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Structural and spectroscopic studies on copper, silver and gold complexes of mixed phosphathia ligands and their chalcogenide derivatives

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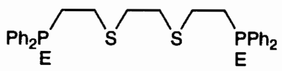
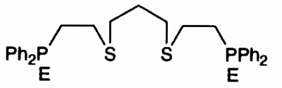
Reaction of $[Cu(MeCN)_4]PF_6$ or $AgBF_4$ with 1 molar equivalent of $Ph_2P(E)(CH_2)_2SZS(CH_2)_2(E)PPh_2$ [Z = $(CH_2)_2$, E = S (L^{1b}) or Se (L^{1c}); Z = $(CH_2)_3$, E = none (L^{2a}), S (L^{2b}) or Se (L^{2c}); Z = o-C_6H_4, E = none (L^{3a}), S (L^{3b}) or Se (L^{3c})] in degassed acetone followed by addition of diethyl ether yielded the mononuclear complexes [ML]X (M = Cu, $X^- = PF_6^-$; M = Ag, $X^- = BF_4^-$) in high yield. The gold(I) species $[AuL]PF_6$ were obtained by reaction of L (= L^{1b}, L^{1c}, L^{2b}, L^{2c} or L^{3a}–L^{3c}) with 1 molar equivalent of [AuCl(tht)] (tht = tetrahydrothiophene) and $TlPF_6$. All of these products have been characterised by ^1H, ^{31}P-$\{^1H\}$ (and in some cases ^{77}Se-$\{^1H\}$ and ^{109}Ag) NMR and IR spectroscopy, FAB or electrospray mass spectrometry and microanalyses. The data indicate four-co-ordination for all of the copper(I) and silver(I) species and this assignment has been confirmed by single-crystal structure determinations on three copper(I) examples. Spectroscopic studies on $[AuL]PF_6$ indicated linear two-co-ordination on average, *via* the phosphine, phosphine sulfide or phosphine selenide functions as appropriate. Variable-temperature ^{31}P-$\{^1H\}$ (and ^{77}Se-$\{^1H\}$) studies showed that the chalcogenide complexes are considerably more labile in solution than the phosphathia ligand complexes. Crystal structure determinations on $[CuL^{3a}]^+$, $[CuL^{1c}]^+$, $[AgL^{1c}]^+$ and $[CuL^{2b}]^+$ each showed the metal ion co-ordinated to all four donor atoms of a single ligand in the solid state, giving an overall distorted-tetrahedral stereochemistry. In the case of $[CuL^{1c}]^+$ there is a slight lengthening of the P–Se bond length compared to that of the unco-ordinated form of L^{3c}. Syntheses for the new pro-ligands are also detailed.

We have been studying the synthesis and co-ordination chemistry of mixed phosphathia macrocycles and their acyclic analogues. As part of this work we have recently prepared and structurally characterised the mixed phosphathia macrocyclic cations $[Pt(Ph_2[14]aneP_2S_2)]^{2+}$ and *trans*-$[RhCl_2(Ph_2[14]aneP_2S_2)]^+$ ($Ph_2[14]aneP_2S_2$ = 4,8-diphenyl-1,11-dithia-4,8-diphosphadithiacyclotetradecane).[1,2] We have also recently reported the syntheses of $[ML^{1a}]^+$ [M = Cu or Ag, L^{1a} = $Ph_2P(CH_2)_2S(CH_2)_2S(CH_2)_2PPh_2$][3] as well as several mono- and bi-nuclear gold(I) complexes involving L^{1a} and $Ph_2P(CH_2)_2S(CH_2)_3S(CH_2)_2PPh_2$ (L^{2a}).[4] Structural studies on $[CuL^{1a}]^+$ showed distorted-tetrahedral co-ordination at Cu^I *via* the P_2S_2 donor set,[3] whereas $[AuL^{1a}]^+$ and $[AuL^{2a}]^+$ showed distorted linear (P_2) co-ordination, with additional long range Au ··· S interactions of *ca.* 3 Å, and the binuclear species $[Au_2L^{1a}{}_2]Cl_2$ involved a highly unusual helical metallocyclic cation hosting a Cl^- anion within the cavity.[4] We have now prepared a complete series of new phosphathia complexes with Cu^I, Ag^I and Au^I and investigated their solution behaviour by variable-temperature ^{31}P-$\{^1H\}$ and, in certain cases, ^{109}Ag NMR spectroscopy and their solid-state structures by X-ray crystallography. We have also attempted to establish the bonding characteristics of the mixed phosphine sulfide–thioether (L^{1b}, L^{2b}, L^{3b}) or phosphine selenide–thioether (L^{1c}, L^{2c}, L^{3c}) derivatives with Cu^I, Ag^I and Au^I. The chemistry of phosphine sulfides and selenides has been well documented,[5,6] although their chemistry with the Group 11 metals is dominated by simple mono- and bi-dentate ligand systems,[7–13] and the potential catalytic applications of such compounds, *e.g.* using $Ph_2PCH_2P(S)Ph_2$, have become apparent only recently.[14,15] Examples of phosphine chalogenides involving other additional donor-atom types are mainly restricted to those involving mixed phosphine oxide–ether functions which have been studied as extractants for alkali- and alkaline-earth metals.[16]

Generally thioethers are considered to be rather poor ligands for transition-metal ions,[17] and very recently we have shown that bidentate Group 16 compounds can form very unusual structures ranging from monomers to linear chain polymers or extended three-dimensional networks with copper(I) and silver(I) centres.[18] In view of these results we were interested to compare the binding of chalcogenide (S or Se) *vs.* thioether functions by incorporating both functionalities within a single ligand. We now report the high-yield syntheses and properties of the complexes $[ML^{2a}]Y$ (M = Cu, Y = PF_6; M = Ag, Y = BF_4), $[ML^{3a}]Y$ (M = Cu or Au, Y = PF_6; M = Ag, Y = BF_4), and their copper(I), silver(I) and gold(I) phosphine sulfide and phosphine selenide derivatives involving ligands L^{1b}–L^{3b} and L^{1c}–L^{3c}. The single-crystal structures of L^{3c}, $[CuL^{3a}]PF_6$, $[CuL^{1c}]PF_6$, $[AgL^{1c}]BF_4$ and $[CuL^{2b}]PF_6$, and routes to L^{1b}, L^{1c}, L^{2b}, L^{2c} and L^{3a}–L^{3c} are also reported.



L^{1a} E = none
L^{1b} E = S
L^{1c} E = Se



L^{2a} E = none
L^{2b} E = S
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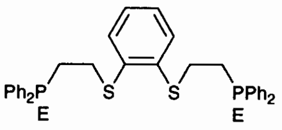

L^{3a} E = none
L^{3b} E = S
L^{3c} E = Se

Table 1 The $^{31}P-\{^1H\}$ and $^{77}Se-\{^1H\}$ NMR spectroscopic data[a]

Compound	$\delta(^{31}P-\{^1H\})$	$\delta(^{77}Se-\{^1H\})$	$^1J(PSe)/Hz$	$^1J(^{107}AgP)/Hz$	$^1J(^{109}AgP)/Hz$
L^{1a}	−16.3	—	—	—	—
L^{1b}	+41.2	—	—	—	—
L^{1c}	+32.8	−352	732	—	—
L^{2a}	−16.3	—	—	—	—
L^{2b}	+41.3	—	—	—	—
L^{2c}	+30.4	−350	732	—	—
L^{3a}	−16.5	—	—	—	—
L^{3b}	+41.2	—	—	—	—
L^{3c}	+32.6	−353	732	—	—
$[CuL^{1a}]PF_6$	+1.0	—	—	—	—
$[CuL^{1b}]PF_6$	+37.5	—	—	—	—
$[CuL^{1c}]PF_6$	+26.2	−369	641	—	—
$[CuL^{2a}]PF_6$	−2.3	—	—	—	—
$[CuL^{2b}]PF_6$	+36.8	—	—	—	—
$[CuL^{2c}]PF_6$	+24.0	−340	641	—	—
$[CuL^{3a}]PF_6$	+3.4	—	—	—	—
$[CuL^{3b}]PF_6$	+38.0	—	—	—	—
$[CuL^{3c}]PF_6$	+26.1	−372	641	—	—
$[AgL^{1a}]BF_4$	−1.7	—	—	445	510
$[AgL^{1b}]BF_4$	+41.5	—	—	n.o.	n.o.
$[AgL^{1c}]BF_4$	+31.0	−412[b]	630	n.o.	n.o.
$[AgL^{2a}]BF_4$	−6.6	—	—	437	490
$[AgL^{2b}]BF_4$	+42.2	—	—	n.o.	n.o.
$[AgL^{2c}]BF_4$	+30.6	n.o.[b]	659	n.o.	n.o.
$[AgL^{3a}]BF_4$	+1.7	—	—	470	535
$[AgL^{3b}]BF_4$	+43.9	—	—	n.o.	n.o.
$[AgL^{3c}]BF_4$	+30.7	−404[b]	601	n.o.	n.o.
$[AuL^{1a}]PF_6$	+32.9	—	—	—	—
$[AuL^{1b}]PF_6$	+42.8	—	—	—	—
$[AuL^{1c}]PF_6$	+30.4	n.o.	562	—	—
$[AuL^{2a}]PF_6$	+29.8	—	—	—	—
$[AuL^{2b}]PF_6$	+45.3	—	—	—	—
$[AuL^{2c}]PF_6$	+30.6	n.o.	532	—	—
$[AuL^{3a}]PF_6$	+33.5	—	—	—	—
$[AuL^{3b}]PF_6$	+44.0	—	—	—	—
$[AuL^{3c}]PF_6$	+31.0	n.o.	554	—	—

n.o. = No resonance observed. [a] Spectra were recorded at 300 K unless stated otherwise (see text). [b] Recorded at 200 K, broad (no spectrum observed at 300 K).

Results and Discussion

Phosphathia systems

The phosphathia compound L^{3a} was prepared by free-radical (azobisisobutyronitrile, aibn) initiated addition of the S–H bonds of benzene-1,2-dithiol across the vinyl function of 2 molar equivalents of $Ph_2PCH{=}CH_2$ at *ca.* 110 °C, followed by recrystallisation from CH_2Cl_2–EtOH (L^{3a}: ^{31}P NMR, δ −16.5). Meek and co-workers[19] previously used a similar route for the preparation of $Ph_2P(CH_2)_2SPh$. This route is not suitable for preparation of L^{1a} or L^{2a} since C–S bond-cleavage reactions also occur in these cases.

