Preparation and properties of cyclic and open-chain Sb/N-donor ligands[†]

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The preparations of both open-chain and cyclic mixed-donor Sb/N ligands, $MeN(CH_2-2-C_6H_4)_2SbMe$ (1), $MeN(CH_2-2-C_6H_4SbMe_2)_2$ (2), $CH_2\{CH_2N(Me)CH_2-2-C_6H_4SbMe_2\}_2$ (3) and $CH_2\{CH_2N(Me)-2-C_6H_4SbMe_2\}_2$ (3) and (3 $CH_2-2-C_6H_4$ }SbMe (4), are described via reaction of chlorostibines with dilithio-reagents, and their spectroscopic properties established. Air-stable stibonium derivatives of (3) and (4) have been isolated by treatment of the compounds with excess MeI, which leads to quaternisation at the Sb atoms exclusively. A crystal structure of a bis(stibonium) derivative of (3), $[CH_2{CH_2N(Me)CH_2-2-C_6H_4SbMe_3}_2]I_2$, reveals hypervalency at Sb through long-range Sb \cdots N interactions (ca. 2.87 Å), giving pseudo-five-membered rings fused to the aromatic rings, and distorted trigonal bipyramidal coordination at Sb. The coordinating properties of compounds (1) to (4) have been investigated through their reactions with Cu(I), Mn(I), Mo(0) and Pt(IV) reagents, and for (1) and (4) by reaction with Fe(0), giving [Fe(CO)₄(L)]. The spectroscopic data (IR, ${}^{1}H$, ${}^{13}C{}^{1}H$ }, ${}^{55}Mn$, ${}^{63}Cu$, ${}^{95}Mo$ and ${}^{195}Pt$ NMR), mass spectrometry and microanalyses for this series of complexes confirm that coordination occurs via the Sb donor atoms in all cases, with N-coordination only present in fac-[Mn(CO)₃(2)](CF₃SO₃). Crystal structures of $[Cu(2)_2]BF_4$, $[Mo(CO)_4(2)]$ and $[PtMe_3I(2)]$ confirm the coordination modes, showing (2) functioning as a wide-angle bidentate distibine. The structures also show the amine N-donor atoms in the complexes are involved in a hypervalent Sb \cdots N interaction (ca. 3.0 Å) with one of the coordinated Sb atoms in each ligand, leading to significant differences in the conformations of the carbon backbones linking the Sb and N atoms. Reaction of $Na_3[RhCl_6]\cdot 12H_2O$ with one mol equiv. of (2), (3) or (4) leads to the bis-ligand complex $[RhCl_2(2)_2]Cl$ and the 1:1 Rh : L complexes $[RhCl_2(3)]Cl$ and [RhCl₃(4)], both of which involve coordination via the Sb and N donor atoms.

Introduction

Developments in the chemistry of stibine ligands have increased significantly in recent years. Traditionally stibines (SbR₃) were considered to be poor ligands in comparison with the much more widely studied phosphines, and together with the practical challenges presented by the reactivity of the Sb-C bonds (which can lead to Sb-C fission and/or scrambling of R groups) and the lack of readily available organoantimony precursors (for antimony(III) only SbPh3 and SbX3, X = Cl, Br or I, are routinely available commercially), this meant that they attracted limited research interest.1-3 However, recent work4-9 has revealed important differences in the chemistry of stibines compared to phosphines and arsines. Significant findings include the first observation of bridging SbⁱPr₃ ligands in rhodium carbene complexes, which also provide an entry into the corresponding PR₃-bridged and AsR₃bridged species (which have not been prepared directly).⁴ The organometallic chemistry of platinum metal stibine complexes has also received renewed interest, leading to different reaction chemistry from the phosphine analogues,^{5,6} and several reports of stibine complexes being used in catalysis, including Rh-catalysed hydrosilylation using binaphthyl distibines,7,8 while the 'poor' σ -donor properties of SbPh₃ has been used to good effect in the

Ni-based catalytic polymerisation of styrene⁹ and norbornene insertion polymerisation.¹⁰ The occurrence of hypervalent bonding in antimony chemistry is also of considerable current interest *vide infra*.¹¹⁻¹⁴

In recent work we have developed synthetic routes to new sterically demanding, wide-angled and chiral stibines, making use of electrophilic reagents (R_2SbCl) to introduce the stibine functions, and typically using Me substituents in order to increase both the basicity and solubility of the resulting compounds (compared to aryl groups).¹⁵⁻¹⁷ Higher denticity stibines are very rare—the only tridentate being the (little studied) MeC(CH₂SbPh₂)₃,¹⁸ while there are no reported examples of macrocycles involving stibine functions. We have also reported the preparations of the potentially tridentate Sb₂-donor chelates to Cu(I), Ag(I) (structural evidence for both), Rh(III) and Pt(II).¹⁹ A small number of potentially tetradentate Sb₂N₂-donor analogues have been described briefly, but no metal complexes are known.²⁰

We report here the preparation and characterisation of a series of new stibine ligands involving mixed Sb/N-donor sets and both cyclic and open-chain structures, utilising 'pre-organised' reagents to aid cyclisation and to promote chelation. The coordinating properties of these compounds towards a selected range of transition metals (Cu(1), Mo(0), Mn(1), Pt(IV), Rh(III)) has been investigated in order to establish the preferred coordination modes and donor properties of the geometrically constrained ligands. These results are also described together with crystal structure determinations of several examples.

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Results and discussion

Ligands

The methods employed for the preparations of the new mixed Sb/N-donor ligands are shown in Scheme 1. The approach used to prepare compound (1) is similar to that reported for a series of stibocine derivatives, which have themselves been studied for the rapid hypervalent antimony-mediated ethylylation of acyl halides.¹³ Thus, reaction of MeN(CH₂-2-C₆H₄Br)₂ with ^tBuLi in diethyl ether at -78 °C gives the dilithiated intermediate, $MeN(CH_2-2-C_6H_4Li)_2$, which was subsequently reacted with either two mol equiv. of SbMe₂Cl or one mol equiv. of SbMeCl₂ (prepared by bubbling HCl (g) through a toluene solution of SbMe₂Ph or SbMePh₂ respectively)¹⁶ over 18 h to give (1) $(MeN(CH_2-2-C_6H_4)_2SbMe)$ and (2) $(MeN(CH_2-2-C_6H_4SbMe_2)_2)$ as off-white solids in 35 and 40% yield, respectively, following hydrolysis, extraction and drying (MgSO₄). Compound (2) is rather more air-sensitive than (1), consistent with the presence of two alkyl (Me) groups on Sb in the former cf. only one in the latter. The EI mass spectra shows peaks with the correct isotope distribution centred at m/z = 330 and $498 ([(1) - Me]^+)$ and $[(2) - Me]^+$ respectively), and microanalyses also support their formulation as (1) and (2). The 1 H NMR spectra of (1) and (2) are consistent with the structures, the most notable features being the SbMe protons which are observed at around 1 ppm-typical of SbMe groups in related compounds.^{15,17,19} The ¹³C{¹H} NMR spectra are also consistent with the structures showing the highly shielded δ (SbMe) at 1.2 and -1.3 ppm, respectively.



Scheme 1 Preparative routes for compounds (1)–(4).

