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FULL PAPER

Synthesis, properties and structures of complexes of platinum metal halides and Group 11 metals with two distibinomethane ligands, $R_2SbCH_2SbR_2$ (R = Me or Ph)

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The reaction of $[Ru(dmf)_6][CF_3SO_3]_3$, LiX and $Ph_2SbCH_2SbPh_2$ (dpsm) yielded *trans*-$[RuX_2(\eta^1\text{-dpsm})_4]$ (X = Cl or Br) or $[RuI_2(\eta^1\text{-dpsm})_2(\eta^2\text{-dpsm})]$. The latter was shown by an X-ray study to contain two monodentate and one chelating dpsm ligands and is the first example with any metal of a distibinomethane acting as a chelate to be authenticated crystallographically. The chelate ring is highly strained as shown by the Sb–Ru–Sb angle (74.3°) and the longer Ru–Sb distances than in the η^1-ligands. Corresponding reactions of *trans*-$[OsX_2(dmso)_4]$ and dpsm produced *trans*-$[OsCl_2(\eta^1\text{-dpsm})_4]$ and $[OsBr_2(\eta^1\text{-dpsm})_2(\eta^2\text{-dpsm})]$ identified spectroscopically. The reactions of RhX_3 (X = Cl, Br or I) with dpsm afford $[RhX_3(dpsm)_2]$ which on the basis of NMR spectroscopic data contain one chelating and one monodentate dpsm ligand. Palladium(II) and platinum(II) halides form both 1 : 1 and 1 : 2 complexes with dpsm. The former are dimeric and crystal structures of $[M_2X_4(dpsm)_2]$ (M = Pt, X = Cl or Br; M = Pd, X = Br) revealed a distibine bridged structure with square-planar MX_2Sb_2 metal centres, one with a *cis* geometry, the other *trans*. The structures *cis,trans*-$[X_2M(\mu\text{-dpsm})_2MX_2]$ are the first examples of this geometry to be established crystallographically. In contrast $[I_2M(\mu\text{-dpsm})_2MI_2]$ are assigned as *trans,trans* isomers on the basis of spectroscopic data. Multinuclear NMR studies show that $[PtX_2(dpsm)_2]$ (X = Cl or Br) contain η^1-dpsm and are a mixture of *cis* and *trans* isomers in solution, but the $[PtI_2(dpsm)_2]$ contains only a single form, probably the *trans* isomer. The $[PdX_2(dpsm)_2]$ have also been characterised and for X = Cl shown to undergo facile fragmentation in solution to form *trans,trans*-$[Pd_2Cl_2(\sigma\text{-Ph})_2(dpsm)_2]$. The complexes $[M(L\text{–}L)_2]Y$ (M = Cu, Ag or Au; Y = BF_4 or PF_6; L–L = dpsm or $Me_2SbCH_2SbMe_2$) and $[Rh_2Cl_2(CO)_2(\mu\text{-L–L})_2]$ have also been prepared. All complexes have been characterised by analysis, IR, UV-VIS, multinuclear NMR (^1H, $^{13}C\text{-}\{^1H\}$, ^{195}Pt, ^{63}Cu and ^{109}Ag) spectroscopies as appropriate. Comparisons are drawn between the various co-ordination modes of the distibines and those of $Ph_2PCH_2PPh_2$ and related ligands.

Introduction

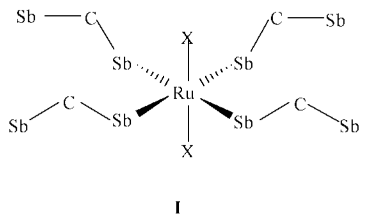
Diphosphines with a single atom bridge between the phosphorus donors, R_2PEPR_2 where E may be CH_2, NH, NR, O, *etc.*, have a particularly rich co-ordination chemistry with the ligands behaving as chelates, monodentates or bridging bidentates. In contrast to ligands with longer (2 or 3 atom) interdonor linkages which usually strongly favour chelation, the single atom bridge results in very strained four-membered chelate rings and other modes of co-ordination are relatively more favoured.[1–3] The behaviour of the corresponding diarsines $R_2AsEAsR_2$ is generally similar. Distibinomethanes $R_2SbCH_2SbR_2$ received cursory examination in the 1970's, but only very limited spectroscopic and no structural data were reported.[4] We have recently re-examined the complexes of two distibines $R_2SbCH_2SbR_2$ (R = Me (dmsm) or Ph (dpsm), L–L) with a variety of metal carbonyls and have identified three co-ordination modes: monodentate *e.g.* $[Fe(CO)_4(\eta^1\text{-dpsm})]$ or $[W(CO)_5(\eta^1\text{-dpsm})]$, bridging bidentate between otherwise unconnected centres *e.g.* $[(OC)_5W(\mu\text{-dpsm})W(CO)_5]$ or $[(OC)_3Ni(\mu\text{-dmsm})Ni(CO)_3]$, and bridging across M–M bonds *e.g.* $[Co_2(CO)_6(\mu\text{-dmsm})]$ or $[Mn_2(CO)_6(\mu\text{-dpsm})_2]$.[5–7] The characterisation of $[Pd_2Cl_2(Ph)_2(dpsm)_2]$ resulting from decomposition of $[PdCl_2(dpsm)_2]$ has also been reported.[8] No compounds in which distibinomethanes behave as chelates were identified.

Results and discussion

Attempts to obtain dmsm complexes often resulted in insoluble or intractable products and only a limited number of examples are described here.

Ruthenium and osmium complexes

The reaction of $[Ru(dmf)_6][CF_3SO_3]_3$[9] with four equivalents of dpsm and an excess of LiX (X = Cl or Br) in refluxing EtOH gave pink $[RuCl_2(dpsm)_4]$ or red $[RuBr_2(dpsm)_4]$. Reaction of *trans*-$[OsCl_2(dmso)_4]$[10] with four equivalents of dpsm gave the corresponding yellow $[OsCl_2(dpsm)_4]$. The complexes are air-stable both as solids and in chlorocarbon solutions. The ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra each show single $\delta(CH_2)$ with only small shifts from the "free" ligand, indicating equivalent η^1 dpsm ligands (Table 1) and the expected *trans* geometry (**I**). In contrast the reaction of $[Ru(dmf)_6][CF_3SO_3]_3$, an excess of LiI and four equivalents of dpsm gave brown $[RuI_2(dpsm)_3]$, and deep yellow $[OsBr_2(dpsm)_3]$ was obtained from *trans*-$[OsBr_2(dmso)_4]$ and dpsm. Unfortunately we have been unable to obtain an osmium iodide complex; the reaction of $[OsI_6]^{2-}$ with the appropriate ligand which gave $[OsI_2(Ph_3Sb)_4]$ with $SbPh_3$[11]



I

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Table 1 Multinuclear NMR data