Reaction of $[Cu(MeCN)_4]PF_6$ or $AgBF_4$ with 1 molar equivalent of L (L = L^{2a} or L^{3a}) in degassed MeCN–CH_2Cl_2, followed by precipitation with Et_2O, yields the complexes $[CuL]PF_6$ or $[AgL]BF_4$ as white solids in good yield. The gold(I) species $[AuL^{3a}]PF_6$ was prepared by the method which we used previously for $[AuL]PF_6$ (L = L^{1a} or L^{2a}),[4] using [AuCl(tht)] (tht = tetrahydrothiophene), L^{3a} and $TlPF_6$ in MeCN solution. For each of the new compounds FAB mass spectrometry showed a molecular ion peak with the correct isotopic distribution in each case corresponding to $[ML]^+$. In some cases partial fragmentation of the ligand was also observed. The IR spectra of $[CuL]PF_6$, $[AgL]BF_4$ and $[AuL^{3a}]PF_6$ were relatively uninformative, but confirmed the presence of ligand and PF_6^- or BF_4^- anion. These data, together with ^1H NMR spectroscopic data and microanalyses, confirm the above formulations.

The $^{31}P-\{^1H\}$ NMR spectroscopic data for the phosphathia complexes are presented in Table 1. The spectra of $[CuL]^+$ (L = L^{1a}–L^{3a}) each show a singlet close to δ 0 due to the co-ordinated P donors of the ligand, as well as a septet at *ca.* δ −146 from the non-co-ordinating PF_6^- anions. These signals integrate as 2:1, consistent with Cu^I co-ordinated to a single P_2S_2-donor ligand. At 300 K the $^{31}P-\{^1H\}$ NMR spectrum of $[AgL^{3a}]BF_4$ shows a broad singlet at δ 1.7. At 220 K this is resolved into two overlapping doublets indicative of the two equivalent ligand phosphines coupling to the two $I = \frac{1}{2}$ silver nuclei, ^{107}Ag (51%) and ^{109}Ag (49%), $J(^{107}AgP)$ = 470 Hz, $J(^{109}AgP)$ = 535 Hz (Fig. 1). Similar Ag–P coupling constants were observed for $[AgL^{1a}]^+$ [$J(^{107}AgP)$ = 445, $J(^{109}AgP)$ = 510 Hz], and these values are consistent with a P_2S_2-donor set at Ag^I. The ^{109}Ag NMR spectrum of $[AgL^{3a}]BF_4$ recorded at 220 K is in accord with this, showing a triplet at δ +1024 arising from the Ag^I ligated to two phosphine donor atoms. This is in good agreement with the triplet observed at δ +1117 for $[AgL^{1a}]^+$.[3] No ^{109}Ag NMR signal was observed for these complexes at 300 K, suggesting that the thioether donor atoms may be exchanging on the NMR time-scale at this temperature. No ^{109}Ag NMR spectrum for $[AgL^{2a}]BF_4$ was obtained even at 220 K due to the limited stability of this particular species in solution.

The $^{31}P-\{^1H\}$ NMR resonance for $[AuL^{3a}]PF_6$ corresponding to the ligand (δ +33.5) occurs at a similar shift to those for $[AuL^{1a}]^+$ (δ +32.9) and $[AuL^{2a}]^+$ (δ +29.8), both of which involved average P_2 co-ordination in solution. In view of the similarity of these species, we expect that in the solid state they also adopt similar structures, involving primary P_2 co-ordination with weak Au···S secondary interactions and a distorted linear geometry.[4]

Crystals of $[CuL^{3a}]PF_6$ suitable for a single-crystal X-ray

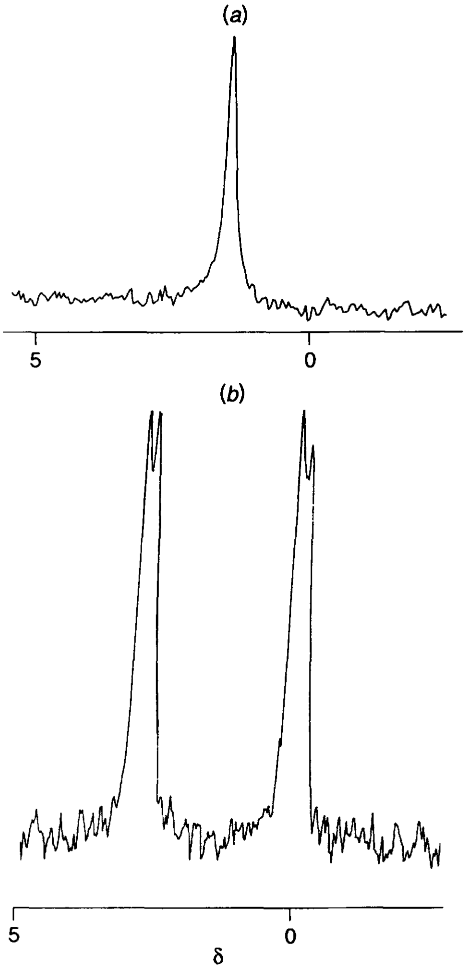

Fig. 1 The $^{31}P-\{^1H\}$ NMR spectrum of $[AgL^{3a}]BF_4$ (145.8 MHz, $CH_2Cl_2-CDCl_3$) at (*a*) 300 and (*b*) 220 K

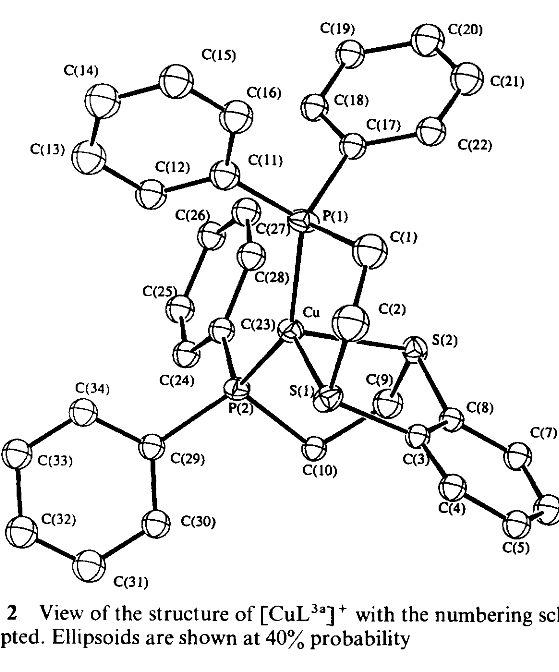

Fig. 2 View of the structure of $[CuL^{3a}]^+$ with the numbering scheme adopted. Ellipsoids are shown at 40% probability

Table 2 Selected bond lengths (Å) and angles (°) for $[CuL^{3a}]^+$

Cu–S(1)	2.336(3)	Cu–S(2)	2.412(3)
Cu–P(1)	2.226(3)	Cu–P(2)	2.217(3)
S(1)–C(2)	1.80(1)	S(1)–C(3)	1.79(1)
S(2)–C(8)	1.79(1)	S(2)–C(9)	1.82(1)
P(1)–C(1)	1.83(1)	P(1)–C(11)	1.79(1)
P(1)–C(17)	1.83(1)	P(2)–C(10)	1.82(1)
P(2)–C(23)	1.80(1)	P(2)–C(29)	1.84(1)
C(1)–C(2)	1.48(2)	C(3)–C(4)	1.38(1)
C(3)–C(8)	1.41(1)	C(4)–C(5)	1.36(2)
C(5)–C(6)	1.37(2)	C(6)–C(7)	1.39(2)
C(7)–C(8)	1.39(1)	C(9)–C(10)	1.54(2)
S(1)–Cu–S(2)	89.0(1)	S(1)–Cu–P(1)	92.8(1)
S(1)–Cu–P(2)	119.9(1)	S(2)–Cu–P(1)	102.9(1)
S(2)–Cu–P(2)	90.6(1)	P(1)–Cu–P(2)	145.0(1)
Cu–S(1)–C(2)	100.0(5)	Cu–S(1)–C(3)	103.2(4)
C(2)–S(1)–C(3)	105.6(6)	Cu–S(2)–C(8)	100.9(4)
Cu–S(2)–C(9)	99.3(4)	C(8)–S(2)–C(9)	102.6(5)
Cu–P(1)–C(1)	97.8(4)	Cu–P(1)–C(11)	122.1(4)
Cu–P(1)–C(17)	117.3(4)	C(1)–P(1)–C(11)	109.1(6)
C(1)–P(1)–C(17)	104.6(6)	C(11)–P(1)–C(17)	104.3(5)
Cu–P(2)–C(10)	100.9(4)	Cu–P(2)–C(23)	114.4(4)
Cu–P(2)–C(29)	124.7(4)	C(10)–P(2)–C(23)	102.7(5)
C(10)–P(2)–C(29)	106.8(5)	C(23)–P(2)–C(29)	104.9(5)
S(2)–C(8)–C(3)	122.4(8)	S(2)–C(8)–C(7)	118.9(8)
C(3)–C(8)–C(7)	118.6(10)	S(2)–C(9)–C(10)	113.9(8)
P(2)–C(10)–C(9)	110.6(7)	P(1)–C(1)–C(2)	114.9(10)
S(1)–C(2)–C(1)	114.9(10)	S(1)–C(3)–C(4)	118.7(8)
S(1)–C(3)–C(8)	122.3(8)	C(4)–C(3)–C(8)	118(1)
C(3)–C(4)–C(5)	121(1)	C(4)–C(5)–C(6)	119(1)
C(5)–C(6)–C(7)	120(1)	C(6)–C(7)–C(8)	120(1)

study were obtained by layering with pentane a solution of the complex in CH_2Cl_2 at *ca.* −20 °C. The structure shows (Fig. 2, Table 2) the Cu^I centre co-ordinated to a distorted-tetrahedral arrangement of all four ligand donor atoms, Cu–P(1) 2.226(3), Cu–P(2) 2.217(3), Cu–S(1) 2.336(3), Cu–S(2) 2.412(3) Å. These bond lengths are in good agreement with those observed for $[CuL^{1a}]^+$ which gave Cu–P 2.233(2), 2.242(2), Cu–S 2.385(2), 2.367(2) Å.[3] In both of these species the angles around the central Cu atom deviate markedly from the 109° expected for a regular tetrahedral environment. In particular, those involving five-membered chelate rings are close to 90°, reflecting the small bite size of the PCH_2CH_2S and $(C_6H_4)S_2$-*o* or SCH_2CH_2S linkages. The result of this is that the stereochemistry at Cu^I is a flattened and severely distorted tetrahedron. The Cu–S and Cu–P distances in these species are similar to those observed for other thioether and phosphine complexes of Cu^I.[20,21]

Chalcogenide derivatives

Reaction of L^{1a}–L^{3a} with an excess of sulfur or selenium powder in refluxing tetrahydrofuran (thf) (S) or toluene (Se) solution affords the chalcogenide derivatives L^{1b}–L^{3b} and L^{1c}–L^{3c} in high yield. The products each show a strong P=S or P=Se stretching vibration at around 600–610 or 520–530 cm^{-1} respectively in their IR spectra, and each shows a single $^{31}P-\{^1H\}$ NMR resonance at around δ 41 (L^{1b}–L^{3b}) or 34 ($^1J_{PSe}$ = 732 Hz), characteristic of phosphine sulfide or selenide functions respectively.[5] Compounds L^{1c}–L^{3c} each show a doublet in the $^{77}Se-\{^1H\}$ NMR spectrum at *ca.* δ −352.