The preparation of the potentially tetradentate ligand (3) $(CH_2(CH_2N(Me)CH_2-2-C_6H_4SbMe_2)_2)$ was achieved

via a similar method, using the dibromodiamine reagent, $CH_2\{CH_2N(Me)CH_2-2-C_6H_4Br\}_2$, which was obtained as a colourless oil in moderate yield from reaction of N.N'-dimethyl-1,3-propanediamine with two mol equiv. of 2-bromobenzyl bromide in CH₂Cl₂-pyridine at 0 °C. Following lithiation of this compound, the SbMe₂Cl was added dropwise as a toluene solution, giving (3) as a yellow, air-sensitive oil in 52% isolated yield, after hydrolysis, extraction and work-up. The EI mass spectrum shows $[(3) - Me]^+$ at m/z = 569. ¹H and ¹³C{¹H} NMR spectra are readily assigned as (3). In order to establish its identity unambiguously, a sample of (3) was converted to the more stable bis-stibonium derivative, [CH₂{CH₂N(Me)CH₂- $2-C_6H_4SbMe_3_2]I_2$, by treatment with an excess of MeI in CH_2Cl_2 solution. The product is an air-stable white solid, and the spectroscopic and analytical data confirm that under these conditions quaternisation occurs exclusively at the Sb atoms, leaving the amine groups unchanged.

A crystal structure determination was also undertaken on $[CH_2{CH_2N(Me)CH_2-2-C_6H_4SbMe_3}_2]I_2\cdot 1/3CHCl_3$. The structure shows (Fig. 1, Table 1) a bis-stibonium dication, with the free iodides balancing the charge. The Sb atoms are directly bonded to three terminal Me substituents as well as the o-phenylene unit in the ligand backbone. There are additional weaker, hypervalent interactions (ca. 2.87 Å) between Sb1 and N1 and between Sb2 and N2, giving pseudo-five-membered rings linking each Sb to the adjacent N atom, leading to distorted trigonal bipyramidal geometry at each Sb atom (the van der Waals radii for N and Sb are 1.55 and 2.0 Å, respectively). Hypervalency involving, for example, Sb ... N and Sb ... O contacts has been well established in a variety of other systems, especially those containing the 2-(R_2NCH_2)C₆H₄ group,¹¹ e.g. [2-{Me₂NCH₂)C₆H₄}{(Me₃Si)₂CH}SbCl (d(Sb \cdots N) = 2.533(7)Å), and is also important in the reactivity of stibocine derivatives.¹³



Fig. 1 View of the structure of the dication in $[CH_2\{CH_2N(Me)CH_2-2-C_6H_4SbMe_3\}_2]I_2\cdot1/3CHCl_3$ with numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation: a = x, y, 1/2 - z.

Table 1 Selected bond lengths (Å) and angles (°) for $[CH_2\{CH_2N-(Me)CH_2-2-C_6H_4SbMe_3\}_2]I_2\cdot 1/3CHCl_3$

Sb1-C1	2.112(6)	Sb1-C2	2.109(6)
Sb1-C3	2.101(6)	Sb1–C4	2.119(5)
N1-C10	1.478(7)	N1-C11	1.477(6)
N1-C12	1.470(7)		
C1-Sb1-C2	101.1(3)	C1–Sb1–C3	115.0(2)
C1-Sb1-C4	117.1(2)	C2-Sb1-C3	105.0(3)
C2-Sb1-C4	102.7(2)	C3–Sb1–C4	113.3(2)
C11-N1-C10	109.5(4)	C12-N1-C10	109.8(4)
C12-N1-C11	110.3(4)		

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Very recently Breunig and co-workers have also studied hypervalency in compounds such as $\{2-(Me_2NCH_2)C_6H_4\}_2SbCH_2SiMe_3$ (R₂SbCH₂SiMe₃) ($d(Sb \cdots N) = 2.971(3)$, 3.189(3) Å) and the related (R₂Sb)₂E (E = O; $d(Sb \cdots N) = 2.775(5)$, 3.240(4) Å; E = S; $d(Sb \cdots N) = 2.855(3)$, 3.025(3) Å).¹² These are similar to the distances found in [CH₂(CH₂N(Me)CH₂-2-C₆H₄SbMe₃)₂]I₂ within this work, although in the latter compound the Sb atoms are formally cationic.

Simultaneous dropwise addition of solutions of the dilithiated derivative of CH₂{CH₂N(Me)CH₂-2-C₆H₄Br}₂ and SbMeCl₂ in a 1:1 mol ratio under similar conditions to those for ligand (1) produces the SbN₂-donor macrocycle (4) (CH₂{CH₂N(Me)CH₂- $2-C_6H_4$ ₂SbMe) in 62% yield as a colourless, waxy solid. Evidence for this formulation follows from the ¹H and ¹³C{¹H} NMR spectra, as well as the EI mass spectrum which shows peaks with the correct isotope distribution corresponding to $[(4)]^+$ (m/z)416) and $[(4) - Me]^+$ (m/z = 401). Treatment of this compound with an excess of MeI in CH₂Cl₂ solution gave the stibonium derivative [CH₂{CH₂N(Me)CH₂-2-C₆H₄}2SbMe₂]I as an air stable white solid, which was characterised by ¹H and ¹³C{¹H} NMR spectroscopy, showing the characteristic high frequency δ (SbMe) shifts associated with quaternisation at Sb, and electrospray mass spectrometry which shows the only significant species at m/z =431 $[(4) + CH_3]^+$. The ready formation of the cyclic species (1) and (4) is attributed in part to the *cis*-directing influence (preorganisation) of the o-phenylene groups in the backbone. We have recently utilised a similar strategy for the preparation of a range of small ring selenoether macrocycles.21,22

Complexes

In order to probe the donor properties and the coordination modes of these unusual Sb/N-donor ligands, we have investigated their reactions with selected transition metal species and characterised the products spectroscopically and in some cases crystallographically.

The acyclic compounds (2) and (3) each react with one mol equiv. of $[Cu(NCMe)_4]BF_4$ in EtOH–CH₂Cl₂ solution to give the 1 : 2 Cu : L complexes $[Cu(2)_2]BF_4$ and $[Cu(3)_2]BF_4$, respectively. Copper-63 (I = 3/2, 69%) NMR spectroscopy provides a useful technique through which to probe the solution speciation, since the large quadrupole moment associated with the ⁶³Cu nucleus ($Q = -0.211 \times 10^{-28} \text{ m}^2$) dictates that only complexes with essentially regular tetrahedral coordination give rise to a ⁶³Cu NMR resonance. Furthermore, previous work shows that Sb₄coordination gives $\delta(Cu)$ around -200 ppm.^{19,23} The ⁶³Cu NMR spectra of $[Cu(2)_2]BF_4$ and $[Cu(3)_2]BF_4$ show single resonances at -203 and -234 ppm, respectively. Together with the 1 : 2 stoichiometry established from the microanalytical data, the ⁶³Cu NMR data strongly suggest that these compounds involve bidentate chelation of the stibine ligands.

