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Journal of Organometallic Chemistry 692 (2007) 5589–5597

Journal of Organo metallic Chemistry

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Synthesis and coordinating properties of the facultative Sb_2O- and As_2O-donor ligands $O\{(CH_2)_2ER_2\}_2$ (E = Sb or As; R = Ph or Me)

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Received 10 July 2007; received in revised form 21 August 2007; accepted 26 August 2007
Available online 4 September 2007

Abstract

The new mixed Sb_2O-donor ligands $O\{(CH_2)_2SbR_2\}_2$ (R = Ph, **1**; R = Me, **2**) with flexible backbones have been prepared in good yields as air-sensitive oils from reaction of $NaSbR_2$ with 0.5 mol equivalents of $O(CH_2CH_2Br)_2$ in thf solution. The As_2O-donor analogues, $O\{(CH_2)_2AsR_2\}_2$ (R = Ph, **3**; R = Me, **4**) were obtained similarly from $LiAsPh_2$ or $NaAsMe_2$, respectively and $O(CH_2CH_2Br)_2$, although ligand **4** appears to be considerably less stable with respect to C–O bond fission under some conditions than the other ligands. Using $O(CH_2CH_2Cl)_2$ leads only to partial substitution by the $SbPh_2^-$ or $AsPh_2^-$ nucleophile. These ligands behave as bidentate chelating Sb_2- or As_2-donors in the distorted tetrahedral $[M(L–L)_2]BF_4$ (M = Cu or Ag; L–L = **1**–**4**) on the basis of solution ^1H and ^{63}Cu NMR spectroscopic studies, mass spectrometry and microanalyses. Crystal structures of three representative examples with Cu(I) and Ag(I) confirm the distorted tetrahedral Sb_4 or As_4 coordination at the metal and allow comparisons of geometric parameters. The crystallographic identification of an unexpected Cu(I)–Cu(I) complex, $[Cu_2\{Me_2As(CH_2)_2OH\}_3](BF_4)_2$, obtained as a by-product via C–O bond fission within ligand **4** is also reported. The distorted octahedral $[RhCl_2(L–L)_2]Cl$ and the distorted square planar *cis*-$[PtCl_2(L–L)]$ (L–L = **1** or **2**) are also described. The ether O atoms are not involved in coordination to the metal ion in any of the late transition metal complexes isolated.

Keywords: Stibine; Arsine; X-ray structures; Copper; Silver

1. Introduction

Stibine ligand chemistry has been much less developed compared to that of the lighter Group 15 donor analogues, phosphines and arsines. This is probably mainly a consequence of the weakness of the Sb–C bonds, the lack of readily available Sb-containing precursor compounds and the early (incorrect) perception that stibines behave the same way as phosphines towards transition metals, but are poorer ligands [1–3]. Recent work from Werner and co-workers [4–6] and ourselves [7–10] has provided clear demonstrations of important differences in the chemistry of stibines compared to phosphines – for example, Werner has identified the first cases of bridging neutral Group 15 ligands in rhodium carbene complexes of Sb^iPr_3. Furthermore, entry into the corresponding P^iPr_3 bridged species requires initial preparation of the bridged stibine species and then substitution of SbR_3 by PR_3, reflecting profoundly different electronic behaviours for the two. Work on the organometallic chemistry of platinum metal stibine complexes from the same research group has also revealed markedly different products are obtained from these compared to those obtained using phosphines. Our own work on Rh(I) stibine chemistry has also identified significant differences in the chemistry of distibines compared to their diphosphine analogues, e.g., reaction of $[Rh(CO)\{Ph_2Sb(CH_2)_3SbPh_2\}_2]^+$ with HCl gas leads to both oxidative addition and cleavage of Ph groups from the stibine (the latter producing chelating $PhClSb(CH_2)_3SbClPh$ on Rh(III)) and the inability of excess $Ph_2Sb(CH_2)_3SbPh_2$ to displace cod from $[Rh(cod)Cl]_2$ [9].

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doi:10.1016/j.jorganchem.2007.08.034

The latter is almost certainly associated with the reduced σ-donor properties of the stibine, and this has recently been used to good effect in the catalytic polymerisation of styrene [11] and norbornene insertion polymerisation [12] by $SbPh_3$ complexes of nickel, in which the rapid and reversible Ni-$SbPh_3$ coordination is thought to be key.

While a range of distibines have been reported (mostly involving reaction of stibides, R_2Sb^- with haloalkanes [1–3] or more recently via reaction of R_2SbCl with di-Grignard reagents [3,7,8]), stibines with higher denticities are very rare – the tripodal $MeC(CH_2SbPh_2)_3$ being the sole example of a tristibine [13], although there are a few examples of mixed donor Sb/O and Sb/N polydentates [15]. In the course of our work towards the development of synthetically viable routes to polydentate and macrocyclic stibines, we have investigated the preparations of the new, potentially tridentate stibine-ether ligands $O\{(CH_2)_2SbR_2\}_2$ (**1**: R = Ph; **2**: R = Me). The analogous arsine-ethers, $O\{(CH_2)_2AsR_2\}_2$ (**3**: R = Ph; **4**: R = Me) have also been prepared to allow comparison of the ligand properties with selected late transition metals. There is an early report of compound **3**, but it was only characterised as its NiI_2 complex [14].

2. Results and discussion

The new Sb_2O-donor ligands **1** and **2** are obtained in good yield from reaction of $NaSbR_2$ (R = Ph or Me) (themselves obtained by treatment of R_2SbCl with Na in liquid NH_3 at −78 °C) with 0.5 mol. equiv. of $O(CH_2CH_2Br)_2$. The α,ω-dibromo precursor is necessary to allow complete substitution (the corresponding $O(CH_2CH_2Cl)_2$ leads only to partial substitution especially by the Ph_2Sb^- nucleophile). Both **1** and **2** are light yellow air-sensitive (especially **2**) oils, hence the compounds were stored and handled in a glove box. ^1H and $^{13}C\{^1H\}$ NMR spectroscopic data for **1** and **2** are fully in accord with the formulations, revealing the two triplets expected for the linking CH_2 groups, and for **2**, the $SbMe_2$ groups significantly shielded as expected. EIMS of **1** reveals a cluster of peaks at $m/z = 624$ consistent with the parent ion, $[M]^+$. As with previous work on new organoantimony compounds, we have prepared and characterised air stable Sb(V) or stibonium derivatives of **1** and **2** to confirm their identities. The tetrabromide derivative of **1** was obtained as a white solid by treatment with 2 mol. equiv. of Br_2 in CH_2Cl_2. NMR spectroscopic studies show a considerable high frequency shift for the CH_2Sb groups ($\delta(^1H)$ shifts from 2.06 to 4.36 ppm; $\delta(^{13}C)$ shifts from 22.53 to 55.27 ppm), consistent with formal oxidation from Sb(III) to Sb(V). The distibonium derivative of **2**, $O\{(CH_2)_2SbMe_3I\}_2$, was isolated as a white solid from reaction of **2** with excess MeI in acetone solution and characterised by NMR spectroscopy, electrospray MS (MeCN) and microanalysis. The analogous As_2O-donor ligands **3** and **4** were obtained from $O(CH_2CH_2Br)_2$ and $LiAsPh_2$ (**3**) or $NaAsMe_2$ (**4**) and characterised similarly. While compound **3** appears to be stable, **4** is much less so and undergoes significant degradation upon standing even under N_2 in the glove box and during distillation and reaction with transition metal salts. The preparation of **4** gave variable yields – in some cases the ^1H and $^{13}C\{^1H\}$ NMR spectra showed **4** to be the only significant product, whereas in others additional resonances were evident. During distillation of **4** from this crude mixture a second, less volatile fraction (74 °C, 0.05 mmHg) was collected in addition to **4** (58 °C, 0.05 mmHg). The NMR features of both fractions show $AsMe_2$, CH_2As and CH_2O resonances, with relative integrals of 3:2:2, and while the Me and $AsCH_2$ resonances are nearly superimposed, that for CH_2O is some 0.2 ppm to low frequency of the CH_2O resonance in **4**. GCEI MS of the by-product shows peaks at $m/z = 150$, consistent with $Me_2As(CH_2)_2OH$, apparently formed via C–O bond fission. Dimethylene linkages are well known to be unstable with respect to elimination of ethene [1,2], however, it is a little surprising that compound **4** appears to be markedly less stable than the other ligands in this study which also incorporate dimethylene linkages. We note that $Ph_2As(CH_2)_2AsPh_2$ is a well known stable compound, whereas $Me_2As(CH_2)_2AsMe_2$ has only been obtained in very low yield and has very little associated chemistry [16]. The compound $Me_2As(CH_2)_2OH$ has been reported as a fragmentation product from $Me_2Si(OCH_2CH_2AsMe_2)_2$ with transition metal compounds and its reaction chemistry with Group 6 carbonyls has been described, although no characterisation data on the arsinoethanol itself have been reported [17].