In order to establish the bond-length distribution in the free phosphine selenide L^{3c}, and to allow comparisons with the co-ordinated L^{1c}–L^{3c}, a single-crystal X-ray analysis on L^{3c} was undertaken. The compound shows (Fig. 3, Table 3) the expected structure, with Se(1)–P(1) 2.099(2) and Se(2)–P(2) 2.111(2) Å, with all of the angles subtended at P being close to tetrahedral.

The phosphine sulfide and selenides were complexed with the Group 11 metals using the same procedures as described above for the phosphathia complexes, and the products were isolated as white powdered solids. They are stable in the solid state, but the silver(I) and particularly the gold(I) species show limited stability in solution, darkening within an hour or so. The solid-state IR spectra of the chalcogenide derivatives [ML]Y (M = Cu, Ag or Au; L = L^{1b}–L^{3b}, L^{1c}–L^{3c}; Y = PF_6 or BF_4) revealed shifts to low frequency (by *ca.* 20–30 cm^{-1}) for the P=S and P=Se stretching vibrations compared to the free ligands,

Table 3 Selected bond lengths (Å) and angles (°) for L^{3c}

Se(1)–P(1)	2.099(2)	Se(2)–P(2)	2.111(2)
S(1)–C(2)	1.827(6)	S(1)–C(3)	1.780(6)
S(2)–C(8)	1.770(6)	S(2)–C(9)	1.799(6)
P(1)–C(1)	1.825(6)	P(1)–C(11)	1.813(6)
P(1)–C(17)	1.803(6)	P(2)–C(10)	1.806(6)
P(2)–C(23)	1.817(6)	P(2)–C(29)	1.812(6)
C(1)–C(2)	1.509(8)	C(3)–C(4)	1.405(8)
C(3)–C(8)	1.394(8)	C(4)–C(5)	1.384(9)
C(5)–C(6)	1.380(9)	C(6)–C(7)	1.371(8)
C(7)–C(8)	1.388(8)	C(9)–C(10)	1.539(8)
C(2)–S(1)–C(3)	100.4(3)	C(8)–S(2)–C(9)	103.5(3)
Se(1)–P(1)–C(1)	111.8(2)	Se(1)–P(1)–C(11)	113.0(2)
Se(1)–P(1)–C(17)	114.5(2)	C(1)–P(1)–C(11)	105.7(3)
C(1)–P(1)–C(17)	105.4(3)	C(11)–P(1)–C(17)	105.7(3)
Se(2)–P(2)–C(10)	112.5(2)	Se(2)–P(2)–C(23)	114.8(2)
Se(2)–P(2)–C(29)	112.4(2)	C(10)–P(2)–C(23)	104.3(3)
C(10)–P(2)–C(29)	106.8(3)	C(23)–P(2)–C(29)	105.2(3)
P(1)–C(1)–C(2)	113.1(4)	S(1)–C(2)–C(1)	108.5(4)
S(1)–C(3)–C(4)	118.6(5)	S(1)–C(3)–C(8)	121.8(5)
C(4)–C(3)–C(8)	119.7(6)	C(3)–C(4)–C(5)	119.9(6)
C(4)–C(5)–C(6)	119.8(6)	C(5)–C(6)–C(7)	120.6(6)
C(6)–C(7)–C(8)	120.8(6)	S(2)–C(8)–C(3)	116.2(5)
S(2)–C(8)–C(7)	124.6(5)	C(3)–C(8)–C(7)	119.2(5)
S(2)–C(9)–C(10)	113.3(4)	P(2)–C(10)–C(9)	111.7(4)

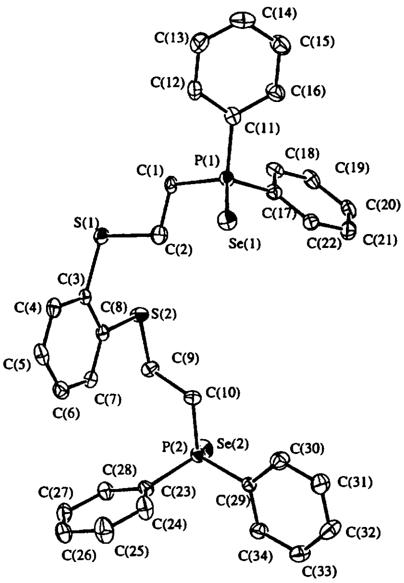

Fig. 3 View of the structure of L^{3c}. Details as in Fig. 2

strongly indicative of metal-ion co-ordination at these functions in the isolated solids. However, solution IR spectra revealed peaks corresponding to free P=S or P=Se as well as co-ordinated P=S and P=Se functions, indicating that these functions are extremely labile in solution.[6] The lability of these ligands is confirmed by $^{31}P\text{-}\{^1H\}$ and $^{77}Se\text{-}\{^1H\}$ NMR spectroscopic data presented in Table 1. At 300 K the $^{31}P\text{-}\{^1H\}$ NMR spectra of the copper(I) complexes each show a small low-frequency shift by *ca.* 5 ppm relative to the free ligands, while the silver(I) and gold(I) species show shifts of only *ca.* 1 ppm. None of the spectra alter significantly upon cooling to 200 K, and in the case of the silver complexes no coupling to ^{107}Ag or ^{109}Ag is observed within this temperature range, consistent with rapid ligand exchange even at low temperature. This contrasts with the silver(I)-phosphathia complexes discussed earlier, where dissociation of the phosphine functions was slow even at 300 K, and for the thioether functions below 230 K. For the complexes of L^{1c}–L^{3c}, satellite couplings to ^{77}Se were also apparent, with J_{PSe} significantly smaller than for the free ligands.

Table 4 Selected bond lengths (Å) and angles (°) for $[CuL^{1c}]^+$

Se(1)–Cu	2.454(1)	Se(1)–P(1)	2.133(2)
Se(2)–Cu	2.444(1)	Se(2)–P(2)	2.135(2)
Cu–S(1)	2.355(2)	Cu–S(2)	2.340(2)
S(1)–C(2)	1.819(6)	S(1)–C(3)	1.810(7)
S(2)–C(4)	1.808(7)	S(2)–C(5)	1.826(6)
P(1)–C(1)	1.807(7)	P(1)–C(7)	1.816(7)
P(1)–C(13)	1.817(6)	P(2)–C(6)	1.819(6)
P(2)–C(19)	1.824(6)	P(2)–C(25)	1.815(6)
C(1)–C(2)	1.521(9)	C(3)–C(4)	1.515(9)
C(5)–C(6)	1.523(9)		
Cu–Se(1)–P(1)	90.82(5)	Cu–Se(2)–P(2)	94.30(5)
Se(1)–Cu–Se(2)	117.08(4)	Se(1)–Cu–S(1)	105.94(5)
Se(1)–Cu–S(2)	118.10(5)	Se(2)–Cu–S(1)	114.44(5)
Se(2)–Cu–S(2)	106.38(5)	S(1)–Cu–S(2)	92.53(6)
Cu–S(1)–C(2)	99.2(2)	Cu–S(1)–C(3)	99.0(2)
C(2)–S(1)–C(3)	99.8(3)	Cu–S(2)–C(4)	97.7(2)
Cu–S(2)–C(5)	98.3(2)	C(4)–S(2)–C(5)	99.4(3)
Se(1)–P(1)–C(1)	111.9(2)	Se(1)–P(1)–C(7)	112.7(2)
Se(1)–P(1)–C(13)	111.7(2)	C(1)–P(1)–C(7)	106.9(3)
C(1)–P(1)–C(13)	109.4(3)	C(7)–P(1)–C(13)	103.9(3)
Se(2)–P(2)–C(6)	113.8(2)	Se(2)–P(2)–C(19)	110.9(2)
Se(2)–P(2)–C(25)	113.4(2)	C(6)–P(2)–C(19)	104.8(3)
C(6)–P(2)–C(25)	107.1(3)	C(19)–P(2)–C(25)	106.2(3)
S(1)–C(3)–C(4)	114.8(4)	S(1)–C(2)–C(1)	112.0(4)
S(2)–C(4)–C(3)	114.7(4)	S(2)–C(5)–C(6)	112.6(4)
P(1)–C(1)–C(2)	116.3(4)	P(2)–C(6)–C(5)	116.1(4)

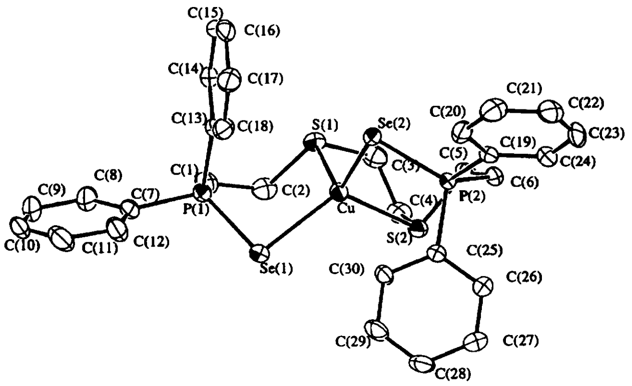

Fig. 4 View of the structure of $[CuL^{1c}]^+$. Details as in Fig. 2

As a result of their limited stability in solution, no $^{77}Se\text{-}\{^1H\}$ NMR data were obtained for the gold(I) phosphine selenides. However, at 300 K the spectra for the copper(I) phosphine selenide complexes each showed a doublet with a co-ordination shift to low frequency of about 15 ppm. This contrasts with the silver(I) analogues which showed no signal at 300 K, and only a broad doublet at best at 200 K (with a low-frequency co-ordination shift of about 50 ppm), suggesting that exchange in the silver(I) species is more rapid than in the copper(I) analogues.