	$^1H^a$			$^{13}C-\{^1H\}^b$			
Complex	δ(CH_2)	δ(CH_3)	δ(Ph)	δ(CH_2)	δ(CH_3)	δ(Ph)	Other
$[Cu(dpsm)_2][PF_6]$	2.1		7.0–7.4	2.5		130–136	(see text)
$[Cu(dmsm)_2][PF_6]$	1.6 (br)	1.2		−3.1	0.0		(see text)
$[Ag(dpsm)_2][BF_4]$	2.2		7.0–7.4	3.4		130–136	+521(^{109}Ag)
$[Ag(dmsm)_2][BF_4]$	1.6 (br)	1.2		−5.2	−0.2		
$[Au(dpsm)_2][PF_6]$	2.7^c		7.0–7.4	5.6		130–136	
$[Au(dmsm)_2][PF_6]$	2.1^c	1.5		1.2	3.4		
$[\{RhCl(CO)(dpsm)\}_2]$	2.8		7.2–7.8	5.7		129–136	186.0 $^1J(^{13}C-^{103}Rh)$ = 66 Hz ^{13}C (CO)
$[\{RhCl(CO)(dmsm)\}_2]$	2.1	1.2		−1.9	1.1		187.1 $^1J(^{13}C-^{103}Rh)$ = 66 Hz ^{13}C (CO)
$[RuCl_2(dpsm)_4]$	2.2		6.7–7.4	6.8		129–137	
$[RuBr_2(dpsm)_4]$	2.3		6.7–7.4	8.1		127–137	
$[RuI_2(dpsm)_3]$	2.2, 4.5		6.8–7.3	8.5, 18.0		127–138	
$[OsCl_2(dpsm)_4]$	2.9		7.0–7.5	1.0		129–138	
$[OsBr_2(dpsm)_3]$	2.9, 3.6		6.8–7.5	2.0, 6.4		127–139	
$[RhCl_3(dpsm)_2]$	2.1, 2.8		6.8–7.6	1.1, 5.4		126–140	
$[RhBr_3(dpsm)_2]$	2.2, 2.7		6.8–7.5	3.2, 8.1 (major)		129–137	
	2.0, 2.8		7.0–7.6	1.0, 9.2 (minor)			
$[RhI_3(dpsm)_2]$	2.2, 3.15		7.0–7.7	8.9, 12.6 (major)		129–137	
	2.2, 3.11		7.0–7.7	8.4, 11.8 (minor)			
$[\{PdCl_2(dpsm)\}_2]$	2.4, 3.0^d		6.8–8.0	7.3		129–137	
$[\{PdBr_2(dpsm)\}_2]$	2.6, 3.1^d		6.7–8.0	9.7		129–137	
$[\{PdI_2(dpsm)\}_2]$	3.0		7.3–8.1	13.7, 14.8		129–136	
$[\{PtCl_2(dpsm)\}_2]$	2.4, 2.9^d		6.7–8.0	1.2		128–138	−4140, −4324 (^{195}Pt)^e
$[\{PtBr_2(dpsm)\}_2]$	2.6, 3.0^d		6.7–8.0	2.2		129–137	−4666, −4722 (^{195}Pt)
$[\{PtI_2(dpsm)\}_2]$	2.6		6.7–8.1	5.7		126–137	−5589 (^{195}Pt)
$[\{PdClPh(dpsm)\}_2]$	2.6		7.0–8.0	4.9		140, 136–126, 123	
$[PdCl_2(dpsm)_2]$	2.75		7.0–7.8	6.8		126–139	
$[PdBr_2(dpsm)_2]$	2.7		7.0–7.6	3.6		126–140	
$[PdI_2(dpsm)_2]$	2.8		7.2–7.6	9.6		126–137	
$[PtCl_2(dpsm)_2]$	2.2, 2.7		6.5–8.0	0.5, 2.7		126–139	−4120, −4305 (^{195}Pt)
$[PtBr_2(dpsm)_2]$	2.6, 2.9		7.0–7.5	3.0, 4.1		126–138	−4647, −4711 (^{195}Pt)
$[PtI_2(dpsm)_2]$	2.6		7.0–7.4	5.0		127–136	−5753 (^{195}Pt)

^{a} In $CDCl_3$. ^{b} In $CDCl_3-CH_2Cl_2$. ^{c} In d^6-Me_2CO. ^{d} AB quartets with $J(^1H-^1H)$ *ca.* 9 Hz. ^{e} Relative to $[PtCl_6]^{2-}$ in water.

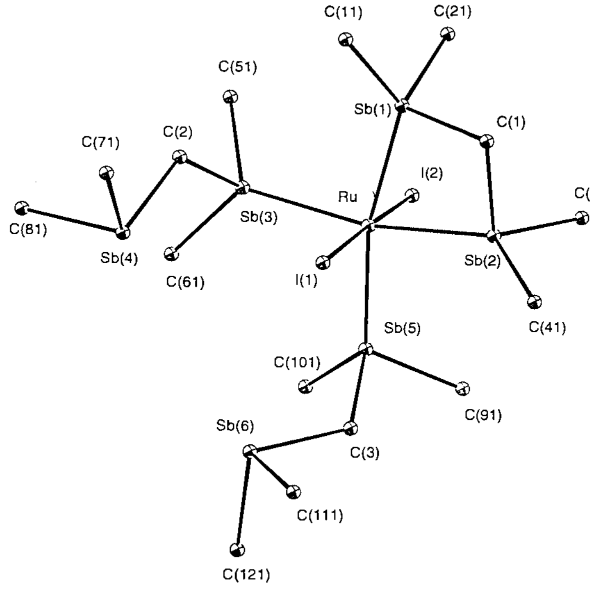


Fig. 1 Structure of $[RuI_2(dpsm)_3]$ showing the atom labelling. Thermal ellipsoids are drawn at the 50% probability level and H atoms and phenyl C atoms other than those bonded to Sb have been omitted for clarity.

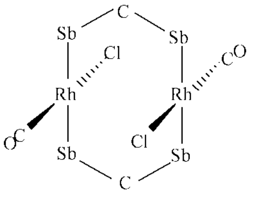
Table 2 Selected bond lengths (Å) and angles (°) for $[RuI_2(dpsm)_3]$

Ru–I(1)	2.7331(8)	Ru–Sb(2)	2.6238(9)
Ru–I(2)	2.7287(8)	Ru–Sb(3)	2.5841(9)
Ru–Sb(1)	2.5988(8)	Ru–Sb(5)	2.5780(8)
Sb–C (methylene)	2.141(8)–2.173(8)	Sb–C (phenyl)	2.122(8)–2.180(9)
Sb(1)–Ru–Sb(2)	74.26(2)	Sb(1)–Ru–Sb(3)	91.56(3)
Sb(1)–Ru–I(1)	91.80(3)	Sb(2)–Ru–Sb(5)	93.15(3)
Sb(1)–Ru–I(2)	91.27(3)	Sb(1)–Ru–Sb(5)	166.80(4)
Sb(2)–Ru–I(1)	87.30(2)	Sb(2)–Ru–I(2)	93.56(3)
Sb(2)–Ru–Sb(3)	164.81(3)	Sb(3)–Ru–I(2)	92.15(3)
Sb(3)–Ru–Sb(5)	101.33(3)	Sb(3)–Ru–I(1)	87.75(3)
Sb(5)–Ru–I(1)	91.54(3)	Sb(5)–Ru–I(2)	85.47(2)
I(1)–Ru–I(2)	176.93(3)		
Sb(1)–C(1)–Sb(2)	93.5(3)	Sb(3)–C(2)–Sb(4)	118.9(4)
Sb(5)–C(3)–Sb(6)	122.2(4)		

failed with dpsm. The ES^+ mass spectra of $[MX_2(dpsm)_x]$ (x = 3 or 4) gave $[MX(dpsm)_3]^+$ as the highest mass ions, but this is inconclusive since the ES^+ spectra of $[RuX_2L_4]$ (L = $AsMe_2Ph$ or $SbMe_2Ph$), which are tetrakis complexes based upon both X-ray studies and spectroscopic data, have $[MXL_3]^+$ as the dominant ions and often $[MXL_4]^+$ are weak or absent.[12] The UV-VIS spectra of all the $[MX_2(dpsm)_x]$ complexes are typical of six-co-ordinate complexes of Ru^{II} or Os^{II} showing weak d–d bands in the range 18 000–25 000 cm^{-1}, and lack the bands at lower energy found for five-co-ordinate complexes of these ions.[13] Distinction of $[MX_2(dpsm)_4]$ and $[MX_2(dpsm)_3]$ is clear in the ^1H and $^{13}C-\{^1H\}$ NMR spectra (Table 1), where the $[MX_2(dpsm)_3]$ show two δ(CH_2) resonances in both ^1H and $^{13}C-\{^1H\}$ NMR spectra, with the weaker one significantly to high frequency, suggesting a formulation $[MX_2(\eta^1\text{-dpsm})_2(\eta^2\text{-dpsm})]$. This was confirmed by a crystal structure of $[RuI_2(dpsm)_3]$ which showed (Table 2, Fig. 1) a distorted six-co-ordinate ruthenium centre, with *trans* iodines, two monodentate dpsm ligands and one chelating dpsm. This is the first complex with any metal in which chelation by a distibinomethane has been established crystallographically. The strain in the chelate ring is evident in the Sb–C–Sb angle of 93.5(3)° compared with 118.9(4), 122.2(4)° in the η^1 ligands and in the Sb–Ru–Sb angle of 74.26(2)°. The *d*(Ru–Sb) involving the chelated dpsm are also longer (2.611 Å (av.)) than those of the η^1 ligands (2.581 Å (av.)). Despite this evidence for significant ring strain, $[RuI_2(dpsm)_3]$ is recovered unchanged after refluxing in CH_2Cl_2 with more dpsm, showing that this structure is preferred to $[RuI_2(\eta^1\text{-dpsm})_4]$. The balance between $[MX_2(dpsm)_3]$ and $[MX_2(dpsm)_4]$ is clearly a subtle function of the M and X involved; possibly the presence of heavier halogens softens the metal centre strengthening the M–Sb bonds and helping to overcome the strain in the chelated ring. The steric crowding will also increase with larger X groups favouring the $[MX_2(dpsm)_3]$, although it should be noted that $[MX_2(SbPh_3)_4]$ are known for both metals and do not show any tendency to dissociate stibines.[11,14] Attempts to prepare dmsm complexes with ruthenium(II) gave only intractable materials which were not further studied.