We have investigated a series of complexes of ligands **1**–**4** with late transition metal ions to probe the coordination modes and to establish whether both the ether O and the As/Sb donor atoms can coordinate simulataneously. Reaction of ligands **1**–**3** (L–L) with $[Cu(MeCN)_4]BF_4$ in MeOH using either a 1:1 or 2:1 ligand:Cu ratio yields only the bis-ligand species $[Cu(L\text{–}L)_2]BF_4$ which were isolated as colourless crystalline solids. Confirmation of the 1:2 Cu:L–L ratio follows from the electrospray MS data (which reveal the main species to be $[Cu(L\text{–}L)_2]^+$ and $[Cu(L\text{–}L)(MeCN)]^+$ for L–L = **1**–**3**), ^{63}Cu NMR spectroscopic measurements and microanalyses. $\delta(^{63}Cu) = -229$ and -194 ppm for the Cu complexes of **1** and **2** respectively, and −139 for the complex of **3**. Copper-63 is quadrupolar with $I = 3/2$ (69%) and as a result of its moderately high quadrupole moment ($Q = -0.211 \times 10^{-28}$ m^2) resonances are typically only observed for high symmetry Cu environments – in the compounds studied here the chemical shifts are consistent with approximately tetrahedral Sb_4 and As_4 donor environments respectively (cf. $[Cu\{Me_2Sb(CH_2)_3SbMe_2\}_2]^+$ $\delta(^{63}Cu) = -167$, $[Cu\{o\text{-}C_6H_4(AsMe_2)_2\}_2]^+$-$\delta(^{63}Cu) = -63$) [18]. A similar reaction of **4** with $[Cu(MeCN)_4]BF_4$ in MeOH solution did not yield $[Cu(\mathbf{4})_2]BF_4$ cleanly, the solution changing from colourless to green and back to colourless during work-up. Electrospray MS (MeCN) on the colourless solid isolated showed peaks at $m/z = 627$, 386 and 345, consistent with $[Cu(\mathbf{4})_2]^+$, $[Cu(\mathbf{4})(MeCN)]^+$ and $[Cu(\mathbf{4})]^+$. The ^{63}Cu NMR spectrum shows a broad resonance associated with the pseudo-tetrahedral Cu(I) cation, $[\mathrm{Cu}(\mathbf{4})_2]^+$ at −16 ppm, confirming the presence of this species in solution. However, the NMR solution also changed to pale green during data acquisition, consistent with some sample degradation, and a structure determination on crystals obtained upon slow evaporation from a solution of the product in $\mathrm{MeOH/Et_2O}$ revealed an unexpected dinuclear Cu(I)–Cu(I) complex incorporating the fragmented ligand $\mathrm{Me_2As(CH_2)_2OH}$ – see below.

The geometry at the metal in the Cu(I) complexes, $[\mathrm{Cu(L{-}L)_2}]\mathrm{BF_4}$, is confirmed from the crystal structure of $[\mathrm{Cu}(\mathbf{3})_2]\mathrm{BF_4}\cdot\mathrm{MeOH}$ (Fig. 1, Table 1) which shows a distorted tetrahedral coordination environment at Cu(I), with the ligands behaving as bidentate $\mathrm{As_2}$-donors and with the ether O atoms not interacting with the metal. The Cu–As bond distances lie in the range 2.4202(9)–2.4652(9) Å respectively, while the As–Cu–As angles within the chelate rings are 106.36(3)° and 107.09(3)°. The bond distances are shorter than those in $[\mathrm{Cu(AsPh_3)_4}]\mathrm{ClO_4}$ 2.493(2)–2.533(1) Å, but significantly longer (by ca. 0.08 Å) than those in $[\mathrm{Cu(Ph_2AsCH{=}CHAsPh_2)_2}]^+$ $d(\mathrm{Cu{-}As}) =$ 2.348(3)–2.358(3) Å, revealing a correlation between increasing ligand steric demands and increased bond lengths [18,19]. The lattice MeOH in $[\mathrm{Cu}(\mathbf{3})_2]\mathrm{BF_4}\cdot\mathrm{MeOH}$ is involved in weak H-bonding interactions with the $[\mathrm{BF_4}]^-$ anion, O3···F2 = 2.97 Å.

Similar coordination is seen for the corresponding (light sensitive) Ag(I) species $[\mathrm{Ag(L{-}L)_2}]\mathrm{BF_4}$ (L–L = **1**–**3**) (obtained from direct reaction of $\mathrm{AgBF_4}$ with L–L in MeOH in a foil-wrapped flask to exclude light). Like the Cu(I) complex of ligand **4** above, reaction of $\mathrm{AgBF_4}$ with **4** did not yield a tractable, pure sample of $[\mathrm{Ag}(\mathbf{4})_2]^+$. Spectroscopic data confirm the presence of this product, however the product is unstable, blackening on standing even in the dark, possibly also due to some C–O fission. The crystal structures of $[\mathrm{Ag}(\mathbf{1})_2]\mathrm{BF_4}\cdot\mathrm{CH_2Cl_2}$ (Fig. 2, Table 2) and $[\mathrm{Ag}(\mathbf{3})_2]\mathrm{BF_4}\cdot\mathrm{MeOH}$ (Fig. 3, Table 3) which show discrete monomeric cations with distorted tetrahedral $\mathrm{Sb_4}$ and $\mathrm{As_4}$ coordination, respectively at Ag(I) via two bidentate L–L units, and with Ag–Sb and Ag–As bond distances in the ranges 2.7020(5)–2.7341(5) and 2.6143(9)–2.6376(9) Å, respectively. These compare very well with *d*(Ag–Sb) of