Crystals of $[Cu(2)_2]BF_4$ were obtained by cooling the filtrate from the reaction solution in the freezer (-18 °C) for several days. The crystal structure shows (Fig. 2, Table 2) the Cu(1) coordinated to a distorted tetrahedral arrangement of four Sb donor atoms from the two molecules of (2), with no Cu…N interactions. The Cu–Sb bond distances are in the range 2.529–2.538 Å, while the Sb–Cu–Sb angles involved in the chelate rings are 102.97(3) and 105.82(3)°—slightly less than those required for a regular

Table 2	Selected	bond	lengths	(Å)	and	angles	(°)	for	[Cu(2)	2]BF
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Cu1–Sb1	2.5291(8)	Cu1–Sb2	2.5317(9)
Cu1–Sb3	2.5289(9)	Cu1–Sb4	2.5380(8)
Sb1-Cu1-Sb2	102.97(3)	Sb1–Cu1–Sb3	111.05(3)
Sb1-Cu1-Sb4	115.61(3)	Sb2-Cu1-Sb3	108.42(3)
Sb2-Cu1-Sb4	112.89(3)	Sb3-Cu1-Sb4	105.82(3)



Fig. 2 View of the structure of the cation in $[Cu(2)_2]BF_4$ with numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

tetrahedron. The Cu–Sb distances are slightly longer than observed for $[Cu\{o-C_6H_4(CH_2SbMe_2)_2\}]^+$ (2.5021(5)–2.5222(5) Å),²³ but shorter than those in $[Cu(SbPh_3)_4]^+$ and $[Cu\{(p-FC_6H_4)_3Sb\}_4]^+$ involving the rather more weakly donating triarylantimony ligands (av. 2.57 Å).²⁴ While the amine N-donor atoms in $[Cu(2)_2]^+$ are not involved in any interactions with the Cu atoms, there are weak, hypervalent interactions between Sb1 and N1 (3.04 Å) and Sb3 and N2 (3.00 Å) (both *ca.* 1.0 Å shorter than the Sb2…N1 and Sb4…N2 distances and significantly shorter than the sum of the van der Waals radii for N and Sb). These distances are longer than d(Sb...N) typically observed in neutral Sb(III) systems showing hypervalency^{11–13} and also compared to those in the stibonium cation $[CH_2\{CH_2N(Me)CH_2-2-C_6H_4SbMe_3)\}_2]^{2+}$ (*vide supra*), possibly due to steric factors.

Treatment of $[Mo(CO)_6]$ with one mol equiv. of (2) and excess NaBH₄ in degassed EtOH gives the tetracarbonyl species $[Mo(CO)_4(2)]$ exclusively as a beige solid in good yield. The presence of four terminal v(CO) vibrations in the IR spectrum is strongly indicative of a *cis*-tetracarbonyl $(C_{2v}: 2a_1 + b_1 + b_2)$ and hence suggests bidentate chelation of (2), and the stretching frequencies are similar to those for other known [Mo(CO)₄(distibine)] compounds.^{15,17,25,26} The ¹³C{¹H} NMR spectrum shows two CO resonances as expected and in both the ¹H and ¹³C{¹H} NMR spectra only one $\delta(Me)$ resonance is evident for $[Mo(CO)_4(2)]$ and this is shifted to high frequency compared to (2) itself, while the resonances associated with the NMe and NCH₂ groups are essentially unaffected. The ⁹⁵Mo NMR spectrum shows one resonance at -1729 ppm—typical of an Sb₂(CO)₄ environment at Mo(0).^{15,17,25,26} Taken together, these data strongly suggest that (2) is coordinated to Mo via the two stibine functions only. Borohydride is effective in promoting CO substitution in Group 6 carbonyl chemistry, however the number of CO groups replaced is dependent upon the particular system,^{18,26} although we note that the tripodal $MeC(CH_2SbPh_2)_3$ (L) forms the *fac*-[Mo(CO)₃(L)] exclusively.¹⁸

Confirmation of the coordination environment in $[Mo(CO)_4(2)]$ follows from a crystal structure determination (Fig. 3, Table 3) which shows the Mo atom in a distorted octahedral environment through four CO ligands and the two Sb donor atoms from a bidentate molecule of (2), with d(Mo-Sb) = 2.7509(6), 2.7792(5) Å. The chelate angle, $Sb1-Mo1-Sb2 = 95.183(18)^{\circ}$. is somewhat larger than observed in other distibine complexes involving the Group 6 metal carbonyls, e.g. $[Mo(CO)_4(2,2'$ bis(Me₂Sb)-1,1'-binaphthyl)] (84.13(4), 84.61(4)°), although the rigidity of the binaphthyl backbone is thought to have a significant role here,¹⁷ and $[W(CO)_4(\{CH_2(o-C_6H_4CH_2SbMe_2)\}_2)]$ (90.34(1) to $93.26(1)^{\circ}$).¹⁶ As expected, the Mo–C distances in [Mo(CO)₄(2)] fall into two distinct sets, those trans to Sb being significantly shorter than those occupying axial (mutually trans) positions reflecting the modest σ -donor/ π -acceptor properties of the stibine compared to CO. The conformation of the ligand backbone in this species is also interesting, adopting an arrangement which places N1 ca. 1.0 Å closer to Sb1 than Sb2, giving $d(Sb1 \cdots N1) = 3.05$ Å; this secondary (hypervalent) interaction presumably adds some

C19 €

Sb2

C18

9

C8

Fig. 3 View of the structure of $[Mo(CO)_4(2)]$ with numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms

C2

C22

Mo1

C23

04

C5

906

C20

C16

C12

C1

¢

C10

C15

C13

are omitted for clarity.

C14



Mo1-C20	1.976(5)	Mo1-C21	1.991(6)
Mo1–C22	2.063(6)	Mo1-C23	2.027(6)
Mo1–Sb1	2.7792(5)	Mo1–Sb2	2.7509(6)
C20-Mo1-C21	90.8(2)	C20-Mo1-C22	91.6(2)
C20-Mo1-C23	86.4(2)	C21-Mo1-C22	90.4(2)
C21-Mo1-C23	86.9(2)	C22-Mo1-C23	176.6(2)
C20-Mo1-Sb1	177.01(16)	C20-Mo1-Sb2	86.60(16)
C21-Mo1-Sb1	87.45(16)	C21-Mo1-Sb2	177.36(16)
C22-Mo1-Sb1	85.97(14)	C22-Mo1-Sb2	89.58(16)
C23-Mo1-Sb1	95.91(14)	C23-Mo1-Sb2	93.04(15)
Sb1-Mo1-Sb2	95.183(18)		. ,

stability to the complex. The Sb atom involved in this interaction is also the one giving the slightly longer Mo–Sb distance.

The Mn(1) compound [MnCl(CO)₅] has been shown to react with the distibutes $R_2Sb(CH_2)_3SbR_2$ (R = Me or Ph) to afford the neutral *fac*-[MnCl(CO)₃(distibute)].²⁷ In order to try to promote tridentate Sb₂N coordination of (**2**) we therefore abstracted the Cl (*via* Ag(CF₃SO₃)) in acetone, prior to adding (**2**). Using this approach we were able to isolate the product [Mn(CO)₃(**2**)](CF₃SO₃) on the basis of microanalysis. Electrospray MS shows peaks with the correct isotope distribution at m/z = 693 ([Mn(CO)₃(**2**)(MeCN)]⁺) and 652 ([Mn(CO)₃(**2**)]⁺), and IR shows v(CO) = 2011 and 1912, consistent with a *fac*-tricarbonyl fragment,²⁸ and conductivity measurements (CH₂Cl₂) confirmed this compound as a 1 : 1 electrolyte, hence incorporating ionic [CF₃SO₃]⁻, and strongly suggesting tridentate Sb₂N-coordinated (**2**).