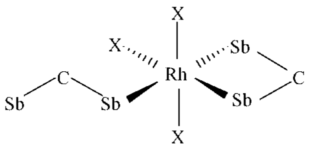
Rhodium complexes

The reaction of $[\{Rh(CO)_2Cl\}_2]$ with dpsm in $CHCl_3$ forms deep red $[\{RhCl(CO)(dpsm)\}_2]$, which has been reported previously.[15] The complex shows a single ν(CO) at 1956 (Nujol) or 1970 cm^{-1} ($CHCl_3$), whilst the $^{13}C\text{-}\{^1H\}$ NMR spectrum shows δ(CO) 186(d), $^1J(^{103}Rh\text{–}^{13}C) = 66$ Hz, and a CH_2 singlet at δ 2.8. The $\delta(CH_2)$ resonances are singlets in both the ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra showing no couplings to the ^{103}Rh ($I = 1/2$, 100%); typically $^2J(^{103}Rh\text{–}^{13}C)$ and $^3J(^{103}Rh\text{–}^1H)$ are small[16] and the line broadening caused by the quadrupolar antimony presumably obscures them. The complex has a molecular weight in $CHCl_3$ corresponding to the dimer formulation.[15] The crystal structure of $[\{RhCl(CO)(Ph_2AsCH_2AsPh_2)\}_2]$ revealed[17] a *trans* ligand bridged dimer and a similar structure (**II**) is proposed for $[\{RhCl(CO)(dpsm)\}_2]$. The reaction of $[\{Rh(CO)_2Cl\}_2]$ with dmsm gave a deep red $[\{RhCl(CO)(dmsm)\}_2]$, which is likely to have an analogous structure based upon its IR (ν(CO) at 1941 cm^{-1} (Nujol) or 1960 cm^{-1} ($CHCl_3$)) and NMR spectra (Table 1). However in contrast to the dpsm complex which appears indefinitely stable, the $[\{RhCl(CO)(dmsm)\}_2]$ decomposes in a few days with loss of the carbonyl groups.



II

The reaction of RhX_3 with two equivalents of dpsm in aqueous acetone gave $[RhX_3(dpsm)_2]$ (X = Cl, Br or I) which were non-electrolytes and monomeric (on the basis of molecular weight measurements in $C_2H_4Cl_2$).[18] Repeating the preparations using an excess of dpsm (Rh : dpsm 1 : 3) gave the same $[RhX_3(dpsm)_2]$ complexes. The FAB and ES^+ mass spectra show $[RhX_2(dpsm)_2]^+$ as the highest significant fragments, and no evidence for Rh–σ-Ph species analogous to those found in the palladium systems (see below) or in the reaction of $RhCl_3$ with $SbPh_3$ which yields a mixture of *mer*-$[RhCl_3(SbPh_3)_3]$ and *mer*-$[RhCl_2Ph(SbPh_3)_3]$.[19] The UV-VIS spectra of $[RhX_3(dpsm)_2]$ have absorptions very similar to those reported for *mer*-$[RhX_3(SbPh_3)_3]$ and with similar very high ε_{mol},[20] and the presence of 6-co-ordinate Rh^{III} seems certain. With the precedent of $[RuI_2(dpsm)_3]$ we propose a structure *mer*-$[RhX_3(\eta^1\text{-dpsm})(\eta^2\text{-dpsm})]$ (**III**). The ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra of $[RhCl_3(dpsm)_2]$ each show two CH_2 singlets of equal intensities (Table 1), the highest frequency in each case being assigned to the η^2-dpsm. The spectra of $[RhBr_3(dpsm)_2]$ are more complex (Table 1), for example in the $^{13}C\text{-}\{^1H\}$ NMR the major CH_2 resonances at δ 3.2 and 8.1 are tentatively assigned to the *mer* isomer, and there are much weaker features (about 20% of the intensity of the major ones) at δ 1.0 and 9.2, with corresponding resonances in the ^1H NMR spectrum. We tentatively suggest this second form is the *fac* isomer. In the $[RhI_3(dpsm)_2]$ two forms are again present.

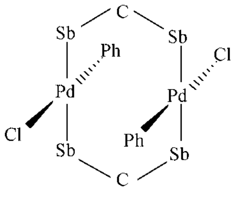


III

Palladium and platinum complexes

The reaction of dmsm with $[MCl_4]^{2-}$ in ethanol or $[MCl_2(MeCN)_2]$ (M = Pd or Pt) in CH_2Cl_2 irrespective of the M : dmsm ratio used precipitated yellow powders with an MCl_2(dmsm) stoichiometry, which are very poorly soluble in organic solvents preventing ^1H, $^{13}C\text{-}\{^1H\}$ or ^{195}Pt NMR studies. The diffuse reflectance UV-VIS spectra are consistent with planar metal centres, and the FAB mass spectra (ES^+ mass spectra could not obtained) showed $[M_2Cl_3(dmsm)_2]^+$ ions, hence $[Cl_2M(\mu\text{-dmsm})_2MCl_2]$ dimers, although we cannot determine which isomer. The corresponding complexes of $Me_2PCH_2PMe_2$[21] and $Me_2AsCH_2AsMe_2$[22] are poorly soluble in common solvents, and their structures similarly uncertain.

The monomeric $[MX_2(dpsm)_2]$ and dimeric $[M_2X_4(dpsm)_2]$ (M = Pd or Pt; X = Cl, Br or I) were described previously,[18] although the isomer(s) present were not established. We have reported that $[PdCl_2(dpsm)_2]$ decomposes photochemically in solution to the σ-Ph complex *trans*,*trans*-$[Pd_2Cl_2Ph_2(dpsm)_2]$ (**IV**), the Ph groups coming from fragmentation of the dpsm.[8]



IV

Ph–Sb cleavage appears to be particularly facile in the chloropalladium systems and crude products often show evidence for significant amounts of these species in addition to the dichloropalladium compounds. In addition to ions of appropriate mass in the ES^+ mass spectra, the σ-Ph groups can be recognised in the ^1H NMR spectra by resonances to low frequency of the dpsm phenyl groups, and by resonances *ca.* δ 123 and 140 in the $^{13}C\text{-}\{^1H\}$ NMR spectra. The corresponding palladium bromo- or iodo-systems seem less prone to Sb–C cleavage, although σ-Ph group fingerprints were often observed as minor features for crude products. Mentes *et al.*[23] observed Sb–C cleavage to form $[PdXPh(SbPh_3)_2]$ on reaction of $SbPh_3$ with $[PdX_2(COD)]$ (X = Cl or Br; COD = cyclooctadiene) or $PdCl_2$, but not with $PdBr_2$, also showing the tendency is greater in the chloropalladium systems. We have not observed σ-Ph complexes in the reactions of dpsm with platinum halides.

$[\{MX_2(dpsm)\}_2]$. The IR and UV-VIS spectra of these complexes have been reported,[18] and our data are in agreement and need not be discussed here. The ES^+ mass spectra contain $[M_2X_3(dpsm)_2]^+$ as the major ion multiplet confirming the dimeric nature. Crystal structures were obtained for $[Pt_2Cl_4(dpsm)_2]$ and $[M_2Br_4(dpsm)_2]$ (M = Pd or Pt) and revealed a new

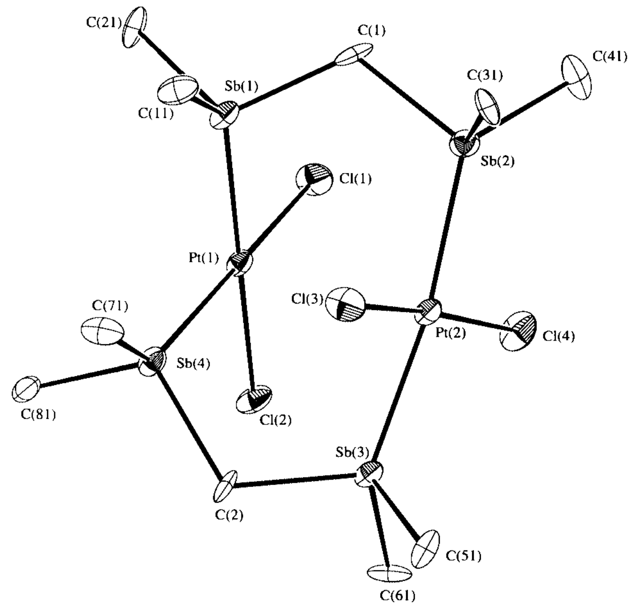
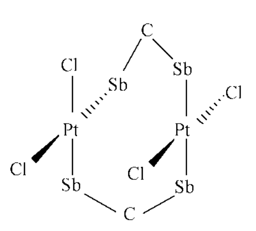


Fig. 2 Structure of $[\{PtCl_2(dpsm)\}_2]\cdot Me_2CO$ showing the atom labelling. Details as in Fig. 1.