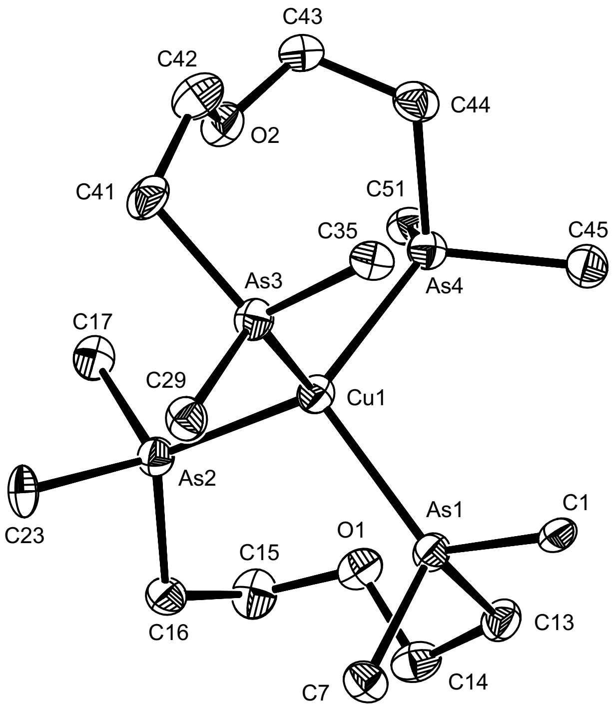

Fig. 1. View of the structure of $[\mathrm{Cu}(\mathbf{3})_2]^+$ with numbering scheme adopted. Ellipsoids are drawn at the 50% probability level. H atoms and the phenyl rings (except the *ipso* C atoms) are omitted for clarity.

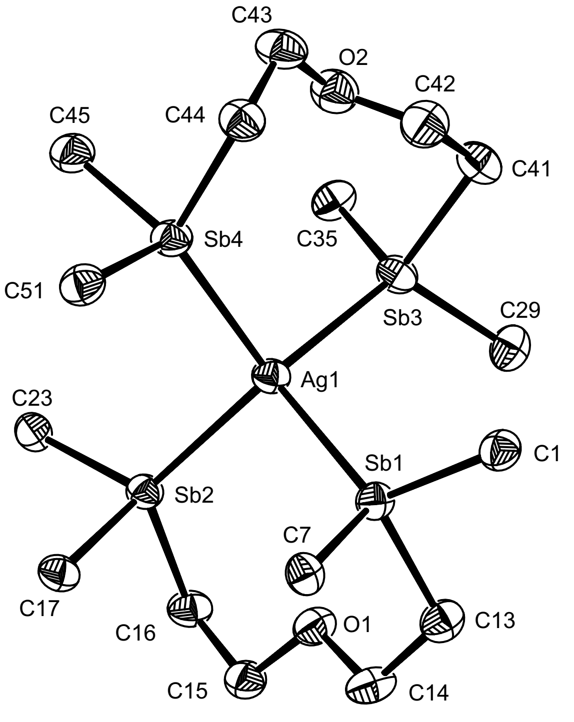

Fig. 2. View of the structure of $[\mathrm{Ag}(\mathbf{1})_2]^+$ with numbering scheme adopted. Ellipsoids are drawn at the 50% probability level. H atoms and the phenyl rings (except the *ipso* C atoms) are omitted for clarity.

Table 1

Selected bond lengths (Å) and angles (°) for $[\mathrm{Cu}(\mathbf{3})_2]\mathrm{BF_4}\cdot\mathrm{MeOH}$

Cu1–As1	2.4212(9)	Cu1–As2	2.4223(9)
Cu1–As3	2.4202(9)	Cu1–As4	2.4652(9)
As3–Cu1–As1	110.64(3)	As3–Cu1–As2	107.65(3)
As1–Cu1–As2	107.09(3)	As3–Cu1–As4	106.36(3)
As1–Cu1–As4	108.09(3)	As2–Cu1–As4	117.00(3)

Table 2

Selected bond lengths (Å) and angles (°) for $[\mathrm{Ag}(\mathbf{1})_2]\mathrm{BF_4}\cdot\mathrm{CH_2Cl_2}$

Ag1–Sb1	2.7268(5)	Ag1–Sb2	2.7341(5)
Ag1–Sb3	2.7020(5)	Ag1–Sb4	2.7194(5)
Sb3–Ag1–Sb4	103.55(2)	Sb3–Ag1–Sb1	107.49(2)
Sb4–Ag1–Sb1	116.26(2)	Sb3–Ag1–Sb2	116.79(2)
Sb4–Ag1–Sb2	109.30(2)	Sb1–Ag1–Sb2	103.95(2)

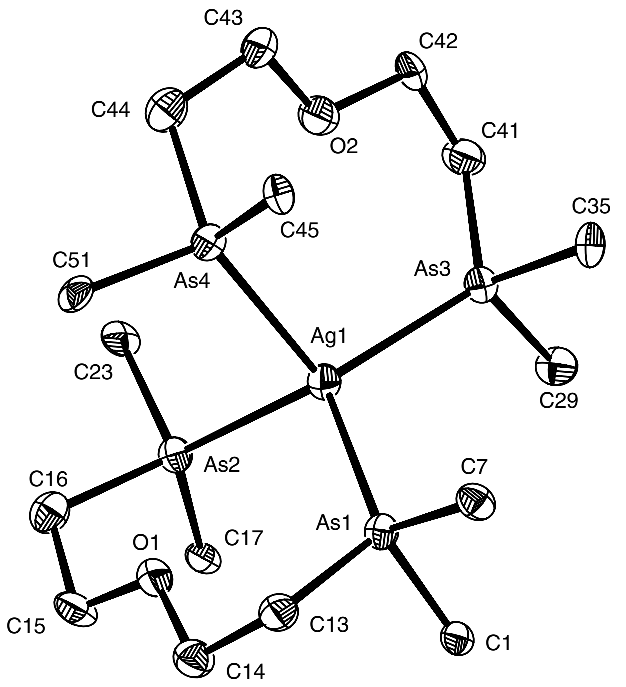

Fig. 3. View of the structure of $[Ag(\mathbf{3})_2]^+$ with numbering scheme adopted. Ellipsoids are drawn at the 50% probability level. H atoms and the phenyl rings (except the *ipso* C atoms) are omitted for clarity.

Table 3
Selected bond lengths (Å) and angles (°) for $[Ag(\mathbf{3})_2]BF_4 \cdot MeOH$

Ag1–As1	2.6376(9)	Ag1–As2	2.6143(9)
Ag1–As3	2.6317(9)	Ag1–As4	2.6296(9)
As2–Ag1–As4	95.67(3)	As2–Ag1–As3	118.83(3)
As4–Ag1–As3	108.09(3)	As2–Ag1–As1	107.60(3)
As4–Ag1–As1	111.63(3)	As3–Ag1–As1	113.65(3)

2.720(1)–2.730(1) Å in $[Ag(SbPh_3)_4]BF_4$ [20] and *d*(Ag–As) of 2.649(2), 2.650(2) Å in $[Ag(AsPh_3)_4]ClO_4$ [19]. We note that the Sb–Ag–Sb angles within the chelates are ca. 4° smaller than the corresponding As–Ag–As chelate angles. The MeOH solvent molecule in $[Ag(\mathbf{3})_2]BF_4 \cdot MeOH$ is also H-bonded to the BF_4^- anion, $O3 \cdots F1 = 2.80$ Å.