In previous work we have shown that PtMe₃I is a very useful reagent against which to probe the preferred coordination modes of new ligands, with ligands favouring bidentate coordination giving the neutral $[PtMe_3I(L_2)]$ (e.g. in distibute complexes),^{19,29} whereas those favouring tridentate coordination can readily displace the coordinated iodide, giving the ionic $[PtMe_3(L_3)]I$ (as for example in [PtMe₃(Se₃-macrocycle)]I).²² NMR spectroscopic measurements (1H, 13C{1H} and 195Pt) allow these species to be distinguished readily. Therefore, ligand (2) was reacted with one mol equiv. of PtMe₃I in refluxing CHCl₃ to give a yellow solid formulated as [PtMe₃I(2)] on the basis of microanalysis. The electrospray mass spectrum shows peaks with the correct isotope distribution due to $[PtMe_3(2)]^+$ (m/z = 752). The ¹H and ¹³C{¹H} NMR spectra each reveal two resonances due to δ (PtMe) groups, with ¹⁹⁵Pt coupling, and also show that the $SbMe_2$ resonances are to high frequency of (2), while the NMe and NCH₂ resonances are unaffected. Finally, the ¹⁹⁵Pt NMR spectrum shows a single resonance at -4400 ppm, similar to [PtMe₃I(distibine)].^{19,29}

The formulation of the product as neutral $[PtMe_3I(2)]$ is confirmed from a crystal structure determination. The structure shows (Fig. 4, Table 4) a distorted octahedral environment at Pt(IV)



Fig. 4 View of the structure of $[PtMe_3I(2)]$ with numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

Pt1-C20	2.105(7)	Pt1–Sb1	2.6321(7)
Pt1-C21	2.090(8)	Pt1–Sb2	2.6053(7)
Pt1-C22	2.092(7)	Pt1–I1	2.7972(7)
C20-Pt1-C21	86.3(3)	C20-Pt1-C22	84.6(3)
C21-Pt1-C22	86.7(3)	Sb1-Pt1-Sb2	97.48(3)
C20-Pt1-I1	176.3(2)	Sb1-Pt1-I1	86.14(2)
C21-Pt1-I1	92.0(2)	Sb2-Pt1-I1	87.65(2)
C22-Pt1-I1	92.1(2)	C20-Pt1-Sb2	95.5(2)
C20-Pt1-Sb1	95.2(2)	C21-Pt1-Sb2	87.7(2)
C21-Pt1-Sb1	174.4(2)	C22-Pt1-Sb2	174.3(2)
C22-Pt1-Sb1	88.2(2)		

via three Me ligands, an iodide and a bidentate Sb₂-coordinated (2), d(Pt-Sb) = 2.6053(7) and 2.6321(7) Å; $\angle(Sb1-Pt1-Sb2) = 97.48(3)^{\circ}$. As in the other complexes of this ligand, in this moiety there is a similar hypervalent Sb1...N1 interaction (2.92 Å); the Sb2...N1 distance is much longer at 4.00 Å. The Pt-Sb bond distances are similar to those in other stibine complexes involving the Me₃PtI fragment, although the chelate angle is slightly larger.^{19,29} Again we note that the slightly longer Pt-Sb distance in [PtMe₃I(2)] is associated with Sb1, which shows the hypervalent Sb...N contact.

We considered that the observation of only bidentate Sb₂chelation in these complexes may reflect the preference for the rather soft metals for antimony over the harder amine N atoms. Therefore we have also investigated reaction of (2) and (3) with Rh(III)-for which many amine complexes are known.³⁰ Ligand (2) reacts with $RhCl_3 \cdot 3H_2O$ (1 : 1 mol ratio) in refluxing EtOH to give a yellow solid formulated, on the basis of IR, electrospray MS (m/z = 1201, [RhCl₂(2)₂]⁺) and microanalysis, as the 1 : 2 complex $[RhCl_2(2)_2]Cl$. Metathesis of the anion with NH_4PF_6 occurs easily, giving the corresponding $[RhCl_2(2)_2]PF_6$, and again under these conditions the Sb₂N-donor ligand favours bidentate Sb₂-coordination, leading to a proposed Cl₂Sb₄ donor set at Rh(III). Reaction of Na₃[RhCl₆]·12H₂O with one mol equiv. of (3) in refluxing EtOH leads to isolation of the 1 : 1 Rh : (3) complex [RhCl₂(3)]Cl. This formulation follows from microanalytical data and electrospray MS (MeCN: m/z = 757 $[RhCl_2(3)]^+$). The ¹H NMR spectrum provides strong evidence for coordination of the N-donor atoms, with δ (NMe) shifted *ca*. 0.5 ppm to high frequency of that in (3) itself, and hence strongly suggesting that (3) behaves as a tetradentate Sb_2N_2 -donor ligand to Rh(III).

Reaction of Na₃[RhCl₆]·12H₂O with one mol equiv. of macrocyclic ligand (4) in EtOH–CH₂Cl₂ (6 : 1) produced an orange solution from which the product [RhCl₃(4)] was isolated as a yellow–orange powder. The IR spectrum shows two peaks attributed to v(Rh–Cl) at 321 and 311 cm⁻¹, respectively, and conductivity measurements confirm the product is a non-electrolyte. These measurements, together with ¹H NMR spectroscopy and microanalysis, support the proposed formulation of the product as the neutral, six-coordinate complex *fac*-[RhCl₃(4)].

In our previous work we have used transition metal carbonyl complexes of new stibine ligands to probe their donor properties by IR and ${}^{13}C{}^{1}H$ NMR spectroscopy. For the cyclic compounds (1) and (4) we have therefore attempted to prepare complexes of nickel, iron and molybdenum carbonyls in which coordination *via* antimony only is anticipated. The products formed by reaction

of (1) and (4) with $[Ni(CO)_4]$; in anhydrous CH_2Cl_2 proved to be very unstable, darkening rapidly, and hence their identification was uncertain and these were not pursued further. Reaction of [Mo(CO)₆] with (1) and excess NaBH₄ in refluxing EtOH led to a mixture of products irrespective of the ratio of Mo : (1) used. IR spectroscopy showed v(CO) at 2070, 1987 and 1922 cm⁻¹ (consistent with a pentacarbonyl species $[Mo(CO)_5(1)]$; C_{4y} theory: $2a_1 + e$) and 2017, 1945, 1904 and 1880 (consistent with *cis*tetracarbonyl species [Mo(CO)₄(1)₂]; C_{2v} theory: $2a_1 + b_1 + b_2$).²⁶ The compound $[Fe(CO)_4(4)]$ was obtained as a dark red solid by reaction of $[Fe_2(CO)_{0}]$ with one mol equiv. of (4) in thf- CH_2Cl_2 (4 : 1). The product is assigned as an axially-substituted tbp containing κ^1 -Sb-coordinated (4) on the basis of the IR data, which show three v(CO) peaks (C_{3v} theory: $2a_1 + e$) at similar frequencies to other stibine complexes.^{15,25} The ¹H NMR spectroscopy shows small high frequency shifts for SbMe, with the NMe resonances essentially unshifted. A κ^1 -Sb-coordinated $[Fe(CO)_4(1)]$ with similar spectroscopic properties was obtained as a dark green oil.

Conclusions

The stibine compounds (1)-(3) have been isolated in moderate yields by reacting the Sb-based electrophiles Me₂SbCl or MeSbCl₂ with appropriate dilithium reagents. Development of this method has produced a very rare example of an Sb-containing macrocyclic ring (4). The ligand properties of these new compounds towards a range of transition metal species has been investigated and reveals a tendency for them to coordinate via the Sb groups only in the majority of reactions investigated. In the cases of (2) and (3) this leads to bidentate chelation, confirmed spectroscopically for Cu(I), Mo(0), Pt(IV) and Rh(III), and structurally for Cu(I), Mo(0) and Pt(IV). The structures of these complexes and of $[CH_2{CH_2N(Me)CH_2-2-C_6H_4SbMe_3}_2]I_2$ also show significant hypervalent Sb...N interactions. Structural evidence of hypervalent interactions in the metal complexes is unusual and has not been found in complexes of hybrid P/N or As/N ligand complexes. In some cases, specifically fac-[Mn(CO)₃(2)](CF₃SO₃), $[RhCl_2(3)]Cl$ and $[RhCl_3(4)]$, tetradentate (Sb_2N_2) and tridentate (SbN_2) coordination respectively is present.