In order to confirm the co-ordination mode with Cu^I, a single-crystal structure determination was undertaken on $[CuL^{1c}]PF_6$. Suitable crystals were obtained by slow evaporation from CH_2Cl_2 solution. The structure confirms (Fig. 4, Table 4) that the Cu^I ion is bound to all four donor atoms of one ligand, giving a mononuclear species with a distorted-tetrahedral arrangement, Cu–Se(1) 2.454(1), Cu–Se(2) 2.444(1), Cu–S(1) 2.355(2) and Cu–S(2) 2.340(2) Å. The S(1)–Cu–S(2) angle which involves the five-membered chelate ring is 92.53(6)°, while those involving the six-membered chelate rings are much closer to tetrahedral, Se(1)–Cu–S(1) 105.94(5), Se(2)–Cu–S(2) = 106.38(5)°. Thus, the overall geometry at Cu^I in this species is much less distorted compared to those of $[CuL^{1a}]^+$ and $[CuL^{3a}]^+$. The P–Se bond lengths in $[CuL^{1c}]^+$ [2.133(2), 2.135(2) Å] are significantly longer than in the free form of the closely related L^{3c}, consistent with removal of electron density from the P–Se bond upon co-ordination to Cu^I, and with both

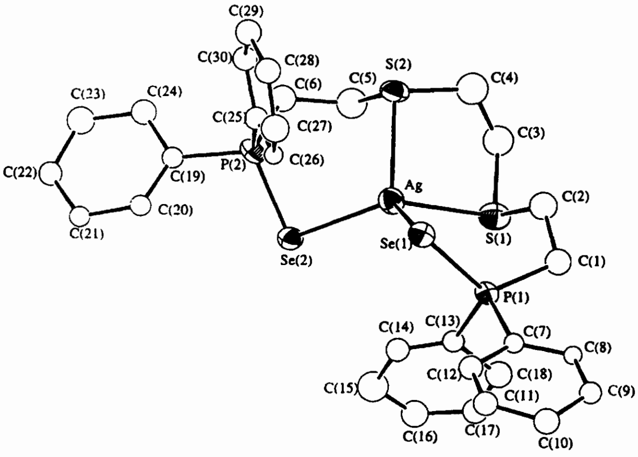

Fig. 5 View of the structure of $[AgL^{1c}]^+$ (details as in Fig. 2): Ag–S(1) 2.63(1), Ag–S(2) 2.57(1), Ag–Se(1) 2.620(5), Ag–Se(2) 2.636(5), Se(1)–P(1) 2.09(1) and Se(2)–P(2) 2.11(1) Å; S(1)–Ag–S(2) 86.8(3), Se(1)–Ag–S(2) 124.3(3), Se(1)–Ag–S(1) 101.8(3), Se(2)–Ag–S(2) 100.8(3), Se(1)–Ag–Se(2) 121.2(2) and Se(2)–Ag–S(1) 117.8(3)°

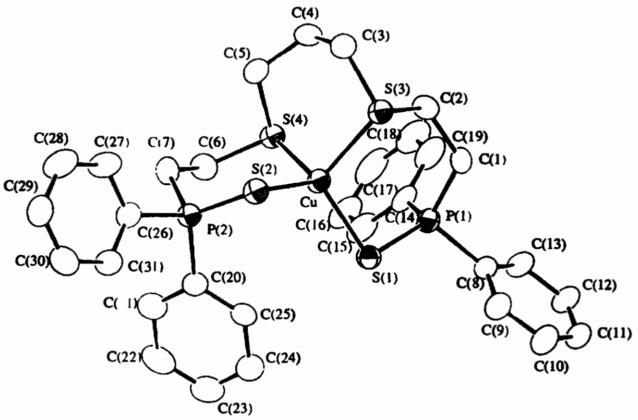

Fig. 6 View of the structure of $[CuL^{2b}]^+$. Details as in Fig. 2

Table 5 Selected bond lengths (Å) and angles (°) for $[CuL^{2b}]^+$

Cu–S(1)	2.296(2)	Cu–S(2)	2.296(2)
Cu–S(3)	2.300(2)	Cu–S(4)	2.314(2)
S(1)–P(1)	1.972(3)	S(2)–P(2)	1.971(3)
S(3)–C(2)	1.817(7)	S(3)–C(3)	1.816(8)
S(4)–C(5)	1.805(7)	S(4)–C(6)	1.802(8)
P(1)–C(1)	1.804(7)	P(1)–C(8)	1.797(7)
P(1)–C(14)	1.819(8)	P(2)–C(7)	1.809(7)
P(2)–C(20)	1.801(8)	P(2)–C(26)	1.814(7)
C(1)–C(2)	1.540(9)	C(3)–C(4)	1.51(1)
C(4)–C(5)	1.523(10)	C(6)–C(7)	1.528(9)
S(1)–Cu–S(2)	118.57(8)	S(1)–Cu–S(3)	109.17(8)
S(1)–Cu–S(4)	113.35(9)	S(2)–Cu–S(3)	106.93(8)
S(2)–Cu–S(4)	107.71(8)	S(3)–Cu–S(4)	99.20(8)
Cu–S(1)–P(1)	100.1(1)	Cu–S(2)–P(2)	99.56(10)
Cu–S(3)–C(2)	101.8(3)	Cu–S(3)–C(3)	107.7(3)
C(2)–S(3)–C(3)	100.7(3)	Cu–S(4)–C(5)	100.5(2)
Cu–S(4)–C(6)	108.0(2)	C(5)–S(4)–C(6)	101.7(4)
S(1)–P(1)–C(1)	115.9(2)	S(1)–P(1)–C(8)	109.5(2)
S(1)–P(1)–C(14)	112.7(3)	C(1)–P(1)–C(8)	104.2(3)
C(1)–P(1)–C(14)	106.6(4)	C(8)–P(1)–C(14)	107.2(3)
S(2)–P(2)–C(7)	116.3(3)	S(2)–P(2)–C(20)	113.9(3)
S(2)–P(2)–C(26)	109.2(3)	C(7)–P(2)–C(20)	106.0(4)
C(7)–P(2)–C(26)	103.0(3)	C(20)–P(2)–C(26)	107.4(3)
S(3)–C(2)–C(1)	110.1(5)	S(3)–C(3)–C(4)	118.7(5)
C(3)–C(4)–C(5)	116.4(6)	S(4)–C(5)–C(4)	112.1(5)
S(4)–C(6)–C(7)	117.4(5)	P(2)–C(7)–C(6)	119.4(5)
P(1)–C(1)–C(2)	118.0(5)		

the reduction in $^1J_{PSe}$ and the shift of ν(PSe) to lower frequency upon co-ordination.

Data collection was also undertaken on a weakly diffracting crystal of $[AgL^{1c}]BF_4{\cdot}2H_2O$, and although the data were of poor quality and hence the final residuals rather high, the analysis was sufficient to establish the nature and geometry of the $[AgL^{1c}]^+$ cation. The structure of this species shows (Fig. 5) a very similar arrangement to that seen for $[CuL^{1c}]^+$ above, with distorted-tetrahedral co-ordination at Ag^I *via* the two phosphine selenide and two thioether functions. Although the poor crystal quality resulted in high estimated standard deviations associated with the geometric parameters, it is clear that the M–Se and M–S bond lengths are longer than observed for $[CuL^{1c}]^+$, consistent with that larger radius of Ag^I *vs.* Cu^I. To our knowledge, these are the first structurally characterised examples of organophosphine selenide complexes of Cu^I and Ag^I. The Cu–Se and Ag–Se bond lengths involving these phosphine selenide functions are similar to those in selenoether complexes.[18]

To allow a comparison between M–S (thioether) and M–S (sulfide) interactions, we also undertook a single-crystal X-ray analysis on $[CuL^{2b}]PF_6$. Crystals of this complex were obtained by layering with hexane a solution of the complex in CH_2Cl_2, and the structure shows (Fig. 6, Table 5) that incorporation of three six-membered chelate rings leads to the arrangement at Cu^I being closer to an ideal tetrahedral geometry (*cf.* the other structures described), with co-ordination *via* all four S-donor atoms of the ligand, S–Cu–S 99.20(8)–118.57(8)°. The Cu–S (sulfide) bond lengths in this species [Cu–S(1) 2.296(2), Cu–S(2) 2.296(2) Å] are not significantly different from the Cu–S (thioether) bond lengths [Cu–S(3) 2.300(2), Cu–S(4) 2.314(2) Å], or from Cu–S distances in other copper(I)–phosphine sulfide or –thioether complexes.[7–10,21]

These results show that although mixed-donor phosphine sulfide–thioethers and phosphine selenide–thioethers do form complexes with Group 11 metal ions which are stable in the solid state and involve bonding *via* the chalcogenide groups, these species are much more labile in solution than the analogous phosphathia ligand complexes. The spectroscopic studies support the conclusions that the P=Se and P=S functions are much poorer ligands than phosphines, and also rather poorer even than the thioether functions, although single-crystal X-ray studies show that the M–S (sulfide) and M–Se (selenide) bond lengths are not significantly longer than M–S (thioether) and M–Se (selenoether) distances in related species.

Experimental

Infrared spectra were measured as KBr or CsI discs or as Nujol mulls using a Perkin-Elmer 983 spectrometer over the range 200–4000 cm^{-1}, mass spectra by electron impact or fast-atom bombardment (FAB) using 3-nitrobenzyl alcohol as matrix on a VG Analytical 70-250-SE normal-geometry double-focusing spectrometer or by electrospray using a VG Biotech platform. Proton and $^{13}C-\{^1H\}$ NMR spectra were recorded at 300 K in $CDCl_3$ solution using a Bruker AM300 spectrometer operating at 300 and 75.47 MHz respectively and are referenced to $SiMe_4$ (δ 0). $^{31}P-\{^1H\}$, $^{77}Se-\{^1H\}$ and ^{109}Ag NMR spectra were recorded in 10 mm NMR tubes containing 10–15% deuteriated solvent using a Bruker AM360 spectrometer operating at 145.8, 68.8 and 16.75 MHz respectively and referenced to 85% H_3PO_4 (^{31}P, δ 0), neat Me_2Se (^{77}Se, δ 0) and 9.1 mol dm^{-3} Ag^+ in water (^{109}Ag, δ +47).[22] 2,2,6,6-Tetramethylpiperidine-*N*-oxyl (TEMPO) was also added to the sample as a relaxation agent prior to recording ^{109}Ag NMR spectra. Microanalyses were obtained from the Imperial College microanalytical laboratory. Compounds L^{1a} (ref. 2) and L^{2a} (ref. 23) were prepared as described previously.