Colourless crystals of $[Cu_2\{Me_2As(CH_2)_2OH\}_3](BF_4)_2$ were obtained as a result of ligand fragmentation in the reaction of $[Cu(MeCN)_4]BF_4$ with 2 mol. equiv. of **4** as described above. The structure of the cation shows (Fig. 4, Table 4) a Cu(I)···Cu(I) dimer with the three dimethylarsinoethanol ligands bridging the metal centres, leading to distorted pyramidal coordination at each Cu atom, with two As and one OH group bonded to Cu1 and with one As and two OH groups bonded to Cu2. The short dimethylene ligand backbone places the Cu atoms only 2.497(1) Å apart. This is towards the short end of the range typically seen for Cu(I)–Cu(I) dimers with bridging ligands [21]. We also note that As2, which is 2.283(1) Å from Cu2, appears to shows a long range interaction (2.934(1) Å) with Cu1. The Cu1–Cu2–As2 angle of 75.58(4)° also suggests that As2 is leaning towards Cu1.

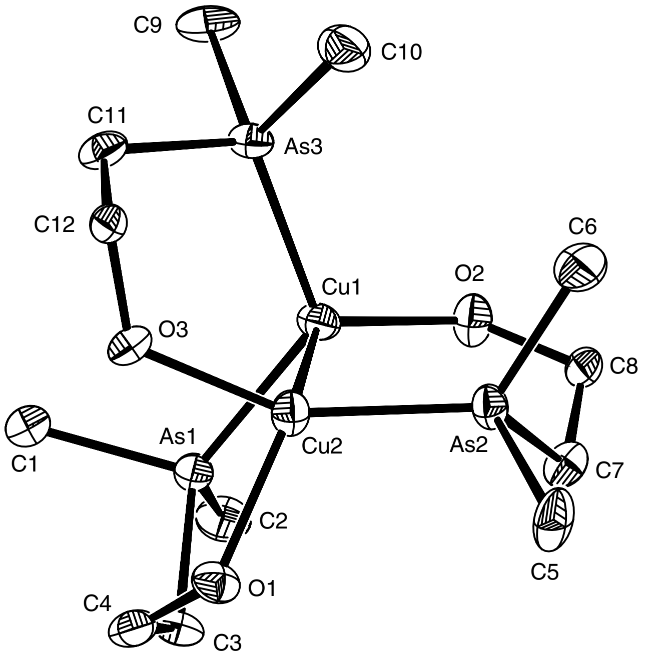

Fig. 4. View of the structure of $[Cu_2\{Me_2As(CH_2)_2OH\}_3]^{2+}$ with numbering scheme adopted. Ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity.

Table 4
Selected bond lengths (Å) and angles (°) for $[Cu_2\{Me_2As(CH_2)_2OH\}_3](BF_4)_2$

Cu1–O2	2.058(6)	Cu2–O3	2.021(5)
Cu1–As3	2.326(1)	Cu2–O1	2.116(6)
Cu1–As1	2.343(1)	Cu2–As2	2.283(1)
Cu1···Cu2	2.497(1)	Cu1···As2	2.934(1)
O2–Cu1–As3	116.77(18)	O2–Cu1–As1	110.87(19)
As3–Cu1–As1	123.12(5)	O2–Cu1···Cu2	126.19(17)
As3–Cu1···Cu2	91.58(5)	As1–Cu1···Cu2	83.99(5)
O2–Cu1···As2	78.38(16)	As3–Cu1···As2	106.81(5)
As1–Cu1···As2	111.67(5)	O3–Cu2–O1	87.8(2)
O3–Cu2–As2	155.21(18)	O1–Cu2–As2	116.05(16)
O3–Cu2···Cu1	98.21(16)	O1–Cu2···Cu1	122.14(17)
As2–Cu2···Cu1	75.58(4)		

The dimethylarsinoethanol ligands clearly result from C–O fission in ligand **4** during the complexation reaction. Although the hydroxyl H atoms were not located in the difference map, the O···F distances strongly suggest H-bonding between the O and F atoms, i.e. O–H···F (O···F ca. 2.7 Å) which, together with the fact the crystals were colouress, are consistent with Cu(I).

The preference for bidentate Sb_2 coordination for **1** and **2** is reinforced by the isolation of $[RhCl_2(\mathbf{1})_2]Cl$ and $[RhCl_2(\mathbf{2})_2]Cl$ from reaction of $Na_3[RhCl_6]$ with 1 mol. equiv. of **1** or **2** in ethanol solution (there is no evidence for $[RhCl_3(\mathbf{1})]$ or $[RhCl_3(\mathbf{2})]$). Spectroscopic data and microanalyses are fully consistent with the formulation of these compounds as distorted octahedral Rh(III) monomers with mutually *trans* Cl ligands and two bidentate chelating L–L units bonded via the Sb atoms only. These complexes were also obtained from the stoichiometric 1:2 Rh:L–L reactions, and the Cl^- anion may be metathesised readily with PF_6^- using NH_4PF_6 in EtOH solution.

Using $[PdCl_2(MeCN)_2]$ or $[PtCl_2(MeCN)_2]$ with **1** or **2** in $MeCN/CH_2Cl_2$ leads to formation of the neutral, distorted square planar monomers *cis*-$[MCl_2(\text{distibine})]$ in high yield. The appearance of two M–Cl stretches in the far-IR spectrum confirms the *cis*-disposition of the Cl ligands, and the ^{195}Pt NMR spectrum of $[PtCl_2(\mathbf{2})]$ shows a single resonance at −4490 ppm, consistent with a Cl_2Sb_2 donor set at Pt(II) [7].

3. Conclusions

We have developed high yielding routes to rare examples of Sb_2O- and As_2O-donor facultative ligands and shown that these behave as Sb_2- (or As_2-) bound bidentates towards tetrahedral Cu(I) and Ag(I), and for **1** and **2**, towards octahedral Rh(III) and square planar Pd(II) and Pt(II) ions. Incorporation of dimethylene linkages between the donor atoms is usually problematic for arsine and stibine ligands, and while ligand **4** shows some C–O bond fission during attempts to purify **4** by distillation and during complexation with Cu(I), the other ligands appear to be significantly more stable. The crystal structure of the Cu(I)–Cu(I) fragmentation product, $[Cu_2\{Me_2As(CH_2)_2OH\}_3](BF_4)_2$ incorporating dimethylarsinoethanol bridging ligands authenticates the occurrence of metal promoted C–O bond fission in compound **4**, leading to unsymmetrical coordination at each Cu atom and a rather short Cu···Cu contact (ca. 2.5 Å).