V

structural type, *cis,trans*-$[X_2M(\mu\text{-dpsm})_2MX_2]$ (**V**). Although discussed as a possible geometry for dppm-bridged dimers,[3] these complexes are the first examples crystallographically identified for any metal/ligand combination, where the two metal centres have identical donor groups, but one has a *cis* and the other a *trans* geometry. The structure of $[Pt_2Cl_4(dpsm)_2]$ which is shown in Fig. 2 (Table 3) is a distibine-bridged dimer, each square-planar platinum(II) centre being co-ordinated to two terminal chlorines and two antimony donors from different dpsm molecules, but with one platinum having a *cis*, and the second a *trans* arrangement of the donors. The $PtSb_2Cl_2$ units are close to planar in each case, and approximately parallel (dihedral angle 6.7°). The Sb–C–Sb angles in the bridging distibine are 114.5(7), 112.5(7)° somewhat more acute than in the "free" ligand (117.3(2)°),[5] but as can be seen from Fig. 3, which shows the molecule as a projection down the Pt(1) · · · Pt(2) vector, the different geometries at the two platinum centres are accommodated by rotation of one end of the molecule to produce a staggered conformation (*e.g.* torsion angle Cl(1)–Pt(1)–Pt(2)–Cl(4) is −36.6(4)°). The structure of $[Pd_2Br_4(dpsm)_2]$ (Fig. 4, Table 4) is very similar; the crystal quality of the platinum bromo complex was poor and the structure is not discussed, although the heavy atom framework is clearly defined.† The Pd–Sb bond lengths are similar to the few examples with $SbPh_3$.[8,23–26] Consideration of the bond lengths about the two platinum centres in $[Pt_2Cl_4(dpsm)_2]$ (Table 3) shows quite large differences in the Pt–Cl ($\text{Pt–Cl}_{\text{transCl}}$ = 2.321(4), 2.312(4), $\text{Pt–Cl}_{\text{transSb}}$ = 2.365(4), 2.353(4) Å) and Pt–Sb ($\text{Pt–Sb}_{\text{transCl}}$ = 2.479(1), 2.494(1), $\text{Pt–Sb}_{\text{transSb}}$ 2.572(1), 2.554(1) Å) distances consistent with the *trans* influence Sb > Cl. The $\text{Pt–Cl}_{\text{transP}}$ in *cis,cis*-$[Pt_2(BuHPCH_2PHBu)_2Cl_4]$ are[21] 2.344(2), 2.360(3) Å suggesting that the *trans* influence of antimony is comparable with that of phosphorus in platinum(II) systems, a conclusion which has been disputed in the past, but is consistent with the most recent data.[24] Very small crystals of $[Pd_2I_4(dpsm)_2]$ were grown from CH_2Cl_2–diethyl ether but the data were too weak to obtain a satisfactory refinement, although the heavy atom skeleton revealed it to be the *trans, trans* isomer (**VI**).

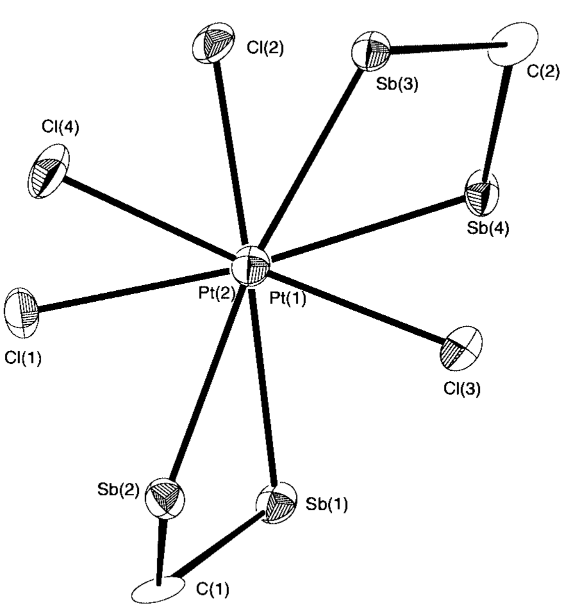


Fig. 3 Structure of $[\{PtCl_2(dpsm)\}_2]\cdot Me_2CO$ viewed down the Pt(1) · · · Pt(2) direction showing the staggered conformation of the two square planar $PtCl_2Sb_2$ groups.

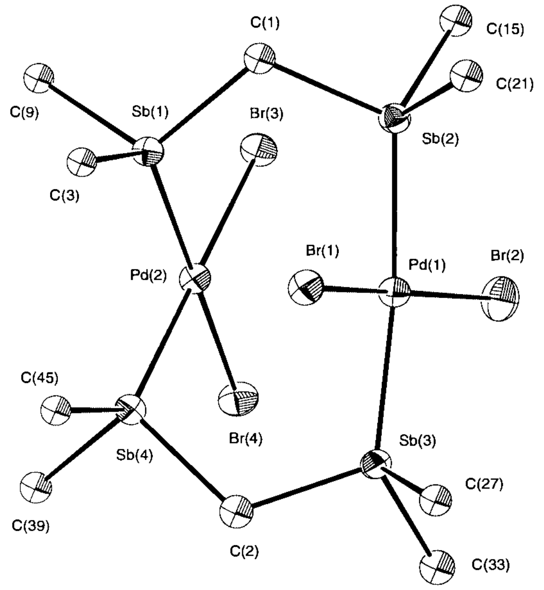
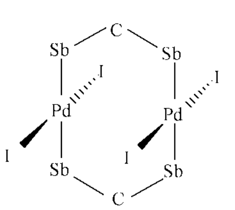


Fig. 4 Structure of $[\{PdBr_2(dpsm)\}_2]\cdot xCH_2Cl_2$ showing the atom labelling. Thermal ellipsoids are drawn at the 50% probability level. Phenyl C atoms other than those bonded to Sb have been omitted for clarity.



VI

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† $[\{PtBr_2(dpsm)\}_2]\cdot CH_2Cl_2$: $C_{51}H_{46}Cl_2Pt_2Sb_4$, $M_r = 1926.63$, triclinic, space group = $P\bar{1}$ (no. 2), $a = 16.008(6)$, $b = 16.990(4)$, $c = 11.934(4)$ Å, $\alpha = 108.61(2)$, $\beta = 109.92(2)$, $\gamma = 79.61(3)$°, $U = 2882.7(1.6)$ Å^3, $T = 150$ K, $Z = 2$, R ($F_o > 4\sigma(F_o)$) = 0.086, wR ($F_o > 4\sigma(F_o)$) = 0.097.

Table 3 Selected bond lengths (Å) and angles (°) for $[\{PtCl_2(dpsm)\}_2]\cdot Me_2CO$

Pt(1)–Cl(1)	2.365(4)	Pt(2)–Cl(3)	2.321(4)
Pt(1)–Cl(2)	2.353(4)	Pt(2)–Cl(4)	2.312(4)
Pt(1)–Sb(1)	2.479(1)	Pt(2)–Sb(2)	2.572(1)
Pt(1)–Sb(4)	2.494(1)	Pt(2)–Sb(3)	2.554(1)
Sb–C	2.09(2)–2.16(2)	C–C	1.32(3)–1.43(3)
Cl(1)–Pt(1)–Cl(2)	93.1(1)	Cl(3)–Pt(2)–Cl(4)	174.5(2)
Cl(1)–Pt(1)–Sb(1)	84.5(1)	Cl(3)–Pt(2)–Sb(2)	88.1(1)
Cl(1)–Pt(1)–Sb(4)	173.0(1)	Cl(3)–Pt(2)–Sb(3)	82.6(1)
Cl(2)–Pt(1)–Sb(1)	177.4(1)	Cl(4)–Pt(2)–Sb(2)	95.4(1)
Cl(2)–Pt(1)–Sb(4)	81.3(1)	Cl(4)–Pt(2)–Sb(3)	94.1(1)
Sb(1)–Pt(1)–Sb(4)	100.91(4)	Sb(2)–Pt(2)–Sb(3)	170.06(4)
Sb(1)–C(1)–Sb(2)	114.5(7)	Sb(3)–C(2)–Sb(4)	112.5(7)
Pt–Sb–C(H$_2$)	Sb(1) 107.8(4); Sb(2) 114.8(4); Sb(3) 114.2(4); Sb(4) 109.5(4)		
Pt–Sb–C (phenyl)	Sb(1) 111.5(5), 127.3(4); Sb(2) 112.6(4), 123.7(6) Sb(3) 110.9(5), 127.0(4); Sb(4) 105.3(4), 128.6(4)		

Table 4 Selected bond lengths (Å) and angles (°) for $[\{PdBr_2(dpsm)\}_2]\cdot xCH_2Cl_2$ ($x = 1.1$)