Syntheses

$\mathrm{L^{1b}}$. To a degassed solution of $\mathrm{L^{1a}}$ (0.5 g, 0.97 mmol) in thf (50 cm^3) was added $\mathrm{S_8}$ (0.035 g, 0.25 mmol) and the reaction mixture was refluxed for 1 h. The volume was reduced (5 cm^3) *in vacuo* and $\mathrm{Et_2O}$ was added to give a white solid which was filtered off and dried *in vacuo* (yield = 0.471 g, 83%). FAB mass spectrum: found m/z = 583, 551 and 519; calc. m/z = 582 ($[\mathrm{L^{1b}}]^+$), 550 ($[\mathrm{L^{1b}} - \mathrm{S}]^+$) and 518 ($[\mathrm{L^{1b}} - 2\mathrm{S}]^+$). NMR: ^{1}H, δ 8.0–7.1 (m, Ph, 20 H) and 3.1–2.4 (br m, $\mathrm{CH_2}$, 12 H); ^{13}C-{^{1}H}, δ 132.2–128.1 (Ph), 33.3 (d, J_{PC} = 52 Hz, $\mathrm{PCH_2}$), 31.8, 25.0 (both $\mathrm{CH_2}$). IR (KBr disc): 3045w, 2908m, 1579w, 1435s, 1397m, 1264w, 1207m, 1101s, 1029w, 998w, 897w, 842m, 729s, 702s, 600s, 508m, 491m and 421w cm^{-1}.

$\mathrm{L^{1c}}$. To a solution of $\mathrm{L^{1a}}$ (0.500 g, 0.96 mmol) in degassed toluene (50 cm^3) was added selenium powder (0.180 g, 2.25 mmol). The reaction mixture was refluxed for 4 h and then the unreacted selenium was filtered off. The toluene was removed on a rotary evaporator and the resulting oil was taken up in $\mathrm{CH_2Cl_2}$ (5 cm^3) and $\mathrm{Et_2O}$ added until the cloud point was reached. On cooling to −15 °C overnight a white solid was produced (yield = 0.386 g, 60%). FAB mass spectrum: found m/z = 679, 599 and 519; calc. m/z = 676 ($[\mathrm{L^{1c}}]^+$), 597 ($[\mathrm{L^{1c}} - \mathrm{Se}]^+$) and 518 ($[\mathrm{L^{1c}} - 2\mathrm{Se}]^+$). NMR: ^{1}H, δ 7.9–7.4 (m, Ph, 20 H) and 2.9–2.6 (br m, $\mathrm{CH_2}$, 12 H); ^{13}C-{^{1}H}, δ 132.0–128.8 (Ph), 33.1 (d, J_{PC} = 44 Hz, $\mathrm{PCH_2}$), 31.8, 25.7 (both $\mathrm{SCH_2}$). IR (KBr disc): 3045m, 2956m, 2905m, 1580w, 1432m, 1421w, 1396w, 1307vw, 1288w, 1262m, 1205m, 1158m, 1096s, 1028m, 997w, 895w, 841m, 802w, 750m, 737m, 702s, 692s, 652w, 597w, 539s, 488m, 418w, 395w and 352w cm^{-1}.

$\mathrm{L^{2b}}$. As for $\mathrm{L^{1b}}$ but using $\mathrm{L^{2a}}$ (0.40 g, 0.75 mmol) and $\mathrm{S_8}$ (0.05 g, 0.19 mmol) in thf (50 cm^3). The product was dried *in vacuo* to give a pale yellow oil (yield = 0.471 g, 83%). Electrospray mass spectrum: found m/z = 595 and 563; calc. m/z = 596 ($[\mathrm{L^{2b}}]^+$) and 564 ($[\mathrm{L^{2b}} - \mathrm{S}]^+$). NMR: ^{1}H, δ 7.8–7.2 (m, Ph, 20 H), 2.7–2.4 (br m, $\mathrm{SCH_2}$, 12 H) and 1.2 (br m, $\mathrm{CH_2}$, 2 H); ^{13}C-{^{1}H}, δ 136.0–130.4 (Ph), 33.4 (d, J_{PC} = 47 Hz, $\mathrm{PCH_2}$), 31.6, 25.0, 24.6 (all $\mathrm{CH_2}$). IR (neat oil, CsI plates): 3050w, 2955s, 2923s, 1582w, 1433m, 1376m, 1259m, 1097m, 1024m, 798m, 728w, 690w, 620w, 608w, 598w, 507w, 490w and 399w cm^{-1}.

$\mathrm{L^{2c}}$. As for $\mathrm{L^{1c}}$ above, using $\mathrm{L^{2a}}$ (0.328 g, 0.62 mmol) and selenium powder (0.105 g, 1.32 mmol) in degassed toluene (50 cm^3). The product was a yellow oil (yield = 0.31 g, 72%). Electrospray mass spectrum: found m/z = 691, 611 and 532; calc. m/z = 690 ($[\mathrm{L^{2c}}]^+$), 611 ($[\mathrm{L^{2c}} - \mathrm{Se}]^+$) and 532 ($[\mathrm{L^{2c}} - 2\mathrm{Se}]^+$). NMR: ^{1}H, δ 7.8–7.2 (m, Ph, 20 H), 2.8–2.4 (br m, $\mathrm{CH_2}$, 12 H) and 1.2 (m, $\mathrm{CH_2}$, 2 H); ^{13}C-{^{1}H}, δ 131.9–128.9 (Ph), 32.6 (d, J_{PC} = 37 Hz, $\mathrm{PCH_2}$), 30.5, 25.8, 25.6 (all $\mathrm{CH_2}$). IR (neat oil, CsI plates): 3049m, 2921s, 2852s, 1585m, 1569m, 1511w, 1477s, 1432s, 1332m, 1308s, 1259s, 1181s, 1158s, 1095s, 1069s, 1026s, 997m, 909m, 796m, 736m, 645w, 617w, 530m, 495m and 392w cm^{-1}.

$\mathrm{L^{3a}}$. To a degassed mixture of benzene-1,2-dithiol (0.50 g, 3.5 mmol) and diphenylvinylphosphine (1.50 g, 7 mmol) at 110 °C was added aibn (0.2 g). The reaction mixture was stirred for 3 h with further addition of aibn (0.1 g) at 30 min intervals. After cooling, the yellow oil was dissolved in $\mathrm{CH_2Cl_2}$ (5 cm^3) and EtOH (20 cm^3) was added to afford a white solid (yield = 1.50 g, 76%). FAB mass spectrum: found m/z = 566, 381, 353 and 321; calc. m/z = 565 ($[\mathrm{L^{3a}}]^+$), 381 {$[\mathrm{Ph_2P(CH_2)_2S(C_6H_4)S(CH_2)_2}]^+$}, 353 {$[\mathrm{Ph_2P(CH_2)_2S(C_6H_4)S}]^+$} and 321 {$[\mathrm{Ph_2P(CH_2)_2SC_6H_4}]^+$}. NMR: ^{1}H, δ 7.5–7.2 (m, aromatic H, 24 H), 2.9 (m, $\mathrm{CH_2}$, 4 H) and 2.3 (m, $\mathrm{CH_2}$, 4 H); ^{13}C-{^{1}H}, δ 137.9–126.7 (aromatic C), 29.7 (d, J_{PC} = 25 Hz, $\mathrm{PCH_2}$), 28.1, 27.9 ($\mathrm{SCH_2}$). IR (KBr disc): 2911m, 1582w, 1479m, 1444m, 1428m, 1309m, 1254w, 1178m, 1095m, 1039m, 1026m, 902m, 802m, 751m, 734s, 693s, 661m, 598m, 511m, 474m, 426m and 352w cm^{-1}.

$\mathrm{L^{3b}}$. As for $\mathrm{L^{1b}}$ above, but using $\mathrm{L^{3a}}$ (0.34 g, 0.6 mmol) and $\mathrm{S_8}$ (0.045 g, 1.3 mmol). The product was isolated as a white solid (yield: 0.24 g, 63%). Electrospray mass spectrum: found m/z = 631; calc. m/z = 630 ($[\mathrm{L^{3b}}]^+$). NMR: ^{1}H, δ 7.9–7.1 (m, aromatic H, 24 H), 3.1 (m, $\mathrm{CH_2}$, 4 H) and 2.7 (m, $\mathrm{CH_2}$, 4 H); ^{13}C-{^{1}H}, δ 136.1–127.3 (aromatic C), 32.3 (d, J_{PC} = 52 Hz, $\mathrm{PCH_2}$) and 26.3 ($\mathrm{CH_2}$). IR (KBr disc): 3040w, 2960w, 1577m, 1478m, 1433m, 1358w, 1253w, 1181w, 1104s, 1042w, 998w, 907w, 782m, 743s, 708m, 690m, 622w, 611m, 490m, 460w and 392w cm^{-1}.

$\mathrm{L^{3c}}$. As for $\mathrm{L^{1c}}$ above, but using $\mathrm{L^{3a}}$ (0.34 g, 0.6 mmol) and selenium powder (0.11 g, 1.3 mmol). The product was isolated as a white solid (yield = 0.18 g, 41%). Electrospray mass spectrum: found m/z = 725; calc. m/z = 724 ($\mathrm{L^{3c}}]^+$) NMR: ^{1}H, δ 7.85–7.1 (m, aromatic H, 24 H), 3.1 (m, $\mathrm{CH_2}$, 4 H) and 2.8 (m, $\mathrm{CH_2}$, 4 H); ^{13}C-{^{1}H}, δ 136.0–127.3 (aromatic C), 32.1 (d, J_{PC} = 44 Hz, $\mathrm{PCH_2}$) and 27.1 ($\mathrm{CH_2}$). IR (KBr disc): 3045w, 2960w, 1578m, 1477w, 1432m, 1357m, 1260w, 1182w, 1102s, 1026w, 996w, 783m, 751m, 738w, 717w, 689m, 664w, 614w, 536m, 497w, 477ww and 454w cm^{-1}.