4. Experimental

Infrared spectra were recorded as CsI discs using a Perkin-Elmer 983G spectrometer over the range 4000–200 cm^{-1}. Mass spectra were run by electron impact on a VG-70-SE Normal geometry double focusing spectrometer or by positive ion electrospray (MeCN solution) using a VG Biotech platform. ^{1}H and $^{13}C\{^1H\}$ NMR spectra were recorded using a Bruker AM300 spectrometer operating at 300 and 75.48 MHz, respectively. ^{63}Cu and ^{195}Pt NMR spectra were recorded using a Bruker DPX400 spectrometer operating at 106.1 or 85.6 MHz respectively and are referenced to $[Cu(MeCN)_4]^+$ and 1 mol dm^{-3} aqueous $Na_2[PtCl_6]$, respectively. Microanalyses were undertaken by the University of Strathclyde microanalytical service.

Solvents were dried prior to use and all preparations were undertaken using standard Schlenk techniques and degassed solvents under a N_2 atmosphere.

4.1. $O\{(CH_2)_2SbPh_2\}_2$ (**1**)

Diphenylchlorostibine [7] (6.23 g, 0.020 mol) was added to a solution of sodium (0.97 g, 0.042 mol) in liquid ammonia (250 mL) maintained at −78 °C (acetone/CO_2 slush). Within 30 min of stirring the colour of the reaction mixture had changed from dark-blue to dark-red. Stirring was continued for a further 1 h, followed by the dropwise addition of bis(2-bromoethyl)ether (2.32 g, 0.010 mol) as a thf solution (100 mL). The reaction was left to stir overnight to allow evaporation of the ammonia. The solution was hydrolysed with degassed H_2O (100 mL) and the organic layer separated. The aqueous layer was washed with diethyl ether (2 × 100 mL), and the combined organics were dried over $MgSO_4$. Following filtration the volatiles were removed under reduced pressure, yielding **1** as a pale yellow oil (3.95 g, 63%). ^{1}H NMR ($CDCl_3$): $\delta = 2.06$ (t) [4H] CH_2Sb, 3.58 (t) [4H] CH_2O, 7.15–7.42 (m) [20H] Ph. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 22.53$ (CH_2Sb), 69.27 (CH_2O), 129.01, 129.32, 136.61 (Ph). EIMS: $m/z = 624$ $[\mathbf{1}]^+$.

Tetrabromide derivative of **1**: compound **1** (0.200 g, 0.32 mmol) was dissolved in CH_2Cl_2 (10 mL) and bromine diluted with CH_2Cl_2 was added dropwise until a permanent orange colour was produced. The reaction mixture was stirred for 1 h, the resulting white solid was filtered off, rinsed with CH_2Cl_2 and dried under reduced pressure (0.22 g, 73%). Anal. Calc. for $C_{28}H_{28}Br_4OSb_2 \cdot CH_2Cl_2$: C, 33.9; H, 2.9. Found: C, 33.4; H, 3.0%. ^{1}H NMR ($CDCl_3$): $\delta = 3.55$ (t) [4H] CH_2O, 4.36 (t) [4H] CH_2Sb, 7.33–7.47 (m) [12H], 8.02–8.13 (m) [8H] Ph. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 55.27$ (CH_2Sb), 67.27 (CH_2O), 130.16, 132.18, 134.69, 139.30 (Ph).

4.2. $O\{(CH_2)_2SbMe_2\}_2$ (**2**)

Hydrogen chloride gas was bubbled through a solution of dimethylphenylstibine (7.00 g, 0.031 mol) in toluene (100 mL) for 15 min. The solution was allowed to stir for a further 20 min and was then purged with N_2 for 30 min. The toluene solution was added to a solution of sodium (1.55 g, 0.067 mol) in liquid ammonia (250 mL) maintained at −78 °C (acetone/CO_2 slush). Within 1 h the colour of the reaction mixture had changed from dark-blue to dark-red. Stirring was continued for a further 2 h, followed by the dropwise addition of bis(2-bromoethyl)ether (3.55 g, 0.015 mol) as a thf solution (100 mL). The reaction mixture was stirred overnight to allow evaporation of the ammonia. The solution was hydrolysed with degassed H_2O (100 mL) and the organic layer separated. The aqueous layer was washed with diethyl ether (2 × 100 mL), and the combined organics were dried over $MgSO_4$. Following filtration the volatiles were removed under reduced pressure yielding (**2**) as a pale yellow oil (2.69 g, 48%). ^{1}H NMR ($CDCl_3$): $\delta = 0.78$ (s) [12H] Me, 1.72 (t) [4H] CH_2Sb, 3.62 (t) [4H] CH_2O. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = -5.27$ (MeSb), 17.90 (CH_2Sb), 69.81 (CH_2O). EIMS: $m/z = 361$ $[\mathbf{2}{-}Me]^+$.

Methiodide of **2**: compound **2** (0.20 g, 0.53 mmol) was dissolved in dry acetone (50 mL) and treated with an excess of methyl iodide. The reaction was left to stir for 30 min and the white solid was filtered, washed with acetone and dried under reduced pressure (Yield: 0.19 g, 54%). Anal. Calc. for $C_{10}H_{26}I_2OSb_2 \cdot 1/3Me_2CO$: C, 19.5; H, 4.2. Found: C, 19.5; H, 4.0%. ^{1}H NMR (d^6-DMSO): $\delta = 1.62$

(s) [18H] Me, 2.59 (t) [4H] CH_2Sb, 3.95 (t) [4H] CH_2O. $^{13}C\{^1H\}$ NMR (d^6-DMSO): $\delta = 1.66$ (MeSb), 22.08 (CH_2Sb), 65.58 (OCH_2). Electrospray MS (MeCN): $m/z =$ 533 $[Me_3Sb(CH_2)_2O(CH_2)_2SbMe_3I]^+$, 203 $[Me_3Sb(CH_2)_2O(CH_2)_2SbMe_3]^{2+}$.

4.3. $O\{(CH_2)_2AsPh_2\}_2$ (**3**)

Lithium metal (0.34 g, 0.048 mol) was added to a solution of triphenylarsine (5.0 g, 0.016 mol) in thf (100 mL). This was refluxed for 1 h to give a dark red solution and then left stirring for 8 h. ^{t}BuCl (1.4 mL, 0.013 mol) was added dropwise to remove the PhLi by-product and the mixture was stirred for 1 h, turning to a lighter orange/red colour. To this was added a solution of $O(CH_2CH_2Br)_2$ (0.70 mL, 5.60 mmol) in thf (10 mL) to give an off-white reaction mixture, which upon refluxing for 2 h turned to a green oil. Aqueous NH_4Cl (50 mL) was added and the organic fraction was separated. The aqueous layer was washed with thf (20 mL) and the combined organic fractions were dried over $MgSO_4$ for 8 h. The solvent was removed in vacuo to give **3** as a yellow waxy oil which was stored in a Schlenk tube over molecular sieves (2.3 g, 77%). ^1H NMR ($CDCl_3$): $\delta = 2.27$ (t) [4H] CH_2As, 3.55 (t) [4H] CH_2O, 7.31–7.44 (m) [20H] Ph. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 28.96$ (CH_2As), 68.86 (CH_2O), 128.96, 129.22, 133.69, 140.96 (Ph). EIMS: $m/z = 530$ [**3**]$^+$, 453 [**3**$-$Ph]$^+$.