Experimental

Infrared spectra were recorded as Nujol nulls between CsI discs or in CH₂Cl₂ solution between NaCl plates using a Perkin-Elmer 983G or a Perkin-Elmer Spectrum 100 spectrometer over the range 4000–200 cm⁻¹. ¹H and ¹³C{¹H} NMR spectra were recorded using a Bruker AV300 spectrometer and are referenced to TMS. ⁵⁵Mn, ⁶³Cu, ⁹⁵Mo and ¹⁹⁵Pt NMR spectra were recorded using a Bruker DPX400 spectrometer operating at 99.1, 106.1, 26.1 or 85.6 MHz respectively and are referenced to external aqueous KMnO₄, [Cu(MeCN)₄]BF₄ in MeCN, aqueous Na₂[MoO₄] and 1 mol dm⁻³ Na₂[PtCl₆] respectively. Mass spectra were run by electron impact on a VG-70-SE Normal geometry double focusing spectrometer

 $CAUTION: Ni(CO)_4$ is volatile and extremely toxic. All reactions were conducted in a good fume cupboard and in sealed equipment fitted with bromine water scrubbers. Spectroscopic samples were also handled in a fume cupboard and residues were destroyed with bromine water.

or by positive ion electrospray (MeCN solution) or APCI using a VG Biotech platform. Microanalyses were undertaken by Medac Ltd.

Solvents were dried by standard procedures prior to use and all preparations were undertaken using standard Schlenk techniques under a N_2 atmosphere. The stibine ligands were stored and handled in a glove box under N_2 . The precursor MeN(CH₂-2-C₆H₄Br)₂ was prepared *via* the literature method.¹³

$CH_2\{CH_2N(Me)CH_2\text{-}2\text{-}C_6H_4Br\}_2$

N,N'-Dimethyl-1,3-propanediamine (5.10 g. 0.05 mol) and pyridine (16 mL, 0.20 mol) were dissolved in CH₂Cl₂ (100 mL) and the mixture was cooled to 0 °C. 2-Bromobenzyl bromide (25.0 g, 0.10 mol) was added as a CH₂Cl₂ solution (100 mL) dropwise, over a period of 3 h. The reaction was stirred for 18 h, followed by the addition of water (100 mL). The organics were separated, washed with water (2×50 mL), and dried over MgSO₄. The solution was filtered and the volatiles were removed under reduced pressure. The crude product was then purified by silica column chromatography (petroleum ether-CH2Cl2, 5 : 1) to yield the compound as a colourless oil. Yield: 8.10 g, 37%. ¹H NMR (CDCl₃): δ 1.75 (m, CH₂) [2H], 2.20 (s, CH₃) [6H], 2.45 (t, CH₂) [4H], 3.50 (s, CH₂) [4H], 7.00 (t, CH) [2H], 7.25 (t, CH) [2H], 7.35 (d, CH) [2H], 7.45 (d, CH) [2H]. ¹³C{¹H} NMR (CDCl₃): δ 25.4 (CH₂), 42.3 (CH₃), 55.9 (NCH₂), 61.5 (NCH₂), 124.5 (C_{ipso}), 127.2, 128.2, 130.8, 132.6 (CH), 138.6 (C_{inso}). EIMS: m/z = 441, [M]⁺. Required for C₁₉H₂₄Br₂N₂: C, 51.8; H, 5.5; N, 6.4. Found: C, 51.6; H, 5.6; N, 6.2%.

$MeN(CH_2-2-C_6H_4)_2SbMe(1)$

 N^1, N^2 -Bis(2-bromobenzyl)- N^1, N^2 -dimethylpropane-1,3-diamine (1.50 g, 3.40 mmol) was dissolved in diethyl ether (100 mL) and cooled to -78 °C. "BuLi (1.6 M in hexane, 4.0 mL) was added dropwise and the reaction was stirred for 2 h, and allowed to warm to RT. SbMeCl₂ was prepared by bubbling HCl (g) through a toluene (100 mL) solution of SbMePh₂ for 30 min, stirring for a further 40 min, and purging the solution with N_2 for 30 min. The chlorostibine solution was added dropwise to the lithiated solution, and the reaction was stirred for 18 h. The mixture was hydrolysed with degassed water (100 mL), the organics separated and the aqueous washed with diethyl ether (2 \times 50 mL). The combined organics were dried over MgSO₄, filtered and the volatiles removed under reduced pressure, yielding (1) as an offwhite solid which was recrystallised from ethanol-CH2Cl2. Yield: 0.41 g, 35%. ¹H NMR (CDCl₃): δ 0.91 (s, SbCH₃) [3H], 2.38 (s, NCH₃) [3H], 3.52–3.85 (m, CH₂) [4H], 6.93–7.54 (m, CH) [8H]. ¹³C{¹H} NMR (CDCl₃): δ1.20 (SbCH₃), 41.3 (NCH₃), 59.9 (CH₂), 126.5, 127.2, 129.0, 132.6 (CH), 136.6, 143.5 (C_{ipso}). EIMS: m/z =330 [(1) - Me]⁺. Required for C₁₆H₁₈NSb·1/3CH₂Cl₂: C, 52.4; H, 5.0; N, 3.7. Found: C, 52.2; H, 5.4; N, 3.2%.

MeN(CH₂-2-C₆H₄SbMe₂)₂ (2)

MeN(CH₂-2-C₆H₄Br)₂ (2.00 g, 5.42 mmol) was dissolved in diethyl ether (100 mL) and cooled to -70 °C. ⁿBuLi (1.6 M in hexane, 6.8 mL) was added dropwise and the reaction was stirred for 2 h, and allowed to warm to RT. SbMe₂Cl was prepared by bubbling HCl (g) through a toluene (100 mL) solution of SbMe₂Ph for

|, 3.50 (s, CH2)[4H], 3.46 (s, CH2) [4H], 7.05 (d, ${}^{3}J = 6.5$ Hz, CH) [2H], 7.16 (m,(d, CH) [2H],(CH2)(5.4 (CH2), 42.3(CH2)(2, 128.2, 130.8)(CH2)(3.1 CH2)(CH2)(4.1 CH2)(CH2)(5.2 (CH2)(CH2)(5.3 CH2)(CH2)(5.4 (CH2))(CH2)(2, 128.2, 130.8)(CH2)(2, 128.2, 130.8)(CH2)(2, 128.2, 130.8)(CH2)(3) - Me]^+.(4.6)(CH2)(5.7, 65.0)(CH2)(7.7, 51.28.5, 133.9)(CH1)(CH2)(7.8)</td

 $CH_{2}{CH_{2}N(Me)CH_{2}-2-C_{6}H_{4}SbMe_{2}}_{2}$ (3)

2.6%.

acetone (50 mL) and an excess of MeI was added to the stirring solution. The reaction was stirred for a further 2 h, before the solution was reduced in volume to give a white precipitate. This was collected by filtration, washed with cold acetone and dried *in vacuo*. Yield: 0.35 g, 80%. ¹H NMR (300 MHz, CDCl₃): δ 1.57 (m, CH₂) [2H], 2.10 (s, SbCH₃) [18H], 2.22 (s, NCH₃) [6H], 2.97 (br m, CH₂) [4H], 3.92 (br m, CH₂) [4H], 7.46 (m, CH) [4H], 7.58 (m, CH) [4H], ¹³C{¹H} NMR (CDCl₃): δ 6.8 (SbCH₃), 22.4 (CH₂), 42.6 (NCH₃), 56.9, 63.2 (CH₂), 130.0, 133.0, 136.1, 137.6 (CH), 145.4, 147.9 (C_{jsso}). Electrospray MS (MeCN): *m*/*z* = 741 [(**3**) + 2CH₃ + I]⁺, 599 [(**3**) + CH₃]⁺, 307 [(**3**) + 2CH₃]²⁺. Required for C₂₅H₄₂I₂N₂Sb₂: C, 34.6; H, 4.9; N, 3.2. Found: C, 35.1; H, 4.9; N, 3.2%.