$[\mathrm{CuL^{2a}}]\mathrm{PF_6}$. Compound $\mathrm{L^{2a}}$ (0.057 g, 0.11 mmol) was dissolved in degassed $\mathrm{CH_2Cl_2}$ (15 cm^3) and to it was added $[\mathrm{Cu(MeCN)_4}][\mathrm{PF_6}]$ (0.041 g, 0.11 mmol) in one portion. The reaction mixture was stirred for 1 h before its volume was reduced (5 cm^3) *in vacuo* and $\mathrm{Et_2O}$ added to afford a white solid (yield = 0.054 g, 66%) (Found: C, 49.6; H, 4.6. $\mathrm{C_{31}H_{34}CuF_6P_3S_2}$ requires C, 50.3; H, 4.6%). FAB mass spectrum: found m/z = 595, 409, 353, 339, 323 and 310; calc. for m/z = 595 ($[^{63}\mathrm{CuL^{2a}}]^+$), 382 ($[^{63}\mathrm{Cu\{Ph_2P(CH_2)_2S(CH_2)_3S\}}]^+$), 350 ($[^{63}\mathrm{Cu\{Ph_2P(CH_2)_2S(CH_2)_3\}}]^+$), 336 ($[^{63}\mathrm{Cu\{Ph_2P(CH_2)_2S(CH_2)_2\}}]^+$) 322 ($[^{63}\mathrm{Cu\{Ph_2P(CH_2)_2S(CH_2)\}}]^+$) and 308 ($[^{63}\mathrm{Cu\{Ph_2P(CH_2)_2S(CH_2)\}}]^+$). ^{1}H NMR: δ 7.6–7.2 (m, Ph, 20 H), 3.0–2.6 (m, $\mathrm{CH_2}$, 12 H) and 2.0 (t, $\mathrm{CH_2}$, 2 H). IR (KBr disc): 3045w, 2963m, 1580w, 1481w, 1433w, 1413w, 1260m, 1083s, 1026m, 833vs, 741s, 696m, 560s, 516w and 483m cm^{-1}.

$[\mathrm{AgL^{2a}}]\mathrm{BF_4}$. Compound $\mathrm{L^{2a}}$ (0.100 g, 0.19 mmol) was dissolved in MeCN (20 cm^3) and cooled to 0 °C. To it was added $\mathrm{AgBF_4}$ (0.038 g, 0.19 mmol) in one portion and the reaction mixture stirred for 1 h. The reaction volume was reduced (5 cm^3) *in vacuo* and $\mathrm{Et_2O}$ added to give a white solid (yield = 0.094 g, 68%). FAB mass spectrum: found m/z = 641, 455, 427, 353 and 321; calc. m/z = 641 ($[^{109}\mathrm{AgL^{2a}}]^+$), 456 ($[^{109}\mathrm{Ag\{Ph_2P(CH_2)_2S(CH_2)_3S(CH_2)_2\}}]^+$), 428 ($[^{109}\mathrm{Ag\{Ph_2P(CH_2)_2S(CH_2)_3S\}}]^+$), 354 ($[^{109}\mathrm{Ag\{Ph_2P(CH_2)_2S\}}]^+$) and 322 ($[^{109}\mathrm{Ag\{Ph_2P(CH_2)_2\}}]^+$). ^{1}H NMR: δ 7.6–7.2 (m, Ph, 20 H), 3.0–2.6 (m, $\mathrm{CH_2}$, 12 H) and 1.8 (br m, $\mathrm{CH_2}$, 2 H). IR (KBr disc): 3045w, 2922m, 1580w, 1484w, 1468w, 1436w, 1311m, 1262m, 1188m, 1057vs, 999s, 838m, 745s, 695s, 516w and 482m cm^{-1}.

$[\mathrm{CuL^{1b}}]\mathrm{PF_6}$. As for $[\mathrm{CuL^{2a}}]\mathrm{PF_6}$, above, but using $\mathrm{L^{1b}}$ (0.075 g, 0.13 mmol) and $[\mathrm{Cu(MeCN)_4}][\mathrm{PF_6}]$ (0.050 g, 0.13 mmol) in acetone (20 cm^3) (yield 0.054 g, 72%) (Found: C, 44.7; H, 3.6. $\mathrm{C_{30}H_{32}CuF_6P_3S_4}$ requires C, 45.6; H, 4.0%). FAB mass spectrum: found m/z = 645; calc. m/z = 645 ($[^{63}\mathrm{CuL^{1b}}]^+$). ^{1}H NMR: δ 8.0–7.4 (m, Ph, 20 H) and 3.2–2.3 (br m, $\mathrm{CH_2}$, 12 H). IR (KBr disc): 3054w, 2918w, 1588w, 1437s, 1104s, 840vs, 584s and 558s cm^{-1}.

$[\mathrm{AgL^{1b}}]\mathrm{BF_4}$. As for $[\mathrm{AgL^{2a}}]\mathrm{BF_4}$ above, but using $\mathrm{L^{1b}}$ (0.075 g, 0.13 mmol) and $\mathrm{AgBF_4}$ (0.033 g, 0.17 mmol) in acetone (20 cm^3) at 0 °C (yield = 0.045 g, 60%) (Found: C, 46.6; H, 3.8. $\mathrm{C_{30}H_{32}AgBF_4P_2S_4}$ requires C, 46.4; H, 4.1%). FAB mass spectrum: found m/z = 691; calc. m/z = 691 ($[^{109}\mathrm{Ag(L^{1b})}]^+$).

^{1}H NMR: δ 8.3–7.4 (m, Ph, 20 H) and 3.1–2.6 (br m, CH_2, 12 H). IR (KBr disc): 3051m, 2905m, 1582w, 1480m, 1436s, 1311w, 1181m, 1104vs, 1060vs, 839m, 695s, 588m and 507m cm^{-1}.

$[AuL^{1b}]PF_6$. To a suspension of L^{1b} (0.075 g, 0.13 mmol) in MeCN (20 cm^3) was added [AuCl(tht)] (0.041 g, 0.13 mmol) in one portion. The reaction mixture was stirred for 10 min, $TlPF_6$ (0.045 g, 0.13 mmol) was added and stirred overnight. The TlCl was filtered off, the filtrate reduced in volume (5 cm^3), and Et_2O (30 cm^3) added to give a white solid (yield = 0.070 g, 93%). (Found: C, 38.8; H, 3.5. $C_{30}H_{32}AuF_6P_3S_4$ requires C, 39.0; H, 3.5%). FAB mass spectrum: found m/z = 779; calc. m/z = 779 ($[AuL^{1b}]^+$). ^{1}H NMR: δ 7.9–7.5 (m, Ph, 20 H) and 3.0–2.8 (br m, CH_2, 12 H). IR (KBr disc): 3052w, 2956m, 2905m, 1582w, 1481w, 1432m, 1421w, 1396w, 1307w, 1288w, 1262m, 1096vs, 1028m, 997w, 895w, 841m, 802w, 750m, 737m, 702s, 692s, 652w, 597w, 539s, 488m, 418w, 395w and 352w cm^{-1}.

$[CuL^{1c}]PF_6$. As for $[CuL^{2a}]PF_6$ above, but using L^{1c} (0.050 g, 0.74 mmol) and $[Cu(MeCN)_4][PF_6]$ (0.028 g, 0.074 mmol) (yield = 0.055 g, 84%). (Found: C, 40.2; H, 3.3. $C_{30}H_{32}CuF_6P_3S_2Se_2$ requires C, 40.7; H, 3.6%). FAB mass spectrum: found m/z = 741, 661 and 581; calc. m/z = 741 ($[^{65}CuL^{1b}]^+$), 662 ($[^{65}Cu\{^{79}SeP_2S_2(C_2)\}]^+$) and 583 ($[^{65}Cu\{P_2S_2(C_2)\}]^+$). ^{1}H NMR: δ 7.9–7.5 (m, Ph, 20 H) and 3.1–2.6 (br m, CH_2, 12 H). IR (CsI disc): 3051m, 2919m, 1576w, 1481w, 1433m, 1413w, 1310w, 1256w, 1185w, 1098m, 997w, 840vs, 746m, 709m, 690m, 665w, 557m, 536m, 522w, 483vw and 394vw cm^{-1}.

$[AgL^{1c}]BF_4$. As for $[AgL^{2a}]BF_4$ above, but using L^{1c} (0.050 g, 0.74 mmol) and $AgBF_4$ (0.015 g, 0.074 mmol) in acetone (20 cm^3) (yield = 0.046 g, 70%) (Found: C, 37.2; H, 3.5. $C_{30}H_{32}AgBF_4P_2S_2Se_2{\cdot}CDCl_3$ requires C, 37.5; H, 3.3%). FAB mass spectrum: found m/z = 785, 705 and 627; calc. m/z = 785 ($[^{109}AgL^{1c}]^+$), 706 ($[^{109}Ag\{^{79}SeP_2S_2(C_2)\}]^+$) and 627 ($[^{109}Ag\{P_2S_2(C_2)\}]^+$). ^{1}H NMR: δ 7.9–7.4 (m, Ph, 20 H) and 3.2–2.7 (br m, CH_2, 12 H). IR (CsI disc): 3052w, 2917m, 1582w, 1481m, 1433s, 1310m, 1284m, 1261m, 1186m, 1099vs, 1083vs, 1059vs, 912m, 813m, 750s, 710s, 690s, 533m, 522s and 490m cm^{-1}.

$[AuL^{1c}]PF_6$. As for $[AuL^{1b}]PF_6$ above, but using L^{1c} (0.050 g, 0.74 mmol), [AuCl(tht)] (0.024 g, 0.074 mmol) and $TlPF_6$ (0.026 g, 0.074 mmol) in acetone (20 cm^3) (yield = 0.057 g, 76%) (Found: C, 33.1; H, 2.9. $C_{30}H_{32}AuF_6P_3S_2Se_2{\cdot}CH_2Cl_2$ requires C, 33.7; H, 3.1%). FAB mass spectrum: found m/z = 875, 795 and 715; calc. m/z = 873 ($[AuL^{1c}]^+$) 794 ($[Au\{^{79}SeP_2S_2(C_2)\}]^+$) and 715 ($[Au\{P_2S_2(C_2)\}]^+$). ^{1}H NMR: δ 7.9–7.5 (m, Ph, 20 H) and 3.2–2.9 (br m, CH_2, 12 H). IR (CsI disc): 3055m, 2907m, 1568w, 1434m, 1382w, 1334vw, 1312w, 1263w, 1187w, 1162w, 1101s, 1026vw, 996w, 836vs, 745m, 688s, 615vw, 598w, 557s, 518m, 487m and 393w cm^{-1}.