Methiodide of **3**: compound **3** (0.2 g, 0.38 mmol) in acetone (5 mL) and MeI (0.2 g, 1.42 mmol) was added and the reaction mixture was stirred for 72 h. The volatiles were removed in vacuo to leave a white solid. ^1H NMR ($CDCl_3$): $\delta = 2.77$ (s) [6H] Me, 3.70–3.77 (m) [8H], CH_2, 7.61–7.90 (m) [20H] Ph. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 10.27$ (MeAs), 27.65 (CH_2As), 65.27 (CH_2O), 122.16 (*ipso* C), 130.60, 132.24, 133.63 (Ph). Electrospray MS (MeCN): $m/z = 687$ $[MePh_2As(CH_2)_2O(CH_2)_2AsPh_2MeI]^+$; 280 $[MePh_2As(CH_2)_2O(CH_2)_2AsPh_2Me]^{2+}$.

4.4. $O\{(CH_2)_2AsMe_2\}_2$ (**4**)

Me_2AsI [22] (8.4 g 0.036 mol) was added dropwise to a flask containing small pieces of sodium metal (2.00 g, 0.087 mol) in thf (200 mL). The reaction mixture was heated to 85 °C for 1 h, whereupon the reaction solution changed from yellow to white and then to green. It was then left stirring for 8 h. $O(CH_2CH_2Br)_2$ (4.20 g, 0.018 mol) was added dropwise, and the mixture was stirred for a further 8 h. Degassed H_2O was added until all the solids dissolved. The organic layer was separated and the aqueous washed with diethyl ether (2×40 mL). The combined organic phases were dried over $MgSO_4$ for 8 h. The solvent was removed in vacuo to give **4** as a yellow oil (3.38 g, 67%). ^1H NMR ($CDCl_3$): $\delta = 0.94$ (s) [12H] Me, 1.68 (t) [4H] CH_2As, 3.75 (t) [4H] CH_2O. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 9.93$ (MeAs), 32.39 (CH_2As), 61.58 (CH_2O). EI MS: $m/z = 267$ [**4**$-$Me]$^+$.

In one case the ^1H NMR spectrum of the product isolated as above showed some additional resonances, hence purification by distillation was attempted, giving two fractions. Fraction 1: B.p. 58 °C at 0.05 mmHg turned out to be ligand **4**, with identical spectroscopic features to those quoted above. Fraction 2: B.p. 74 °C at 0.05 mm Hg; ^1H NMR spectrum ($CDCl_3$): $\delta = 0.93$ (s) [6H] Me, 1.70 (t) [2H] CH_2As, 3.54 (t) [2H] CH_2O. GCEI MS: $m/z = 150$ $[Me_2As(CH_2)_2OH]^+$.

4.5. $[Cu($**1**$)_2]BF_4$

$[Cu(MeCN)_4]BF_4$ (0.31 g, 1.00 mmol) was dissolved in degassed ethanol (75 mL), (**1**) (0.62 g, 1.00 mmol) was added dropwise as a CH_2Cl_2 solution (10 mL). The reaction stirred for 2 h at room temperature and the resulting white precipitate was filtered, washed with ethanol and dried under reduced pressure. The filtrate was reduced in volume and placed in the freezer to yield white crystals (0.15 g) giving a combined yield of 0.33 g, 94% based on **1**. Anal. Calc. for $C_{56}H_{56}BCuF_4O_2Sb_4$: C, 48.1; H, 4.0. Found: C, 47.9; H, 3.6%. ^1H NMR ($CDCl_3$): $\delta = 2.33$ (t) [4H] CH_2Sb, 3.62 (t) [4H] CH_2O, 7.15–7.45 (m) [20H] Ph. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 22.71$ (CH_2Sb), 67.10 (CH_2O), 130.22, 130.78, 132.17, 135.98 (Ph). ^{63}Cu NMR ($MeCN/CDCl_3$): $\delta = -229$ ($w_{1/2} = 2000$ Hz). Electrospray MS (MeCN): $m/z = 1311$ [Cu(**1**)$_2$]$^+$, 728 [Cu(**1**)(MeCN)]$^+$. IR (Nujol): 1072 (BF_4^-) cm^{-1}.

4.6. $[Ag($**1**$)_2]BF_4$

This reaction was carried out in the absence of light and the product was treated as light sensitive. $AgBF_4$ (0.19 g, 1.00 mmol) was dissolved in degassed methanol (30 mL). The ligand (**1**) (0.62 g, 1.00 mmol) was dissolved in CH_2Cl_2 (10 mL) and added dropwise to the methanolic solution. The reaction was stirred for 3 h and the resulting off-white precipitate was filtered, washed with methanol and dried under reduced pressure (0.21 g, 58% based on **1**). Anal. Calc. for $C_{56}H_{56}AgBF_4O_2Sb_4$: C, 46.6; H, 3.9. Found: C, 46.8; H, 4.0%. ^1H NMR ($CDCl_3$): $\delta = 2.33$ (t) [4H] CH_2Sb, 3.64 (t) [4H] CH_2O, 7.11–7.49 (m) [20H] Ph. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 22.25$ (CH_2Sb), 67.3 (CH_2O), 129.37, 129.90, 135.69 (Ph). Electrospray MS (MeCN): $m/z = 1355$ [Ag(**1**)$_2$]$^+$. IR (Nujol): 1078 (BF_4^-) cm^{-1}.

4.7. $[RhCl_2($**1**$)_2]Cl$

$Na_3RhCl_6 \cdot 12H_2O$ (0.30 g, 0.50 mmol) was dissolved in degassed water (40 mL), the ligand (**1**) (0.62 g, 1.00 mmol) was added dropwise as an ethanolic solution (50 mL). The solution turned orange with a yellow precipitate forming and the reaction mixture stirred for a further 1 h. The yellow solid was filtered, washed with diethyl ether and then recystallised from $EtOH/CH_2Cl_2$ before drying under reduced pressure. (0.48 g, 66%). Anal. Calc. for $C_{56}H_{56}Cl_3O_2RhSb_4 \cdot CH_2Cl_2$: C, 44.4; H, 3.8. Found: C, 44.4; H, 3.6. ^{1}H NMR ($CDCl_3$): $\delta = 2.2$–2.6 (br m) [4H] CH_2Sb, 3.7–4.0 (br m) [4H] CH_2O, 7.0–7.7 (m) [20H] Ph. Electrospray MS (MeCN): $m/z = 1421$ $[Rh(\mathbf{1})_2Cl_2]^+$. IR (Nujol): 332 ν(Rh–Cl) cm^{-1}. UV/Vis (nm/CH_2Cl_2): 382 br ($\varepsilon_{mol} = 1450$ cm^{-1} mol^{-1} dm^3).