30 min, stirring for a further 20 min, and purging the solution with

 N_2 for 30 min. The chlorostibine solution was added dropwise

to the lithiated solution, and the reaction was stirred for 18 h.

The mixture was hydrolysed with degassed water (100 mL), the

organics separated and the aqueous washed with diethyl ether ($2 \times$

50 mL). The combined organics were dried over MgSO₄, filtered

and the volatiles removed under reduced pressure, yielding the title compound as an off-white crystalline solid. Yield: 1.10 g, 40%. ¹H

NMR (CDCl₃): δ 0.75 (s, SbCH₃) [12H], 1.92 (s, NCH₃) [3H], 3.72 (s, CH₂) [4H], 7.28 (m, CH) [4H], 7.35 (d, ³*J* = 7 Hz, CH)

[2H], 7.51 (d, ${}^{3}J = 7$ Hz, CH) [2H]. ${}^{13}C{}^{1}H{}$ NMR (CDCl₃): δ

-1.3 (SbCH₃), 40.4 (NCH₃), 64.5 (CH₂), 127.3, 127.9, 129.3, 133.7

(CH), 138.9, 143.9 (C_{ipso}). EIMS: $m/z = 498 [(2) - Me]^+$. Required

for C₁₉H₂₇NSb₂: C, 44.5; H, 5.3; N, 2.7. Found: C, 44.8; H, 5.3; N,

Synthesised using the method for ligand (2) above, but using

the precursor $CH_2\{CH_2N(Me)CH_2-2-C_6H_4Br\}_2$, yielding a pale

yellow oil. Yield: 52%. ¹H NMR (CDCl₃): δ 0.74 (s, SbCH₃) [12H],

1.69 (m, CH₂) [2H], 1.97 (s, NCH₃) [6H], 2.37 (t, ${}^{3}J = 7.5$ Hz, CH₂)

$CH_{2}\{CH_{2}N(Me)CH_{2}-2-C_{6}H_{4}\}_{2}SbMe$ (4)

Synthesised using the method for ligand (2) above, but using the dibromodiamine precursor, CH₂{CH₂N(Me)CH₂-2-C₆H₄Br}₂. The concentrations of lithiated precursor and the chlorostibine reagent were kept below 0.025 mol dm⁻³, and the solutions of the reactants were added slowly dropwise over a period of 3 h, yielding a pale yellow solid. Yield: 62%. ¹H NMR (CDCl₃): δ 1.16 (s, SbCH₃) [3H], 1.89 (m, CH₂) [2H], 1.97 (s, NCH₃) [6H], 2.21 (m, CH₂) [4H], 3.55 (s, CH₂) [4H], 7.05 (m, CH) [2H], 7.16 (m, CH) [6H]. ¹³C{¹H} NMR (CDCl₃): δ 1.65 (SbCH₃), 22.3 (CH₂), 41.1 (NCH₃), 55.9, 65.6 (NCH₂), 127.5, 127.7, 128.9, 136.4 (CH), 143.6, 145.0 (C_{ipso}). EIMS: *m*/*z* = 416 [(4)]⁺ (7%), 401 [(4) – Me]⁺ (60%). Required for C₂₀H₂₇N₂Sb: C, 57.5; H, 6.5; N, 6.7. Found: C, 57.1; H, 6.7; N, 5.9%.

Compound (4) (0.21 g, 0.5 mmol) was dissolved in degassed acetone (50 mL) and an excess of MeI was added to the stirring solution. The reaction was stirred for 2 h, the solution was reduced in volume and the resulting white precipitate was filtered off and washed with cold acetone. Yield: 0.30 g, 86%. ¹H NMR (CDCl₃): δ 1.23 (s, SbCH₃) [6H], 1.80 (m, CH₂) [2H], 2.05 (s, NCH₃) [6H], 3.40 (m, CH₂) [4H], 6.98 (m, CH) [6H]. ¹³C{¹H} NMR (CDCl₃): δ 11.2 (SbCH₃), 21.6 (CH₂), 40.1 (NCH₃), 54.4, 65.9 (NCH₂), 129.2, 129.8, 130.1, 131.2 (CH). Electrospray MS (MeCN): m/z = 431 [(4) + CH₃]⁺.

[Fe(CO)₄(1)]

Fe₂(CO)₉ (0.10 g, 0.29 mmol) was dissolved in dry thf (20 mL) and filtered. Ligand (1) (0.10 g, 0.29 mmol) was added dropwise as a CH₂Cl₂ solution (5 mL). On addition of the ligand the solution turned a dark green colour and the reaction was left to stir for 15 h. The solvent was reduced to dryness and the dark green oil was dried *in vacuo*. ¹H NMR (CDCl₃): δ –0.10 (s, SbCH₃) [3H], 2.72 (s, NCH₃) [3H], 3.46–3.89 (m, CH₂) [4H], 6.93–7.54 (m, CH) [8H]. ¹³C{¹H} NMR (CDCl₃): δ 4.4 (SbCH₃), 34.4 (NCH₃), 63.3 (CH₂), 129.0, 129.3, 129.7 (CH), 136.6, 136.4, 138.9 (C_{*ipso*}), 212.3 (CO). IR (CH₂Cl₂/cm⁻¹): 2042 (s), 1966 (m), 1930 (br, s).

[Cu(2)₂]BF₄

[Cu(MeCN)₄]BF₄ (0.094 g, 0.3 mmol) was dissolved in degassed ethanol (70 mL) and ligand (**2**) (0.153 g, 0.3 mmol) was added dropwise as a CH₂Cl₂ solution under N₂. The reaction stirred at room temperature for 4 h, after which the volume was reduced to *ca.* 10 mL and the yellow solid formed was filtered, washed with diethyl ether and dried *in vacuo.* Yield: 0.13 g, 74%. ¹H NMR (CDCl₃): δ 1.10 (s, SbCH₃) [12H], 1.65 (s, NCH₃) [3H], 3.44 (s, CH₂) [4H], 6.95 (d, ³J = 8 Hz, CH) [2H], 7.31 (m, CH) [4H], 7.54 (d, ³J = 8 Hz, CH) [2H], ¹³C{¹H} NMR (CDCl₃): δ 1.81 (SbCH₃), 41.5 (NCH₃), 65.2 (CH₂), 129.2, 129.3, 133.9 (CH), 159.9 (C_{ipso}). ⁶³Cu NMR (CHCl₃-CDCl₃): -203 ($w_{1/2}$ = 2200 Hz). Electrospray MS (MeCN): m/z = 1089 [Cu(**2**)₂]⁺, 617 [Cu(**2**)(MeCN)]⁺, 576 [Cu(**2**)]⁺, 514 [(**2**)]⁺, 360 [(**2**) – SbMe₂]⁺. Required for C₃₈H₅₄BCuF₄N₂Sb₄: C, 38.8; H, 4.6; N, 2.4. Found: C, 38.2; H, 4.6; N, 2.4%.