$[CuL^{2b}]PF_6$. As for $[CuL^{2a}]PF_6$ above, but using L^{2b} (0.046 g, 0.077 mmol) and $[Cu(MeCN)_4][PF_6]$ (0.030 g, 0.077 mmol) (yield 0.031 g, 50%) (Found: C, 43.1; H, 3.9. $C_{31}H_{34}CuP_3F_6S_4{\cdot}CH_2Cl_2$ requires C, 43.1; H, 4.0%). Electrospray mass spectrum: found m/z = 659; calc. m/z = 659 ($[^{63}CuL^{2b}]^+$). ^{1}H NMR: δ 8.0–7.3 (m, Ph, 20 H), 3.3–2.7 (br m, SCH_2, PCH_2, 12 H) and 2.1–2.0 (br m, CH_2, 2 H). IR (KBr disc): 3054w, 2918w, 1580w, 1434s, 1104s, 840vs, 748w, 693w, 664vw, 558s, 518m, 415vw and 393vw cm^{-1}.

$[AgL^{2b}]BF_4$. As for $[AgL^{2a}]BF_4$ above, but using L^{2b} (0.067 g, 0.11 mmol) and $AgBF_4$ (0.023 g, 0.11 mmol) in CH_2Cl_2 (20 cm^3) (yield = 0.048 g, 54%) (Found: C, 44.5; H, 4.0. $C_{31}H_{34}AgBF_4P_2S_4{\cdot}CH_2Cl_2$ requires C, 44.4; H, 4.2%). Electrospray mass spectrum: found m/z = 704; calc. for m/z = 705 ($[^{109}AgL^{2b}]^+$). ^{1}H NMR: δ 8.0–7.5 (m, Ph, 20 H), 3.3–2.6 (br m, SCH_2, PCH_2, 12 H) and 2.0–1.7 (br m, CH_2, 2 H). IR (KBr disc): 3057m, 2905m, 1584w, 1481m, 1434s, 1105vs, 1063vs, 834m, 693s, 587m and 507m cm^{-1}.

$[AuL^{2b}]PF_6$. As for $[AuL^{1b}]PF_6$ above, but using L^{2b} (0.066 g, 0.11 mmol), [AuCl(tht)] (0.035 g, 0.11 mmol) and $TlPF_6$ (0.039 g, 0.11 mmol) (yield = 0.044 g, 42%) (Found: C, 39.5; H, 3.7. $C_{31}H_{34}AuF_6P_3S_4$ requires C, 39.7; H, 3.6%). Electrospray mass spectrum: found m/z = 793; calc. m/z = 793 ($[AuL^{2b}]^+$). ^{1}H NMR: δ 7.8–7.3 (m, Ph, 20 H), 3.0–2.5 (br m, SCH_2, PCH_2, 12 H) and 2.0–1.9 (br m, CH_2, 2 H). IR (KBr disc): 3051w, 2958m, 2919m, 1578w, 1481m, 1433s, 1310w, 1282w, 1258w, 1104s, 1026m, 997w, 839vs, 736w, 712m, 690s and 559s cm^{-1}.

$[CuL^{2c}]PF_6$. As for $[CuL^{2a}]PF_6$ above, but using L^{2c} (0.085 g, 0.12 mmol) and $[Cu(MeCN)_4]PF_6$ (0.05 g, 0.12 mmol) (yield 0.078 g, 87%) (Found: C, 40.7; H, 3.7. $C_{31}H_{34}CuF_6P_3S_2Se_2$ requires C, 41.0; H, 3.8%). Electrospray mass spectrum: found m/z = 754; calc. m/z = 755 ($[^{65}CuL^{2c}]^+$). ^{1}H NMR: δ 7.9–7.4 (m, Ph, 20 H), 3.4–2.9 (br m, SCH_2, PCH_2, 12 H) and 2.0 (t, CH_2, 2 H). IR (CsI disc): 3054w, 2934w, 1561w, 1481m, 1434m, 1260m, 1100s, 997m, 840vs, 745m, 727m, 690m, 558s, 522s and 477m cm^{-1}.

$[AgL^{2c}]BF_4$. As for $[AuL^{2a}]BF_4$ above, but using L^{2c} (0.108 g, 0.15 mmol) and $AgBF_4$ (0.031 g, 0.15 mmol) (yield 0.060 g, 43%) (Found: C, 35.2; H, 3.4. $C_{31}H_{34}AgBF_4P_2S_2Se_2{\cdot}2CHCl_3$ requires C, 35.2; H, 3.2%). Electrospray mass spectrum: found m/z = 799; calc. m/z = 799 ($[^{109}AgL^{2c}]^+$). ^{1}H NMR: δ 7.9–7.4 (m, Ph, 20 H), 3.4–2.8 (br m, SCH_2, PCH_2, 12 H) and 1.9 (t, CH_2, 2 H). IR (CsI disc): 3054w, 2938w, 1562w, 1481m, 1433m, 1260m, 1100s, 1061vs, 996m, 840m, 750m, 690m, 525s, 490m and 442w cm^{-1}.

$[AuL^{2c}]PF_6$. As for $[AuL^{1b}]PF_6$ above, but using L^{2c} (0.060 g, 0.085 mmol), [AuCl(tht)] (0.027 g, 0.085 mmol) and $TlPF_6$ (0.027 g, 0.085 mmol) (yield 0.0625 g, 71%) (Found: C, 36.0; H, 3.2. $C_{31}H_{34}AuF_6P_3S_2Se_2$ requires C, 36.0; H, 3.3%). Electrospray mass spectrum: found m/z = 888; calc. m/z = 887 ($[AuL^{2c}]^+$). ^{1}H NMR: δ 7.9–7.4 (m, Ph, 20 H), 3.2–2.4 (br m, SCH_2, PCH_2, 12 H) and 1.8 (t, CH_2, 2 H). IR (CsI disc): 3054w, 2925w, 1561w, 1481m, 1433s, 1310w, 1187m, 1103m, 997w, 841vs, 744m, 688m, 558s, 520m and 487w cm^{-1}.

$[CuL^{3a}]PF_6$. As for $[CuL^{2a}]PF_6$ above, but using L^{3a} (0.038 g, 0.067 mmol) and $[Cu(MeCN)_4][PF_6]$ (0.026 g, 0.067 mmol) in acetone (20 cm^3) (yield = 0.050 g, 95%) (Found: C, 52.7; H, 4.1. $C_{34}H_{32}CuF_6P_3S_2$ requires C, 52.7; H, 4.1%). FAB mass spectrum: found m/z = 629, 443 and 416; calc. m/z = 629 ($[^{63}CuL^{3a}]^+$), 444 ($[^{63}Cu\{Ph_2P(CH_2)_2S(C_6H_4)S(CH_2)_2\}]^+$) and 416 ($[^{63}Cu\{Ph_2P(CH_2)_2S(C_6H_4)S\}]^+$). ^{1}H NMR: δ 7.9–7.4 (m, aromatic H, 24 H), 3.3–3.2 (m, CH_2, 4 H) and 2.6–2.5 (m, CH_2, 4 H). IR (CsI disc): 3048w, 2923m, 1570w, 1481m, 1432m, 1246w, 1155w, 1101s, 1083m, 1035m, 1026m, 997w, 839vs, 786w, 770m, 758m, 748m, 704m, 694m, 657w, 557m, 522m and 487w cm^{-1}.

$[AgL^{3a}]BF_4$. As for $[AuL^{2a}]BF_4$ above, but using $AgBF_4$ (0.014 g, 0.067 mmol) and L^{3a} (0.038 g, 0.067 mmol) in acetone (25 cm^3) (yield = 0.0440 g, 85%) (Found: C, 48.0; H, 3.5. $C_{34}H_{32}AgBF_4P_2S_2{\cdot}CDCl_3$ requires C, 47.7; H, 3.7%). FAB mass spectrum: found m/z = 675, 489 and 461; calc. m/z = 675 ($[^{109}AgL^{3a}]^+$), 490 ($[^{109}Ag\{Ph_2P(CH_2)_2S(C_6H_4)S(CH_2)_2\}]^+$) and 462 ($[^{109}Ag\{Ph_2P(CH_2)_2S(C_6H_4)S\}]^+$). NMR: ^{1}H, δ 7.7–7.3 (m, aromatic H, 24 H), 3.3–3.2 (m, CH_2, 4 H) and 2.6–2.5 (m, CH_2, 4 H); ^{109}Ag (16.75 MHz, CH_2Cl_2–$CDCl_3$, 220 K), δ +1024 [t, $^1J(^{109}AgP)$ = 535 Hz]. IR (KBr disc): 3049w, 2923m, 1578w, 1481m, 1432m, 1258w, 1054vs, 997m, 826m, 750s, 693m, 514m and 480w cm^{-1}.