Pd(1)–Br(1)	2.439(3)	Pd(2)–Br(3)	2.487(3)
Pd(1)–Br(2)	2.418(3)	Pd(2)–Br(4)	2.474(3)
Pd(1)–Sb(2)	2.567(2)	Pd(2)–Sb(1)	2.507(2)
Pd(1)–Sb(3)	2.556(2)	Pd(2)–Sb(4)	2.510(2)
Sb–C	2.09(2)–2.20(2), 2.14(3) av.	C–C	1.33(3)–1.48(3)
Br(1)–Pd(1)–Br(2)	172.6(1)	Br(3)–Pd(2)–Br(4)	96.4(1)
Br(1)–Pd(1)–Sb(2)	84.53(8)	Br(3)–Pd(2)–Sb(1)	81.41(8)
Br(1)–Pd(1)–Sb(3)	83.94(8)	Br(3)–Pd(2)–Sb(4)	179.4(1)
Br(2)–Pd(1)–Sb(2)	96.0(1)	Br(4)–Pd(2)–Sb(1)	176.9(1)
Br(2)–Pd(1)–Sb(3)	95.4(1)	Br(4)–Pd(2)–Sb(4)	83.02(9)
Sb(2)–Pd(1)–Sb(3)	168.46(8)	Sb(1)–Pd(2)–Sb(4)	99.16(7)
Sb(1)–C(1)–Sb(2)	111.3(9)	Sb(3)–C(2)–Sb(4)	115(1)
Pd–Sb–C(H$_2$)	111.2(6)–115.4(6)		

The *cis,trans*-$[M_2X_4(dpsm)_2]$ (M = Pd or Pt, X = Cl or Br) show single $\delta(CH_2)$ resonances in the $^{13}C\text{-}\{^1H\}$ NMR spectra (Table 1), but in the ^1H NMR data the CH_2 groups produce an AB quartet since the methylene protons in each ligand are inequivalent. In contrast the *trans,trans*-$[Pd_2I_4(dpsm)_2]$ exhibits singlet CH_2 resonances in both the ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra. For the *cis,trans*-$[Pt_2X_4(dpsm)_2]$ (X = Cl or Br) the ^{195}Pt NMR spectra each show two broad resonances (the broadening reflects the effect of the substantial quadrupoles of both antimony isotopes and is observed for other platinum stibines)[27,28] due to the *cis* and *trans* PtX_2Sb_2 centres present; the higher frequency and relatively sharper resonance in each is assigned to the *trans* centre.[29] The case of $[Pt_2I_4(dpsm)_2]$ is less clear in that it shows only singlets in both the ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra and is thus not a *cis,trans* isomer, but could be either the *cis,cis* or *trans,trans* form. It also exhibits a single ^{195}Pt NMR resonance at δ −5589. Whilst for many complexes the ^{195}Pt chemical shift distinguishes the geometry satisfactorily,[28,29] this criterion fails with the heavier donor sets when the characteristic chemical shift ranges merge. For example *trans*-$[PtI_2(SbPh_3)_2]$ has δ(Pt) −5798 and *cis*-$[PtI_2\{Me_2Sb(CH_2)_3SbMe_2\}]$ δ(Pt) −5800.[27] Based upon the geometry of the palladium iodo complex and the *trans* geometry favoured[24] in $[PtI_2(SbPh_3)_2]$ it seems very probable that $[Pt_2I_4(dpsm)_2]$ is also *trans,trans*. The formation of the *cis, trans* isomers was unexpected and the underlying reason(s) are unclear. As far as we are aware, despite the very many complexes of dppm and related ligands characterised,[1–3] only *cis,cis* or *trans,trans* forms have been crystallographically identified, and no example of a *cis,trans* isomer with identical donor sets about each metal has been isolated, although in a few cases all three forms have been tentatively suggested to be present in solution. The $[PtX_2(dpsm)_2]$ (X = Cl or Br) complexes discussed below show that both mononuclear *cis* and *trans* geometries exist in solution and are hence of similar stabilities. It is possible that the isolation of *cis,trans* forms results from them preferentially crystallising, but the NMR spectra show no evidence for other isomers, although the slow decomposition of the complexes in solution limits attempts to promote isomerisation, for example by heating in high boiling solvents.

$[MX_2(dpsm)_2]$. The complexes are relatively unstable in solution with the $[\{MX_2(dpsm)\}_2]$ among the decomposition products, as well as σ-Ph species for M = Pd. The NMR data (Table 1) were collected from freshly prepared solutions. The effect of the quadrupolar antimony is to broaden the lines in both the $^{13}C\text{-}\{^1H\}$ and ^1H NMR spectra and similar broadening of the ^{195}Pt satellites[28] means that these are rarely clearly observed. The NMR data (Table 1) on $[PtCl_2(dpsm)_2]$ show the presence of two isomers *cis* and *trans* in the ratio 5 : 1 in CH_2Cl_2, whereas in $[PtBr_2(dpsm)_2]$ the *cis*:*trans* ratio is 2 : 1. The IR data[18] also indicated a *cis* structure for the chloro complex in the solid state, but the structure of the solid bromo complex is unknown. The $[PtI_2(dpsm)_2]$ in contrast shows evidence for only a single isomer in solution, probably the *trans*. The palladium systems are simpler in that only one isomer was detected in CH_2Cl_2 solution for each complex by NMR studies, and the spectra are unchanged on cooling to 220 K so fast ligand exchange (between *cis* and *trans* isomers) seems unlikely. The $[PdCl_2(dpsm)_2]$ is the *cis* isomer in the solid state based upon its far-IR spectrum,[18] and it is probable that this isomer persists in solution. In contrast the bromide and iodide are probably *trans* in solution, support for the change in geometry coming from the irregular chemical shifts ($\delta(CH_2)$) along the series Br < Cl < I in both the ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra (Table 1).

Group 11 metals. The reaction of $[Cu(MeCN)_4]Y$ ($Y = BF_4$ or PF_6) with dpsm or dmsm (L–L) in CH_2Cl_2, irrespective of the Cu : ligand ratio used, gave white $[Cu(L\text{–}L)_2]Y$. The silver analogues $[Ag(L\text{–}L)_2]Y$ were prepared similarly from anhydrous $AgBF_4$ or $AgPF_6$ in CH_2Cl_2, although since the silver complexes are light sensitive in solution these preparations were conducted in foil-wrapped flasks to exclude light. The properties of the complexes seem little influenced by the anion used, and only one example of each is described here. The gold complexes $[Au(L\text{–}L)_2]PF_6$ were prepared from [AuCl(tht)] (tht = tetrahydrothiophene), L–L and $TlPF_6$ in a 1 : 2 : 1 mol ratio in CH_2Cl_2. The ES^+ or FAB mass spectra show $[M(L\text{–}L)_2]^+$ as the major ions, with sometimes weaker $[M(L\text{–}L)]^+$, but with no clear evidence of polymetallic ions. However, we have observed previously[30] that polymeric complexes of Cu or Ag of dithio- or diseleno-ethers give only monometallic ions in their mass spectra, and this result should not be taken as evidence that the present complexes are monomeric in the solid state. The IR spectra show the vibrations of $[PF_6]^-$ (*ca.* 840, 560 cm^{-1}) or $[BF_4]^-$ (*ca.* 1060, 520 cm^{-1}) ions.

The ^{1}H or ^{13}C-{^{1}H} NMR spectra in chlorocarbon solvents at 300 K of the dmsm complexes show only single rather broad δ(Me) and $\delta(CH_2)$ resonances to high frequency of the "free" ligand values (Table 1). Adding more dmsm to these solutions still results in single δ(Me) and $\delta(CH_2)$ resonances although the chemical shifts vary with the amount of added ligand, which demonstrates fast ligand exchange in solution. Similar results are observed for the dpsm complexes. Fast ligand exchange in solution has been reported in $[Cu(SbR_3)_4]^+$ and $[Ag(SbR_3)_4]^+$ systems.[31,32] The $[Ag(dmsm)_2]BF_4$ was too poorly soluble in chlorocarbons to obtain a ^{109}Ag NMR spectrum, but $[Ag(dpsm)_2]BF_4$ exhibited a weak resonance at δ 521; since $[Ag(SbR_3)_4]^+$ and $[Ag\{R_2Sb(CH_2)_3SbR_2\}_2]^+$ which contain $AgSb_4$ moieties have $\delta(^{109}Ag)$ in the range 1000–1100 (relative to Ag^+ in water),[32] the observed value is reasonable for silver co-ordinated to fewer antimony atoms, approximating to a weighted average of $AgSb_2$ that might be expected from the stoichiometry. Neither copper complex showed a ^{63}Cu resonance in CH_2Cl_2 solution over the temperature range 180–300 K, but on adding a large excess of ligand ^{63}Cu resonances were observed at ambient temperature for $[Cu(dpsm)_2]^+$ (δ −197, $w_{1/2}$ = 1200 Hz) and $[Cu(dmsm)_2]^+$ (δ −170, $w_{1/2}$ = 800 Hz) which are within the range observed for $CuSb_4$ species.[31] Unless the copper is in an environment approaching cubic symmetry, fast quadrupolar relaxation (^{63}Cu, $I = 3/2$) results in unobservably broad lines, and thus these results are consistent with the formation of tetrahedral $[Cu(\eta^1\text{-L–L})_4]^+$ in the presence of an excess of L–L; in its absence, it is probable that a variety of species with lower co-ordination numbers are present unobservable by ^{63}Cu NMR spectroscopy due to the fast relaxation. However it is notable that concentration of these solutions leads to the isolation of $[M(L–L)_2]Y$ complexes. The gold complexes were poorly soluble in CH_2Cl_2 but more soluble in acetone, in which they exhibited similar ^{1}H and ^{13}C-{^{1}H} NMR spectra to those of the copper or silver analogues.