[Mo(CO)₄(2)]

[Mo(CO)₆] (0.053 g, 0.2 mmol), NaBH₄ (0.017 g, 0.45 mmol) and ligand (**2**) (0.205 g, 0.4 mmol) were suspended in ethanol (30 mL) and heated to reflux for 1 h. The solution was stirred at room temperature for 18 h and then reduced in volume (~5 mL) *in vacuo*. Hexane (10 mL) was added and the suspension was stirred for 1 h. The off-white solid was filtered off and dried *in vacuo*, the filtrate was refrigerated to produce a crop of single crystals suitable for X-ray structure analysis. Yield: 0.08 g, 55%. ¹H NMR (CDCl₃): δ 1.03 (s, SbCH₃) [12H], 1.78 (s, NCH₃) [3H], 3.55 (s, CH₂) [4H], 7.17 (m, CH) [2H], 7.25 (m, CH) [4H], 7.46 (m, CH) [2H]. ¹³C{¹H} NMR (CDCl₃): δ 1.8 (SbCH₃), 41.4 (NCH₃), 64.5 (CH₂), 128.2, 129.1, 131.6, 133.8 (CH), 135.2, 142.7 (C_{4ps0}), 210.8, 216.1 (CO). ⁹⁵Mo NMR (CDCl₃): δ -1729. IR (Nujol/cm⁻¹): 1860, 1882, 1909, 2012 (all s). Required for $C_{23}H_{27}MoNO_4Sb_2$: C, 38.3; H, 3.8; N, 1.9. Found: C, 38.2; H, 3.8; N, 2.0%.

[Mn(CO)₃(2)][CF₃SO₃]

[Mn(CO)₅Cl] (0.057 g, 0.25 mmol) was dissolved in acetone (40 mL), AgCF₃SO₃ (0.064 g, 0.25 mmol) was added to the solution which was then refluxed for 1 h. The solution was filtered into a clean Schlenk tube and ligand (2) (0.128 g, 0.25 mmol) was added as an acetone solution (15 mL) under N2. The mixture was refluxed for 20 min and then stirred for 18 h. The volume was reduced to ~10 mL in vacuo and the off-white solid filtered off and dried under reduced pressure. Yield: 0.13 g, 65%. ¹H NMR (CDCl₃): δ 1.15 (s, SbCH₃) [12H], 1.85 (s, NCH₃) [3H], 3.48 (br, CH₂) [4H], 6.95–7.54 (m, CH) [8H]. ⁵⁵Mn NMR (CDCl₃): δ -850 ($w_{1/2}$ = 4200 Hz). Electrospray MS (MeCN): m/z = 693 [Mn(CO)₃(2)(MeCN)]⁺, 652 [Mn(CO)₃(2)]⁺. IR (Nujol/cm⁻¹): 1912 (br), 2011 (s). Required for C₂₃H₂₇F₃MnNO₆SSb₂: C, 34.5; H, 3.4; N, 1.7. Found: C, 34.8; H, 3.8; N, 1.6%. Conductivity measurement ($1 \times 10^{-3} \text{ mol dm}^{-3} \text{ in CH}_2 \text{Cl}_2$): $\Lambda_M = 26 \,\Omega^{-1} \,\text{cm}^2 \,\text{mol}^{-1}$ (1:1 electrolyte).

[PtMe₃I(2)]

PtMe₃I (0.100 g, 0.27 mmol) was dissolved in CHCl₃ (10 mL), ligand (2) (0.140 g, 0.27 mmol) was added as CHCl₃ solution (10 mL) under N₂. The solution was stirred for 18 h, the volume was then reduced to <5 mL and Et₂O (10 mL) was added to yield an off white precipitate. The solid was filtered off and dried in vacuo and the filtrate was cooled to yield a crop of crystals. Yield: 0.14 g, 58%. ¹H NMR (CDCl₃): δ 0.88 (s, PtCH₃) [3H] $({}^{2}J_{PtH} = 73 \text{ Hz}), 1.01 \text{ (br s, SbCH}_{3}) [6H], 1.27 \text{ (s, SbCH}_{3}) [6H],$ 1.40 (s, PtCH₃) [6H] (${}^{2}J_{PtH}$ = 79 Hz), 2.08 (s, NCH₃) [3H], 3.42 (br s, CH₂) [4H], 7.31 (m, CH) [6H], 7.55 (d, ${}^{3}J = 6.2$ Hz) [2H]. ¹³C{¹H} NMR (CDCl₃): δ -10.33, -7.62 (SbCH₃), -3.31 (¹J_{PtC} = 724 Hz) (PtCH₃), -1.24 (¹ $J_{PtC} = 616$ Hz) (PtCH₃), 44.62 (NCH₃), 65.01 (CH₂), 128.2, 129.4, 132.0, 136.1 (CH), 143.3 (C_{ipso}). ¹⁹⁵Pt NMR (CDCl₃): δ –4400. Electrospray MS (MeCN): m/z = 752[PtMe₃(2)]⁺. Required for C₂₂H₃₆INPtSb₂·CHCl₃: C, 27.6; H, 3.7; N, 1.4. Found: C, 27.7; H, 3.8; N, 1.4%.

[RhCl₂(2)₂]Cl

Na₃RhCl₆·12H₂O (0.15 g, 0.25 mmol) was dissolved in degassed ethanol (40 mL), ligand (2) (0.13 g, 0.25 mmol) was added dropwise as an ethanolic solution (50 mL) under N₂, giving an orange solution. The reaction mixture was stirred for a further 12 h, at which stage the solution was concentrated in vacuo, producing a yellow solid which was filtered off, washed with diethyl ether and dried in vacuo. Yield: 0.12 g, 78% (based on (2)). ¹H NMR (CDCl₃): δ 1.21 (s, SbCH₃) [12H], 2.45 (br, s, NCH₃) [3H], 3.54–3.91 (m, CH₂) [4H], 6.92–7.51 (m, CH) [8H]. Electrospray MS (MeCN): m/z = 1201 [RhCl₂(2)₂]⁺. Required for $C_{38}H_{54}Cl_3N_2RhSb_4$: C, 36.9; H, 4.4; N, 2.3. Found: C, 36.9; H, 3.8; N, 2.4%. Addition of an EtOH solution of NH_4PF_6 to a solution of [RhCl₂(2)₂]Cl, gave [RhCl₂(2)₂]PF₆ as a yellow solid which was collected by filtration, washed with EtOH and dried *in vacuo*. Electrospray MS (MeCN): $m/z = 1201 [RhCl_2(2)_2]^+$. IR $(Nujol/cm^{-1}): 842 (s), 558 (s) (PF_6).$

$[Cu(3)_2]BF_4$

[Cu(MeCN)₄]BF₄ (0.094 g, 0.3 mmol) was dissolved in ethanol (50 mL) and ligand (3) (0.175 g, 0.3 mmol) was added dropwise as a CH₂Cl₂ solution (10 mL) under N₂. The reaction was stirred for 4 h, after which the volume was reduced to *ca*. 10 mL and the beige solid formed was filtered off, washed with diethyl ether and dried under reduced pressure. Yield: 0.14 g, 71%. ¹H NMR (CDCl₃): δ 1.21 (s, SbCH₃) [12H], 1.92 (m, CH₂) [2H], 2.43 (s, NCH₃) [6H], 2.80 (m, CH₂) [4H], 3.55 (m, CH₂) [2H], 4.07 (m, CH₂) [2H], 7.21 (m, CH) [2H], 7.37 (m, CH) [4H], 7.52 (m, CH). ⁶³Cu NMR (CHCl₃-CDCl₃): –234 ($w_{1/2}$ = 5300 Hz). Electrospray MS (MeCN): m/z = 647 [Cu(3)]⁺. Required for C₄₆H₇₂BCuF₄N₄Sb₄: C, 41.9; H, 5.5; N, 4.2. Found: C, 41.7; H, 5.4; N, 4.2%.