4.8. $[PtCl_2(\mathbf{1})]$

$PtCl_2$ (0.13 g, 0.50 mmol) was suspended in acetonitrile (50 mL) and heated to reflux for 2 h until a yellow solution formed. The ligand **1** (0.31 g, 0.5 mmol) was added dropwise as a CH_2Cl_2 solution (5 mL), the solution turned orange initially then back to yellow after 20 min. The reaction was left to stir for a further 2 h and the solvent was reduced in volume under reduced pressure. The solid was filtered, washed with diethyl ether (10 mL), and dried under reduced pressure to yield a yellow solid (0.15 g, 33%). Anal. Calc. for $C_{28}H_{28}Cl_2OPtSb_2 \cdot 1/2CH_2Cl_2$: C, 36.7; H, 3.1. Found: C, 36.5; H, 2.5%. ^{1}H NMR (d^6-dmso): $\delta = 6.9$–7.8 (br m) [20H] Ph, 3.2–4.1 (br m) [4H] OCH_2, 2.1–2.8 (br m) [4H] $SbCH_2$. IR (Nujol): 318, 332 ν(Pt–Cl) cm^{-1}.

4.9. $[Cu(\mathbf{2})_2]BF_4$

$[Cu(MeCN)_4]BF_4$ (0.31 g, 0.01 mol) was dissolved in degassed ethanol (75 mL), (**2**) (0.38 g, 0.01 mol) was added dropwise as a CH_2Cl_2 solution (10 mL). The reaction mixture was stirred for 2 h and the resulting white precipitate was filtered off, washed with ethanol and dried under reduced pressure (0.17 g). The filtrate was reduced in volume and placed in the freezer to yield white crystals (0.07 g) giving a combined yield of 0.24 g, 53%. Anal. Calc. for $C_{16}H_{40}BCuF_4O_2Sb_4$: C, 21.3; H, 4.5. Found: C, 20.7; H, 3.9%. ^{1}H NMR ($CDCl_3$): $\delta = 1.53$ (s) [12H] Me, 2.33 (t) [4H] $SbCH_2$, 3.62 (t) [4H] CH_2O. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = -2.56$ (Me), 19.89 (CH_2Sb), 67.83 (CH_2O). ^{63}Cu NMR ($CH_2Cl_2/CDCl_3$): $\delta = -194$ ($w_{1/2} = 400$ Hz). Electrospray MS (MeCN): $m/z = 816$ $[Cu(\mathbf{2})_2]^+$, 481 $[Cu(\mathbf{2})(CH_3CN)]^+$. IR (Nujol): 1060 ($BF_4^-$) cm^{-1}.

4.10. $[Ag(\mathbf{2})_2]BF_4$

This reaction was carried out in the absence of light and the product was treated as light sensitive. $AgBF_4$ (0.19 g, 0.01 mol) was dissolved in degassed methanol (30 mL). The ligand (**2**) (0.38 g, 0.01 mol) was dissolved in CH_2Cl_2 (10 mL) and added dropwise to the methanolic solution. The reaction mixture was stirred for 3 h and the off-white precipitate was filtered off, washed with methanol and dried under reduced pressure (0.21 g, 74%). Anal. Calc. for $C_{16}H_{40}AgBF_4O_2Sb_4 \cdot H_2O$: C, 19.9; H, 4.4. Found: C, 19.5; H, 4.0%. ^{1}H NMR ($CDCl_3$): $\delta = 0.98$ (s) [12H] Me, 2.01 (t) [4H] CH_2Sb, 3.72 (t) [4H] CH_2O. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = -3.30$ (Me), 19.15 (CH_2Sb), 67.10 (CH_2O). Electrospray MS: $m/z = 860$ $[Ag(\mathbf{2})_2]^+$. IR (Nujol): 3350 br $\nu(H_2O)$, 1650 $\delta(H_2O)$, 1071 $\nu(BF_4)^-$ cm^{-1}.

4.11. $[RhCl_2(\mathbf{2})_2]Cl$

$Na_3RhCl_6 \cdot 12H_2O$ (0.15 g, 0.25 mmol) was dissolved in degassed water (40 mL), the ligand (**1**) (0.18 g, 0.50 mmol) was added dropwise as an ethanolic solution (50 mL). The solution turned orange and the reaction mixture was stirred for a further 2 h. The solution was reduced in volume and the yellow solid filtered off, washed with diethyl ether and then recrystallised from chloroform and dried under reduced pressure (0.16 g, 68%). Anal. Calc. for $C_{16}H_{40}Cl_3O_2RhSb_4 \cdot 2CHCl_3$: C, 18.0; H, 3.5. Found: C, 17.3; H, 3.3%. ^{1}H NMR ($CDCl_3$): $\delta = 1.35$ (s) [12H] Me, 2.2–2.6 (m) [4H] CH_2Sb, 3.6–4.0 (m) [4H] CH_2O. Electrospray MS: $m/z = 926$ $[Rh(\mathbf{2})_2Cl_2]^+$. IR (Nujol): 322 ν(Rh–Cl) cm^{-1}.

4.12. $[PtCl_2(\mathbf{2})]$

$PtCl_2$ (0.13 g 0.50 mmol) was suspended in acetonitrile (50 mL) and heated to reflux for 2 h until the suspension dissolved to give a yellow solution. The ligand **2** (0.18 g, 0.50 mmol) was added dropwise as a CH_2Cl_2 solution (5 mL), the solution turned orange initially then back to yellow after 20 min. The reaction was left to stir for a further 2 h and the solvent was reduced in volume under reduced pressure. The solid was filtered, washed with diethyl ether (10 mL), and dried under reduced pressure to yield a yellow solid (0.18 g, 58%). Anal. Calc. for $C_8H_{20}Cl_2OPtSb_2$: C, 15.0; H, 3.1. Found: C, 15.4; H, 2.9%. ^{1}H NMR ($CDCl_3$): $\delta = 1.18$ (s) [12H] Me, 2.11 (t) [4H] $SbCH_2$, 3.82 (t) [4H] OCH_2. ^{195}Pt NMR ($CH_2Cl_2/CDCl_3$): $\delta = -4490$ ($w_{1/2} = 2000$ Hz). IR (Nujol): 279, 301 ν(Pt–Cl) cm^{-1}.

4.13. $[PdCl_2(\mathbf{2})]$

$PdCl_2$ (0.09 g, 0.50 mmol) was suspended in acetonitrile (50 mL) and heated to reflux for 2 h until the suspension dissolved to give a yellow solution. The solution was left to cool and the ligand **2** (0.18 g, 0.50 mmol) was added dropwise as a CH_2Cl_2 solution (5 mL), the reaction was left to stir for a further 2 h. The solid was filtered, washed with diethyl ether (10 mL), and dried under reduced pressure to yield a yellow solid (0.13 g, 49%). Anal. Calc. for $C_8H_{20}Cl_2OPdSb_2$: C, 17.4; H, 3.6. Found: C, 17.1; H, 3.4%. ^{1}H NMR ($CDCl_3$): $\delta = 1.31$ (s) [12H] Me, 2.11 (t) [4H] $SbCH_2$, 3.86 (t) [4H] OCH_2. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 1.71$ (MeSb), 20.75 (CH_2Sb), 67.63 (CH_2O). IR (Nujol): 296, 336 ν(Pd–Cl) cm^{-1}.