Unfortunately, despite many attempts in a variety of solvents we have been unable to obtain crystals of any of these complexes of Cu, Ag or Au for X-ray studies to establish their structures in the solid state. Owing to the weak donor properties and the strain in a four-membered chelate ring, we do not expect chelation in complexes involving labile metals which prefer tetrahedral geometry with even larger L–M–L angles. The closest analogies are probably with the $[M(L'–L')_2]BF_4$ complexes of $MeSCH_2SMe$ and $MeSeCH_2SeMe$ (L′–L′) which are polymeric with the Cu or Ag bound to one S or Se atom of four different ligands which bridge to other copper or silver ions, giving either polymeric ribbons or large channels which host the counter anions.[33]

Conclusions

This work has resulted in the characterisation of the first example of chelation by a distibinomethane ligand in $[RuI_2(dpsm)_3]$, and several other examples have been identified spectroscopically. The formation of *cis,trans*-$[M_2X_4(dpsm)_2]$ (M = Pd or Pt, X = Cl or Br) isomers is also unprecedented. Comparison with complexes of dppm and related diphosphinomethane ligands[1–3] shows three major differences in the chemistry of dpsm: (a) much reduced tendency to chelation and a greater preference for η^1 co-ordination, (b) greater tendency to fragmentation (Sb–C bond fission), although this is very metal dependent, and (c) similar stabilities for *cis or trans* geometric isomers in some systems, whereas the phosphines usually have a clear preference for one geometry.

Experimental

Physical measurements were made as described previously.[5] The dpsm and dmsm were made as described.[5] All preparations were conducted in dry solvents under a dinitrogen atmosphere. Since dmsm is pyrophoric, rigorous exclusion of air during the synthesis of its complexes is essential.

Preparations

$[Cu(dpsm)_2][PF_6]\cdot CH_2Cl_2$. A solution of $[Cu(MeCN)_4][PF_6]$ (0.316 g, 0.85 mmol) in dichloromethane (30 ml) was heated to reflux and added to a solution of dpsm (0.96 g, 1.7 mmol) in dichloromethane (30 ml). The solution was reduced in volume to *ca.* 5 ml and diethyl ether (20 ml) added. The white solid precipitated was filtered off, washed with diethyl ether (2 × 10 ml) and dried *in vacuo*. Yield 0.164 g, 43% (Found: C, 43.3; H, 2.9. Calc. for $C_{51}H_{46}Cl_2CuF_6PSb_4$: C, 43.0; H, 3.2%). IR (CsI) 558, 840 cm^{-1}. MS (ES): m/z = 1194. Calc. for $[C_{50}H_{44}{}^{63}Cu^{121}Sb_4]^+$ 1192.

$[Cu(dmsm)_2][PF_6]$ was made similarly from $[Cu(MeCN)_4][PF_6]$. Yield 40% (Found: C, 14.6; H, 3.4. Calc. for $C_{10}H_{28}CuF_6PSb_4$: C, 14.2; H, 3.3%). IR (CsI) 560, 842 cm^{-1}. MS FAB (3-nitrobenzyl alcohol) m/z 695 and 379. Calc. for $[C_{10}H_{28}{}^{63}Cu^{121}Sb_4]^+$ 695 and $[C_5H_{14}{}^{63}Cu^{121}Sb_2]^+$ 379.

$[Ag(dpsm)_2][BF_4]$. $AgBF_4$ (0.058 g, 0.30 mmol) and dpsm (0.34 g, 0.60 mmol) were stirred together in acetone (20 ml) in the absence of light at 0 °C for 1 h. After filtration the filtrate was reduced in volume to *ca.* 5 ml and pentane (20 ml) added. The white solid precipitated was filtered off, washed with pentane (2 × 10 ml) and dried *in vacuo*. Yield 0.20 g, 50% (Found: C, 45.6; H, 2.8. Calc. for $C_{50}H_{44}AgBF_4Sb_4$: C, 45.3; H, 3.3%). IR (Nujol) 519 and 1064 cm^{-1}. MS (ES): m/z = 1239. Calc. for $[C_{50}H_{44}{}^{109}Ag^{121}Sb_4]^+$ 1237.

$[Ag(dmsm)_2][BF_4]$ was made similarly from $AgBF_4$. Yield 45% (Found: C, 14.8; H, 3.2. Calc. for $C_{10}H_{28}AgBF_4Sb_4$: C, 14.5; H, 3.4%). IR (Nujol) 525 and 1050 cm^{-1}. MS(ES): m/z = 745 and 425. Calc. for $[C_{10}H_{28}{}^{109}Ag^{121}Sb_4]^+$ 741 and $[C_5H_{14}{}^{109}Ag^{121}Sb_2]^+$ 425.

$[Au(dpsm)_2][PF_6]\cdot CH_2Cl_2$. [AuCl(tht)] (0.07 g, 0.2 mmol), dpsm (0.23 g, 0.4 mmol) and $TlPF_6$ (0.07 g, 0.2 mmol) were stirred in degassed dichloromethane (20 ml) for 20 min. The solution was filtered and the filtrate reduced in volume to *ca.* 5 ml. Diethyl ether (25 ml) was added and the light yellow precipitate filtered off, washed with diethyl ether (2 × 10 ml) and dried *in vacuo*. Yield 0.24 g, 80% (Found: C, 39.1; H, 2.7. Calc. for $C_{51}H_{46}Cl_2AuF_6PSb_4$: C, 39.3; H, 2.9%). IR (Nujol) 556 and 836 cm^{-1}. MS (ES): m/z = 1329. Calc. for $[C_{50}H_{44}{}^{197}Au^{121}Sb_4]^+$ 1325.

$[Au(dmsm)_2][PF_6]$ was made similarly. Yield 55% (Found: C, 11.5; H, 2.7. Calc. for $C_{10}H_{28}AuF_6PSb_4$: C, 12.3; H, 2.9%). IR (Nujol) 557 and 842 cm^{-1}. MS (ES): m/z = 833 and 515. Calc. for $[C_{10}H_{28}{}^{197}Au^{121}Sb_4]^+$ 828 and $[C_5H_{14}{}^{197}Au^{121}Sb_2]^+$ 513.

$[\{RhCl(CO)(dpsm)\}_2]$. $[\{RhCl(CO)\}_2]$ (0.05 g, 0.13 mmol) and dpsm (0.15 g, 0.26 mmol) were stirred together in chloroform (20 ml) for 10 min. The dark red solution was reduced in volume to *ca.* 5 ml and pentane (20 ml) added. The dark red precipitate was filtered off, washed with pentane (2 × 10 ml) and dried *in vacuo*. Yield 0.13 g, 68% (Found: C, 42.4; H, 3.0. Calc. for $C_{26}H_{22}ClORhSb_2$: C, 42.6; H, 3.0%). IR: ν(CO) (Nujol) 1956, (chloroform) 1970 cm^{-1}.

$[\{RhCl(CO)(dmsm)\}_2]$. Yield 48%. IR: ν(CO) (Nujol) 1941, (chloroform) 1960 cm^{-1}.