[RhCl₂(3)]Cl

Na₃RhCl₆·12H₂O (0.150 g, 0.25 mmol) was dissolved in degassed ethanol (40 mL), ligand (3) (0.146 g, 0.25 mmol) was added dropwise as an ethanolic solution (50 mL) under N₂, giving an orange solution. The reaction mixture was stirred for a further 12 h at which stage the solution was concentrated *in vacuo*, producing a yellow solid which was filtered off, washed with diethyl ether and dried in *vacuo*. Yield: 0.135 g, 68%. ¹H NMR (CDCl₃): δ 1.26 (br, SbCH₃) [12H], 1.88 (m, CH₂) [2H], 2.43 (br, NCH₃) [6H], 2.89 (m, CH₂) [4H], 3.50 (m, CH₂) [2H], 4.07 (m, CH₂) [2H], 7.11 (m, CH) [2H], 7.37 (m, CH) [4H], 7.59 (m, CH). Electrospray MS (MeCN): m/z = 757 [RhCl₂(3)]⁺. Required for C₂₃H₃₆Cl₃N₂RhSb₂·1/2CH₂Cl₂: C, 36.5; H, 4.3; N, 3.2. Found: C, 36.3; H, 4.2; N, 3.6%. Conductivity measurement (1 × 10⁻³ mol dm⁻³ in CH₂Cl₂): $\Lambda_{\rm M} = 18 \ \Omega^{-1} \ {\rm cm}^2 \ {\rm mol}^{-1}$ (1 : 1 electrolyte).

[RhCl₃(4)]

 $Na_3RhCl_6 \cdot 12H_2O$ (0.15 g, 0.25 mmol) was dissolved in degassed ethanol (60 mL), ligand (4) (0.21 g, 0.25 mmol) was added dropwise as an CH₂Cl₂ solution (10 mL) under N₂, and stirred

 Table 5
 Crystallographic parameters^a

under N₂ for 48 h, giving an orange solution with an offwhite precipitate which was filtered off. The orange filtrate was concentrated *in vacuo* (~10 mL) and the resulting yellow–orange solid was collected by filtration, washed with a small volume of cold CHCl₃ and dried under reduced pressure. Yield: 0.103 g, 66%. ¹H NMR (CDCl₃): δ 1.45 (br s, SbCH₃) [3H], 1.85 (m, CH₂) [2H], 2.00 (s, NCH₃) [6H], 2.35 (m, CH₂) [4H], 3.70 (br s, CH₂) [2H], 6.80–7.55 (m, CH) [8H]. IR (Nujol/cm⁻¹): 321 (s), 311 (m) (Rh–Cl). Required for C₂₀H₂₇Cl₃N₂RhSb·1¹/₂CHCl₃: C, 32.1; H, 3.6; N, 3.5. Found: C, 32.2; H, 3.6; N, 2.4%. Conductivity measurement (1 × 10⁻³ mol dm⁻³ in CH₂Cl₂): non-electrolyte ($\Lambda_{\rm M} < 1 \Omega^{-1} \, {\rm cm}^2 \, {\rm mol}^{-1}$).

[Fe(CO)₄(4)]

Fe₂(CO)₉ (0.087 g, 0.24 mmol) was dissolved in dry thf (20 mL) and filtered. Ligand (4) (0.10 g, 0.24 mmol) was added dropwise as a CH₂Cl₂ solution (5 mL). On addition of the ligand the solution turned a dark red colour and the reaction was left to stir for 15 h. The solvent was reduced to dryness and the dark red solid was dried *in vacuo.* ¹H NMR (CDCl₃): δ 0.82 (s, SbCH₃) [3H], 1.62–2.30 (m, CH₂) [6H], 1.80 (s, NCH₃) [6H], 3.50 (br, CH₂) [4H], 6.89–7.52 (m, CH) [8H]. IR (CH₂Cl₂/cm⁻¹): 2038 (s), 1955 (sh), 1924 (vbr, s).

X-Ray crystallography

Details of the crystallographic data collection and refinement parameters are given in Table 5. Crystals of $[CH_2{CH_2N(Me)CH_2-2-C_6H_4SbMe_3}_2]I_2\cdot1/3CHCl_3$ were obtained by cooling an acetone–CHCl_3 solution of the compound at -18 °C, while crystals of $[Cu(2)_2]BF_4$, $[Mo(CO)_4(2)]$ and $[PtMe_3I(2)]$ were grown by cooling the filtrates from the reaction mixtures at -18 °C. Data collection used a Nonius Kappa CCD diffractometer (T = 120 K) and with monochromated (graphite or confocal mirrors) Mo-K α X-radiation ($\lambda = 0.71073$ Å). Structure solution and refinement were routine^{31,32} except for the following compound, with H atoms added to the model in calculated positions and using the

Compound	$[Cu(2)_2]BF_4$	[Mo(CO) ₄ (2)]	$[PtMe_{3}I(2)]$	$[CH_{2}\{CH_{2}N(Me)CH_{2}\text{-}2\text{-}C_{6}H_{4}SbMe_{3}\}_{2}]I_{2}\text{-}1/3CHCl_{3}$
Formula	C ₃₈ H ₅₄ BCuF ₄ N ₂ Sb ₄	C ₂₃ H ₂₇ MoNO ₄ Sb ₂	C ₂₂ H ₃₆ INPtSb ₂	C _{25,33} H _{42,33} ClI ₂ N ₂ Sb ₂
Μ	1176.18	720.90	880.01	907.70
Crystal system	Monoclinic	Monoclinic	Monoclinic	Hexagonal
Space group (no.)	$P2_1/c$ (14)	$P2_1/n$ (14)	$P2_1/c$ (14)	$P6_3/m$ (176)
a/Å	15.517(3)	9.9439(10)	16.843(4)	13.7732(10)
b/Å	20.044(4)	7.1462(10)	10.645(3)	13.7732(10)
c/Å	14.2102(15)	36.806(5)	15.405(3)	29.544(3)
β/°	102.588(10)	97.694(5)	110.431(15)	90
U/Å ³	4313.5(13)	2591.9(6)	2588.2(10)	4853.6(7)
Ζ	4	4	4	6
μ (Mo-K α)/mm ⁻¹	3.003	2.573	8.665	3.676
No. data collected	53978	21865	29377	28258
No. unique data	9867	5554	5919	3789
R _{int}	0.096	0.044	0.068	0.095
No. parameters	461	285	252	162
$R1, wR2 (I > 2\sigma(I))^b$	0.050, 0.083	0.044, 0.101	0.042, 0.095	0.034, 0.064
R1, wR2 (all data)	0.090, 0.095	0.049, 0.104	0.065, 0.104	0.051, 0.069

^{*a*} Details in common: temperature = 120 K; wavelength (Mo-K α) = 0.71073 Å; $\theta_{\text{max}} = 27.5^{\circ}$. ^{*b*} $R1 = \sum ||F_{\circ}| - |F_{c}|| / \sum |F_{\circ}|$; $wR_{2} = [\sum w(F_{\circ}^{2} - F_{c}^{2})^{2} / \sum wF_{\circ}^{4}]^{1/2}$.

default C–H distance. The hexagonal $[CH_2{CH_2N(Me)CH_2-2-C_6H_4SbMe_3}_2]I_2\cdot1/3CHCl_3$ was eventually solved in the lower symmetry Laue group although all of the possible space groups arising from the systematic absence showed promisingly low CFOM values. The space group $P6_3/m$ (no. 176) together with the Shelxl TWIN command provided a satisfactory solution. The iodide ions required for charge balance arise from I1 (4f site), I2 (6h) and I3 (4e, and sof 0.5) with a partial CHCl₃ solvate molecule located in the vicinity of I3. Selected bond lengths and angles are given in Tables 1–4.

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