR data (Table II) showing the ether groups are uncoordinated, leads to the postulate of a halide-bridged dimer perhaps similar to $[Ru(PR_3)_2(CO)Cl_2]_2$ [37].

In conclusion it seems likely that the Rh(III), Ir(III) and Ru(II) complexes are dimeric, possibly with bridging dsde, although the poor solubility has so far frustrated attempts to obtain single crystals for an X-ray study.

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