4.14. $[Cu(\mathbf{3})_2]BF_4$

Ligand **3** (0.53 g, 1.0 mmol) in CH_2Cl_2 was added dropwise to a solution of $[Cu(MeCN)_4]BF_4$ (0.315 g, 1.0 mmol) in methanol (10 mL). The reaction mixture was stirred for 0.5 h and the light yellow solution was then concentrated to half the volume in vacuo. Colourless crystals were obtained by cooling this solution in the freezer over several days. These were filtered off to give a white solid which was dried in vacuo (0.36 g, 60%). Anal. Calc. for $C_{56}H_{56}As_4BCuF_4O_2 \cdot 2CH_2Cl_2$: C, 50.5; H, 4.4. Found: C, 51.0; H, 4.8%. ^{1}H NMR ($CDCl_3$): $\delta = 2.62$ (br) [4H] CH_2As, 3.84 (br) [4H] OCH_2, 7.28–7.39 (m) [20H] Ph. ^{63}Cu NMR (CH_2Cl_2): $\delta = -139$. IR (Nujol): 1050 (BF_4^-) cm^{-1}.

4.15. [Ag(**3**)$_2$]BF$_4$

Ligand **3** (0.57 g, 1.1 mmol) in CH_2Cl_2 was added dropwise to a solution of $AgBF_4$ (0.21 g, 1.1 mmol) in methanol (10 mL) in a foil-wrapped flask. The reaction mixture was stirred for 1 h, the brown solution was then filtered and colourless crystals were obtained by leaving the filtrate in the dark for one month. (0.29 g, 43%). Anal. Calc. for $C_{56}H_{56}AgAs_4BF_4O_2 \cdot 2MeOH$: C, 52.8; H, 4.9. Found: C, 52.1; H, 4.4%. Electrospray MS (MeCN): $m/z = 1167$ [Ag(**3**)$_2$]$^+$. ^{1}H NMR ($CDCl_3$): $\delta = 2.41$ (br) [4H] CH_2As, 3.48 (br) [4H] OCH_2, 7.17–7.39 (m) [20H] Ph. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 29.17$ (CH_2As), 66.89 (CH_2O), 129.26, 129.88, 132.75, 134.95 (Ph). IR (Nujol): 1060 (BF_4^-) cm^{-1}.

4.16. [Cu(**4**)$_2$]BF$_4$

Ligand **4** (0.07 g, 0.25 mmol) was added dropwise to a solution of $[Cu(MeCN)_4]BF_4$ (0.156 g, 0.50 mmol) in degassed methanol (10 mL), this was stirred for 2 h before the solution was then reduced in vacuo to give a green paste. This dissolved partially in methanol (10 mL), the colourless mother liquor was then transferred and diethyl ether (10 mL) added to produce a green fluffy solid. This was left to stand, the solvent was decanted off and the solid was dried in vacuo. Electrospray MS (MeCN): $m/z = 627$ [Cu(**4**)$_2$]$^+$, 386 [Cu(**4**)(MeCN)]$^+$, 345 [Cu(**4**)]$^+$. ^{1}H NMR ($CDCl_3$): $\delta = 1.38$ (s) [12H] CH_3, 2.08 (t) [4H] CH_2As, 3.99 (br) [4H] OCH_2. ^{63}Cu NMR (CH_2Cl_2): $\delta = -16$. IR (Nujol): 1065 (BF_4^-) cm^{-1}.

4.17. [Ag(**4**)$_2$]BF$_4$

Ligand **4** (0.07 g, 0.25 mmol) was added dropwise to a solution of $AgBF_4$ (0.10 g, 0.50 mmol) in degassed methanol (10 mL) in a foil-wrapped schlenk. After stirring for ca. 2 h the solvent was then removed in vacuo to give a light brown oily paste. Electrospray MS (MeCN): $m/z = 539$ [Ag(**4**)(**4**−$CH_2CH_2AsMe_2$)]$^+$, 407 [Ag(**4**)(H_2O)]$^+$, 389 [Ag(**4**)]$^+$. ^{1}H NMR ($CDCl_3$): $\delta = 1.42$ (s) [12H] Me, 2.13 (t) [4H] CH_2As, 3.95 (t) [4H] OCH_2. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 8.88$ (Me), 31.79 (CH_2As), 58.72 (CH_2O). IR (Nujol): 1057 (BF_4^-) cm^{-1}.

4.18. X-ray crystallography

Details of the crystallographic data collection and refinement parameters are given in Table 5. Colourless crystals of [Ag(**1**)$_2$]BF$_4$ · CH$_2$Cl$_2$, [Cu(**3**)$_2$]BF$_4$ · MeOH, [Ag(**3**)$_2$]BF$_4$ · MeOH and $[Cu_2\{Me_2As(CH_2)_2OH\}_3](BF_4)_2$ were grown by cooling concentrated solutions of the complexes in MeOH (ca. −18 °C). Data collection used a Nonius Kappa CCD diffractometer ($T = 120$ K) and with monochromated (graphite or confocal mirrors) Mo Kα X-radiation ($\lambda = 0.71073$ Å). Structure solution and refinement were routine [23–25] and H atoms were included in calculated positions. Selected bond lengths and angles are given in Tables 1–4.

Table 5
Crystallographic parameters

Complex	[Cu(**3**)$_2$]BF$_4$ · MeOH	[Ag(**1**)$_2$]BF$_4$ · CH$_2$Cl$_2$	[Ag(**3**)$_2$]BF$_4$ · MeOH	$[Cu_2\{Me_2As(CH_2)_2OH\}_3](BF_4)_2$
Formula	$C_{57}H_{60}As_4BCuF_4O_3$	$C_{57}H_{58}AgBCl_2F_4O_2Sb_4$	$C_{57}H_{60}AgAs_4BF_4O_3$	$C_{12}H_{33}As_3B_2Cu_2F_8O_3$
M	1243.08	1527.61	1287.41	750.84
Crystal system	Monoclinic	Monoclinic	Triclinic	Orthorhombic
Space group	$P2_1/c$ (#14)	$P2_1/c$ (#14)	$P\bar{1}$ (#2)	$P2_12_12_1$ (#19)
a (Å)	11.209(3)	13.1670(10)	11.387(2)	8.1798(10)
b (Å)	17.931(4)	16.5702(15)	13.633(3)	15.120(3)
c (Å)	26.177(5)	26.543(3)	17.061(3)	20.506(5)
α (°)	90	90	91.285(10)	90
β (°)	90.359(10)	101.943(6)	93.574(10)	90
γ (°)	90	90	92.830(10)	90
U (Å^3)	5261.4(19)	5665.8(9)	2639.4(8)	2536.1(8)
Z	4	4	2	4
μ (mm^{-1})	2.970	2.370	2.928	5.631
Total number of reflections	62586	73096	57994	16310
Unique reflections	12178	12971	12167	5726
R_{int}	0.142	0.065	0.175	0.068
Number of parameters	633	640	633	271
R_1 $[I_0 > 2\sigma(I_0)]$	0.057	0.044	0.066	0.057
wR_2 $[I_0 > 2\sigma(I_0)]$	0.101	0.096	0.112	0.090
R_1 [all data]	0.143	0.067	0.162	0.099
wR_2 [all data]	0.128	0.104	0.141	0.104

$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum (F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$.

Acknowledgements

We thank the EPSRC for support (GR/T09613/01 and EP/D003148) and Johnson Matthey plc for precious metal loans.

Appendix A. Supplementary material

CCDC 652335, 652336, 652337 and 652338 contain the supplementary crystallographic data for (Cu/**3**), (Ag/**1**), (Ag/**3**) and Cu. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.08.034.

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