$[RuCl_2(dpsm)_4]$. $[Ru(dmf)_6][CF_3SO_3]_3$ (0.2 g, 0.2 mmol) and dpsm (0.46 g, 0.8 mmol) were refluxed in ethanol (20 ml) for 10 min. LiCl (0.0017 g, 0.4 mmol) in warm ethanol (5 ml) was added and the solution refluxed for 10 min. On cooling the yellow solid was filtered off, washed with ethanol (2 × 10 ml) and dried *in vacuo*. Yield 0.13 g, 27% (Found: C, 48.9; H, 3.5. Calc. for $C_{100}H_{88}Cl_2RuSb_8$: C, 49.3; H, 3.6%). MS (ES):

m/z = 1833. Calc. for $[C_{75}H_{66}{}^{35}Cl^{101}Ru^{121}Sb_6]^+$ 1828. UV/VIS (CH_2Cl_2 10^3 cm^{-1} (ε_{mol}/dm^3 mol^{-1} cm^{-1})) 33.0 (56 200), 23.9 (sh, 730) and 19.1 (590).

[RuBr$_2$(dpsm)$_4$]. [Ru(dmf)$_6$][CF$_3$SO$_3$]$_3$ (0.18 g, 0.18 mmol) and dpsm (0.42 g, 0.72 mmol) were refluxed in ethanol (20 ml) for 10 min. LiBr (0.031 g, 0.36 mmol) in warm ethanol (5 ml) was added and the solution refluxed for 10 min. On cooling the deep red solid was filtered off, washed with ethanol (2 × 10 ml) and dried *in vacuo*. Yield 0.17 g, 33% (Found: C, 46.9; H, 2.8. Calc. for $C_{100}H_{88}Br_2RuSb_8$: C, 47.6; H, 3.5%). MS (ES): *m/z* = 1877 and 1313. Calc. for $[C_{75}H_{66}{}^{79}Br^{101}Ru^{121}Sb_6]^+$ 1872 and $[C_{50}H_{44}{}^{79}Br^{101}Ru^{121}Sb_4]^+$ 1308. UV/VIS (CH_2Cl_2 10^3 cm^{-1} (ε_{mol}/dm^3 mol^{-1} cm^{-1})) 31.8 (41 500), 24.1 (sh, 760) and 18.4 (530).

[RuI$_2$(dpsm)$_3$]. [Ru(dmf)$_6$][CF$_3$SO$_3$]$_3$ (0.26 g, 0.26 mmol) and dpsm (0.56 g, 1.04 mmol) were refluxed in ethanol (20 ml) for 10 min. LiI (0.07 g, 0.52 mmol) in warm ethanol (5 ml) was added and the solution refluxed for 10 min. On cooling the brown solid was filtered off, washed with ethanol (2 × 10 ml) and dried *in vacuo*. Yield 0.40 g, 75% (Found: C, 43.7; H, 3.0. Calc. for $C_{75}H_{66}I_2RuSb_6$: C, 43.9; H, 3.2%). MS (ES): *m/z* = 1926, 1488 and 1358. Calc. for $[C_{75}H_{66}I^{101}Ru^{121}Sb_6]^+$ 1920, $[C_{50}H_{44}I_2{}^{101}Ru^{121}Sb_4]^+$ 1483 and $[C_{50}H_{44}I^{101}Ru^{121}Sb_4]^+$ 1356. UV/VIS (CH_2Cl_2 10^3 cm^{-1} (ε_{mol}/dm^3 mol^{-1} cm^{-1})) 30.5 (16 000), 28.3 (13 700), 25.6 (sh, 4000) and 18.0 (190).

[OsCl$_2$(dpsm)$_4$]. [OsCl$_2$(dmso)$_4$] (0.04 g, 0.07 mmol) and dpsm (0.16 g, 0.28 mmol) were refluxed in ethanol (20 ml) for 30 min. On cooling the yellow solid precipitated was filtered off, washed with ethanol (2 × 10 ml) and dried *in vacuo*. Yield 0.07 g, 40% (Found: C, 47.2; H, 3.5. Calc. for $C_{100}H_{88}Cl_2OsSb_8$: C, 47.6; H, 3.5%). MS (ES): *m/z* = 1925 and 1357. Calc. for $[C_{75}H_{66}{}^{35}Cl^{192}Os^{121}Sb_6]^+$ 1919 and $[C_{50}H_{44}{}^{35}Cl^{192}Os^{121}Sb_4]^+$ 1355. UV/VIS (CH_2Cl_2 10^3 cm^{-1} (ε_{mol}/dm^3 mol^{-1} cm^{-1})) 29.4(sh).

[OsBr$_2$(dpsm)$_3$] was made as a deep yellow solid in a similar way from [OsBr$_2$(dmso)$_4$] and 4 equivalents of dpsm in refluxing ethanol. Yield 45% (Found: C, 43.6; H, 3.0. Calc. for $C_{75}H_{66}Br_2OsSb_6$: C, 43.9; H, 3.2%). MS (ES): *m/z* 1968. Calc. for $[C_{75}H_{66}{}^{79}Br^{192}Os^{121}Sb_6]^+$ 1963. UV-VIS (CH_2Cl_2 10^3 cm^{-1} (ε_{mol}/dm^3 mol^{-1} cm^{-1})) 30.3(sh) and 26.3(sh).

[RhCl$_3$(dpsm)$_2$] made as described[18] (Found: C, 44.9; H, 3.0. Calc. for $C_{50}H_{44}Cl_3RhSb_4$: C, 44.7; H, 3.2%). MS FAB: *m/z* = 1305. Calc. for $[C_{50}H_{44}{}^{35}Cl_2Rh^{121}Sb_4]^+$ 1301. UV-VIS (CH_2Cl_2 10^3 cm^{-1} (ε_{mol}/dm^3 mol^{-1} cm^{-1})) 26.3 (16 500).

[RhBr$_3$(dpsm)$_2$] (Found: C, 39.9; H, 3.0. Calc. for $C_{50}H_{44}Br_3RhSb_4$: C, 40.7; H, 3.0%). MS FAB: *m/z* = 1395. Calc. for $[C_{50}H_{44}{}^{79}Br_2Rh^{121}Sb_4]^+$ 1389. UV-VIS (CH_2Cl_2 10^3 cm^{-1} (ε_{mol}/dm^3 mol^{-1} cm^{-1})) 25.5 (12 500).

[RhI$_3$(dpsm)$_2$] (Found: C, 37.4; H, 2.2. Calc. for $C_{50}H_{44}I_3RhSb_4$: C, 37.2; H, 2.7%). MS FAB: *m/z* = 1489. Calc. for $[C_{50}H_{44}I_2Rh^{121}Sb_4]^+$ 1485. UV-VIS (CH_2Cl_2 10^3 cm^{-1} (ε_{mol}/dm^3 mol^{-1} cm^{-1})) 28.0 (sh) and 23.8 (9300).

[{PdCl$_2$(dpsm)}$_2$]. A solution of dpsm (0.34 g, 0.6 mmol) in acetone (15 ml) was added to a solution of [PdCl$_2$(MeCN)$_2$] (0.15 g, 0.6 mmol) in acetone (15 ml) and stirred in the absence of light for 30 min. The volume was reduced to *ca.* 5 ml and diethyl ether (15 ml) added. The orange solid precipitated was filtered off, washed with diethyl ether (2 × 10 ml) and dried *in vacuo*. Yield 0.12 g, 27% (Found: C, 40.6; H, 3.5. Calc. for $C_{50}H_{44}Cl_4Pd_2Sb_4$: C, 40.4; H, 3.0%). MS (ES): *m/z* = 1441. Calc. for $[C_{50}H_{44}{}^{35}Cl_3{}^{106}Pd_2{}^{121}Sb_4]^+$ 1445.

[{PdBr$_2$(dpsm)}$_2$] made as described[18] (Found: C, 36.4; H, 2.3. Calc. for $C_{25}H_{22}Br_2PdSb_2$: C, 36.1; H, 2.7%). MS (ES): *m/z* = 1582. Calc. for $[C_{50}H_{44}{}^{79}Br_3{}^{106}Pd_2{}^{121}Sb_4]^+$ 1577.

[{PdI$_2$(dpsm)}$_2$] (Found: C, 31.9; H, 1.8. Calc. for $C_{25}H_{22}I_2PdSb_2$: C, 32.4; H, 2.4%). MS (ES): *m/z* = 1725. Calc. for $[C_{50}H_{44}I_3{}^{106}Pd_2{}^{121}Sb_4]^+$ 1721.

[{PdCl$_2$(dmsm)}$_2$]. The ligand dmsm (0.27 g, 0.85 mmol) was added to a solution of [PdCl$_2$(MeCN)$_2$] (0.22 g, 0.85 mmol) in acetone (20 ml) with stirring in the absence of light. The mixture was stirred for 5 min, the yellow–orange solid formed filtered off, washed with acetone (2 × 10 ml) and dried *in vacuo*. Yield 0.35 g, 42% (Found: C, 12.2; H, 3.0. Calc. for $C_5H_{14}Cl_2PdSb_2$: C, 12.1; H, 2.8%). MS (FAB): *m/z* = 954. Calc. for $[C_{10}H_{28}{}^{35}Cl_3{}^{106}Pd_2{}^{121}Sb_4]^+$ 951.

[{PtCl$_2$(dpsm)}$_2$]. A solution of dpsm (0.28 g, 0.5 mmol) in acetone (15 ml) was added to a solution of [PtCl$_2$(MeCN)$_2$] (0.17 g, 0.5 mmol) in acetone (15 ml) and stirred in the absence of light for 30 min. The volume was reduced to *ca.* 5 ml and diethyl ether (15 ml) added. The orange solid precipitated was filtered off, washed with diethyl ether (2 × 10 ml) and dried *in vacuo*. Yield 0.13 g, 32% (Found: C, 35.4; H, 2.7. Calc. for $C_{25}H_{22}Cl_2PtSb_2$: C, 36.1; H, 2.6%). MS (ES): *m/z* = 1630, 1362. Calc. for $[C_{50}H_{44}{}^{35}Cl_3{}^{195}Pt_2{}^{121}Sb_4]^+$ 1623 and $[C_{50}H_{44}{}^{35}Cl^{195}Pt^{121}Sb_4]^+$ 1358.

[{PtBr$_2$(dpsm)}$_2$] made as described[18] (Found: C, 31.9; H, 2.6. Calc. for $C_{50}H_{44}Br_4Pt_2Sb_4$: C, 32.6; H, 2.4%). MS (ES): *m/z* = 1763. Calc. for $[C_{50}H_{44}{}^{79}Br_3{}^{195}Pt_2{}^{121}Sb_4]^+$ 1755.

[{PtI$_2$(dpsm)}$_2$] (Found: C, 28.8; H, 2.4. Calc. for $C_{25}H_{22}I_2PtSb_2$: C, 29.6; H, 2.2%). MS (ES): *m/z* = 1904. Calc. for $[C_{50}H_{44}I_3{}^{195}Pt_2{}^{121}Sb_4]^+$ 1899.

[{PtCl$_2$(dmsm)}$_2$]. dmsm (0.33 g, 1.0 mmol) was added to a solution of [PtCl$_2$(MeCN)$_2$] (0.36 g, 1.0 mmol) in acetone (20 ml) with stirring in the absence of light. The mixture was stirred for 5 min, the yellow precipitate formed filtered off, washed with diethyl ether (2 × 10 ml) and dried *in vacuo*. Yield 0.44 g, 38% (Found: C, 10.0; H, 2.3. Calc. for $C_5H_{14}Cl_2PtSb_2$: C, 10.3; H, 2.4%). MS (FAB): *m/z* = 1134. Calc. for $[C_{10}H_{28}{}^{35}Cl_3{}^{195}Pt_2{}^{121}Sb_4]^+$ 1127.

[PdCl$_2$(dpsm)$_2$]. A solution of dpsm (0.34 g, 0.60 mmol) in acetone (15 ml) was added to a solution of [PdCl$_2$(MeCN)$_2$] (0.078 g, 0.30 mmol) in acetone (15 ml) and stirred in the absence of light for 30 min. The volume was reduced to *ca.* 5 ml and diethyl ether (15 ml) added. The yellow solid precipitated was filtered off, washed with diethyl ether (2 × 10 ml) and dried *in vacuo*. Yield 0.20 g, 52% (Found: C, 46.3; H, 3.3. Calc. for $C_{50}H_{44}Cl_2PdSb_4$: C, 45.9; H, 3.4%).

[PtCl$_2$(dpsm)$_2$] was made similarly from [PtCl$_2$(MeCN)$_2$], Yield 63% (Found: C, 43.2; H, 3.3. Calc. for $C_{50}H_{44}Cl_2PtSb_4$: C, 42.9; H, 3.1%). MS (EI) *m/z* = 1363. Calc. for $[C_{50}H_{44}{}^{35}Cl^{195}Pt^{121}Sb_4]^+$ 1358.

[PtBr$_2$(dpsm)$_2$] made as described[18] (Found: C, 40.0; H, 3.2. Calc. for $C_{50}H_{44}Br_2PtSb_4$: C, 40.4; H, 3.0%). MS (EI) *m/z* = 1405. Calc. for $[C_{50}H_{44}{}^{79}Br^{195}Pt^{121}Sb_4]^+$ 1402.

[PtI$_2$(dpsm)$_2$] (Found: C, 37.6; H, 2.5. Calc. for $C_{50}H_{44}I_2PtSb_4$: C, 37.9; H, 2.9%). MS (EI) *m/z* = 1454. Calc. for $[C_{50}H_{44}I^{195}Pt^{121}Sb_4]^+$ 1450.

[PdBr$_2$(dpsm)$_2$]. Yield 55% (Found: C, 43.1; H, 3.1. Calc. for $C_{50}H_{44}Br_2PdSb_4$: C, 42.9; H, 3.2%).

[PdI$_2$(dpsm)$_2$]. Yield 48% (Found: C, 40.4; H, 3.1. Calc. for $C_{50}H_{44}I_2PdSb_4$: C, 40.2; H, 3.0%).

Crystallography

Crystals of [RuI$_2$(dpsm)$_3$] and [{PtCl$_2$(dpsm)}$_2$]·Me$_2$CO were obtained by vapour diffusion of diethyl ether into an acetone solution of the complex; crystals of [{MBr$_2$(dpsm)}$_2$]·xCH$_2$Cl$_2$ were obtained by vapour diffusion from CH$_2$Cl$_2$ solutions with the sealed vessel held at −20 °C (M = Pd; hexane; M = Pt; EtOH). Crystallographic details are shown in Table 5 and footnote.† Data were collected on a Rigaku AFC7S (Pd and Pt) or Nonius CCD diffractometer (Ru (due to the small crystal size)), both fitted with Mo-Kα radiation (λ = 0.71073 Å) and a graphite monochromator. Selected crystals were mounted on

Table 5 Crystallographic details

	$[RuI_2(dpsm)_3]$	$[\{PtCl_2(dpsm)\}_2]\cdot Me_2CO$	$[\{PdBr_2(dpsm)\}_2]\cdot xCH_2Cl_2$
Formula	$C_{75}H_{66}I_2RuSb_6$	$C_{53}H_{50}Cl_4OPt_2Sb_4$	$C_{50}H_{44}Br_4Pd_2Sb_4\cdot xCH_2Cl_2$ ($x = 1.1$)
M_r	2052.65	1721.97	1664.36 + x84.93
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
a/Å	23.8997(5)	18.964(6)	15.953(5)
b/Å	11.2289(1)	12.729(4)	17.000(4)
c/Å	25.5004(5)	23.090(4)	11.943(3)
α/°			109.18(2)
β/°	93.340(1)	107.50(2)	109.95(2)
γ/°			79.65(2)
U/Å^3	6831.9(2)	5316.0(2.3)	2867.2(1.4)
T/K	293	150	150
Z	4	4	2
Total observations	77356	10166	10476
No. unique observations (R_{int})	15670 (0.135)	9850 (0.059)	10080 (0.051)
μ/cm^{-1}	34.97	74.60	53.73 ($x = 1.1$)
R ($F_o > n\sigma(F_o)$)	0.047 ($n = 4$, 8915 reflections)	0.055 ($n = 4$, 6448 reflections)	0.065 ($n = 4$, 5415 reflections)
(all data)	0.121	—	—
$wR2$ (all data)	0.087	—	—
wR ($F_o > n\sigma$ (F_o))	—	0.062 ($n = 4$)	0.076 ($n = 4$)

glass fibres using an adhesive for room temperature data (Ru) or the oil-film technique for 150 K data (Pd, Pt). Structure solution was by means of DIRDIF[34] followed by full-matrix least-squares refinement on either F using the TEXSAN package[35] (Pd and Pt) or F^2 using SHELXL 97[36] (Ru). There was some evidence for H atoms in both the ruthenium compound and $[\{PtCl_2(dpsm)\}_2]\cdot Me_2CO$ and all were introduced in calculated positions. The large peaks in the residual electron density for the Pt–Cl compound are close to heavy atoms. For the Pd–Br compound the inclusion of anisotropic atomic displacement parameters (adp) for C atoms gave on refinement a number of non-positive definite ellipsoids together with others which were very elongated suggestive of disorder and with no real improvement in the fit to the data. Accordingly, all the C atoms were retained with isotropic adp values and no H atoms were included in the model. During the structure solution two CH_2Cl_2 solvate molecules became apparent in electron density maps and these were included with a partial occupancy (0.66 and 0.42) to avoid unreasonably large isotropic adp values.

CCDC reference number 186/1820.

See http://www.rsc.org/suppdata/dt/a9/a908296d/ for crystallographic files in .cif format.

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