Table 6 Crystallographic data

	L^{3c}	$[CuL^{3a}]PF_6$	$[CuL^{1c}]PF_6$	$[CuL^{2b}]PF_6$
Formula	$C_{34}H_{32}P_2S_2Se_2$	$C_{34}H_{32}CuF_6P_3S_2$	$C_{30}H_{32}CuF_6P_3S_2Se_2$	$C_{31}H_{34}CuF_6P_3S_4$
M	724.61	775.20	885.08	805.31
Colour, morphology	Colourless, column	Colourless, column	Colourless, column	Yellow, block
Crystal dimensions/mm	0.90 × 0.20 × 0.20	0.40 × 0.10 × 0.10	0.90 × 0.20 × 0.20	0.70 × 0.50 × 0.50
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P2_1/c$
a/Å	10.226(7)	10.160(2)	15.179(5)	12.216(4)
b/Å	18.869(6)	20.971(4)	11.182(7)	16.636(8)
c/Å	9.192(5)	15.423(4)	20.118(4)	18.049(3)
α/°	90.23(3)			
β/°	113.80(4)	92.74(2)	94.52	109.20(2)
γ/°	85.10(4)			
U/Å^3	1616(1)	3282(1)	3404(2)	3463(1)
Z	2	4	4	4
F(000)	732	1584	1760	1648
D_c/g cm^{-3}	1.489	1.568	1.727	1.544
μ(Mo-Kα)/cm^{-1}	25.08	9.98	30.99	10.65
Transmission factors (maximum, minimum)	—	1.000, 0.837	1.000, 0.902	1.000, 0.830
No. unique observed reflections	5711	5113	6331	6350
R_{int} (based on F^2)	0.035	0.101	0.040	0.084
Unique observed reflections with $[I_o > n\sigma(I_o)]$	3378 $(n = 3)$	2259 $(n = 2)$	3751 $(n = 3)$	3514 $(n = 2.5)$
No. parameters	361	245	398	406
Goodness of fit	1.88	1.84	1.63	2.93
$R(F_o)$	0.038	0.064	0.036	0.055
$R'(F_o)$	0.038	0.074	0.041	0.048
Maximum, minimum residual peaks/e Å^{-3}	0.68, −0.60	0.65, −0.76	0.65, −0.65	0.70, −0.68

$R = \Sigma(|F_o|_i - |F_c|_i)/\Sigma|F_o|_i$, $R' = [\Sigma w_i(|F_o|_i - |F_c|_i)^2/\Sigma w_i|F_o|_i^2]^{\frac{1}{2}}$, goodness of fit $= [\Sigma(|F_o|_i - |F_c|_i)/\sigma_i]/(n - m) \approx 1$.

[AuL^{3a}]PF$_6$. As for [AuL^{1b}]PF$_6$ above, but using L^{3a} (0.040 g, 0.071 mmol), [Au(tht)Cl] (0.023 g, 0.071 mmol) and TlPF$_6$ (0.025 g, 0.071 mmol) (yield = 0.057 g, 88%) (Found: C, 43.6; H, 3.5. $C_{34}H_{32}AuF_6P_3S_2\cdot CH_2Cl_2$ requires C, 43.6; H, 3.4%). FAB mass spectrum: found m/z = 763, 577, 550 and 441; calc. m/z = 763 ([AuL^{3a}]$^+$), 578 ([Au{$Ph_2P(CH_2)_2S(C_6H_4)S(CH_2)_2$}]$^+$), 550 ([Au{$Ph_2P(CH_2)_2S(C_6H_4)_2S$}]$^+$) and 442 ([Au{$Ph_2P(CH_2)_2S$}]$^+$). ^{1}H NMR: δ 7.8–7.3 (m, aromatic H, 24 H), 3.5–3.3 (m, CH$_2$, 4 H) and 2.7–2.6 (m, CH$_2$, 4 H). IR (CsI disc): 3052w, 2915m, 1580w, 1481m, 1433s, 1332w, 1309w, 1255w, 1186w, 1165m, 1102s, 1040m, 1025w, 998m, 836vs, 741s, 718m, 705m, 690s, 617w, 598w, 557s, 522m and 493m cm^{-1}.

[CuL^{3b}]PF$_6$. As for [CuL^{2a}]PF$_6$ above, but using [Cu(MeCN)$_4$]PF$_6$ (0.046 g, 0.12 mmol) and L^{3b} (0.075 g, 0.12 mmol) (yield = 0.09 g, 89%) (Found: C, 45.6; H, 3.6. $C_{34}H_{32}CuF_6P_3S_4\cdot CH_2Cl_2$ requires C, 45.5; H, 3.7%). Electrospray mass spectrum: found m/z = 693; calc. m/z = 693 ([CuL^{3b}]$^+$). ^{1}H NMR: δ 7.9–7.4 (m, aromatic H, 24 H), 3.3 (m, CH$_2$, 4 H) and 2.7 (m, CH$_2$, 4 H). IR (CsI disc): 3052w, 2975w, 1584w, 1522w, 1480m, 1435m, 1358w, 1277w, 1103s, 997w, 839vs, 752m, 708m, 690m, 669w, 614m, 578w, 557s, 509w and 492m cm^{-1}.

[AgL^{3b}]BF$_4$. As for [AgL^{2a}]BF$_4$ above, but using AgBF$_4$ (0.023 g, 0.12 mmol) and L^{3b} (0.075 g, 0.012 mmol) (yield = 0.09 g, 92%) (Found: C, 41.7; H, 3.2. $C_{34}H_{32}AgBF_4P_2S_4\cdot 2CHCl_3$ requires C, 40.6; H, 3.2%). FAB mass spectrum: found m/z = 738; calc. m/z = 737 ([AgL^{3b}]$^+$). ^{1}H NMR: δ 8.0–7.4 (m, aromatic H, 24 H), 3.4 (m, CH$_2$, 4 H) and 3.0 (m, CH$_2$, 4 H). IR (CsI disc): 3050w, 2965w, 1580w, 1435m, 1357m, 1104vs, 996w, 834w, 750m, 693m, 611m, 582w and 512w cm^{-1}.

[AuL^{3b}]PF$_6$. As for [AuL^{1b}]PF$_6$ above, but using [AuCl(tht)] (0.031 g, 0.10 mmol), L^{3b} (0.062 g, 0.10 mmol) and TlPF$_6$ (0.035 g, 0.10 mmol) (yield = 0.051 g, 59%) (Found: C, 41.7; H, 3.3. $C_{34}H_{32}AuF_6P_3S_4$ requires C, 42.0; H, 3.3%). Electrospray mass spectrum: found m/z = 827; calc. m/z = 827 ([AuL^{3b}]$^+$). ^{1}H NMR: δ 7.8–7.4 (m, aromatic H, 24 H), 3.3 (m, CH$_2$, 4 H) and 3.1 (m, CH$_2$, 4 H). IR (CsI disc): 3052w, 2965w, 1583w, 1481w, 1435m, 1356m, 1186wm, 1105m, 996w, 839vs, 740m, 688m, 558s and 502w cm^{-1}.

[CuL^{3c}]PF$_6$. As for [CuL^{2a}]PF$_6$ above, but using [Cu(MeCN)$_4$]PF$_6$ (0.024 g, 0.062 mmol) and L^{3c} (0.050 g, 0.07 mmol) (yield = 0.052 g, 81%) (Found: C, 45.6; H, 3.6. $C_{34}H_{32}CuF_6P_3S_2Se_2\cdot CH_2Cl_2$ requires C, 45.5; H, 3.7%). Electrospray mass spectrum: found m/z = 789; calc. m/z = 789 ([CuL^{3c}]$^+$). ^{1}H NMR: δ 7.9–7.4 (m, aromatic H, 24 H), 3.4 (m, CH$_2$, 4 H) and 3.2 (m, CH$_2$, 4 H). IR (CsI disc): 3051w, 1585w, 1481w, 1434m, 1390w, 1364w, 1315w, 1102m, 997w, 863m, 836vs, 752m, 705w, 692s, 557s, 516s and 448w cm^{-1}.

[AgL^{3c}]BF$_4$. As for [AgL^{2a}]BF$_4$ above, but using AgBF$_4$ (0.020 g, 0.057 mmol) and L^{3c} (0.042 g, 0.057 mmol) (yield = 0.045 g, 78%) (Found: C, 35.2; H, 3.4. $C_{34}H_{32}AgBF_4P_2S_2Se_2\cdot 2CHCl_3$ requires C, 35.2; H, 3.2%). Electrospray mass spectrum: found m/z = 833; calc. m/z = 833 ([AgL^{3c}]$^+$). ^{1}H NMR: δ 7.9–7.4 (m, aromatic H, 24 H), 3.4 (m, CH$_2$, 4 H) and 3.1 (m, CH$_2$, 4 H). IR (CsI disc): 3050w, 2930w, 1564w, 1481m, 1434s, 1364m, 1259w, 1099vs, 1060vs, 966m, 834w, 750m, 713w, 689m, 584w, 522s and 490w cm^{-1}.

[AuL^{3c}]PF$_6$. As for [AuL^{1b}]PF$_6$ above, but using [AuCl(tht)] (0.026 g, 0.08 mmol), L^{3c} (0.060 g, 0.08 mmol) and TlPF$_6$ (0.029 g, 0.08 mmol) (yield = 0.029 g, 91%) (Found: C, 39.4; H, 2.3. $C_{34}H_{32}AuF_6P_3S_2Se_2$ requires C, 38.3; H, 3.0%). Electrospray mass spectrum: found m/z = 923; calc. m/z = 921 ([AuL^{3c}]$^+$). ^{1}H NMR: δ 7.8–7.3 (m, aromatic H, 24 H), 3.3 (m, CH$_2$, 4 H) and 3.1 (m, CH$_2$, 4 H). IR (CsI disc): 3054m, 2923m, 1584w, 1568w, 1481w, 1434s, 1372m, 1312w, 1252w, 1185m, 1160m, 1102s, 1040w, 909w, 839vs, 745s, 688s, 557s, 520m and 489w cm^{-1}.

X-Ray crystallography

Single crystals of compound L^{3c}, [AgL^{1c}]BF$_4$,[*] [CuL^{2b}]PF$_6$ and [CuL^{3a}]PF$_6$ were obtained by layering a solution of the complex in CH_2Cl_2 with hexane at *ca.* −15 °C, while for $[CuL^{1c}]PF_6$ crystals were obtained by slow evaporation from a solution in CH_2Cl_2. For each compound the selected crystal was coated with mineral oil and mounted on a glass fibre. Data collection used a Rigaku AFC7S four-circle diffractometer equipped with an Oxford Cryostreams low-temperature attachment operating at 150 K, using graphite-monochromated Mo-Kα X-radiation (λ_{max} = 0.710 73 Å), ω–2θ scans. The intensities of three standard reflections were monitored every 150. No significant crystal decay or movement was observed. As there were no identifiable faces the raw data were corrected for absorption using ψ scans (except for L^{3c} where no absorption correction was applied). The weighting scheme $w^{-1} = \sigma^2(F)$ gave satisfactory agreement analyses for L^{3c} and for each of the copper complexes. Crystallographic data are presented in Table 6.

The structure of compound L^{3c} was solved by direct methods[27] and developed by iterative cycles of full-matrix least-squares refinement and Fourier-difference syntheses which located all non-H atoms in the ordered molecule in the asymmetric unit.[25] The structures of the copper(I) complexes were all solved by heavy-atom methods[24] and developed by using iterative cycles of full-matrix least-squares refinement and Fourier-difference syntheses which located all non-H atoms in an ordered $[CuL]^+$ cation and PF_6^- anion in the asymmetric unit.[25] All non-H atoms in the structures were refined anisotropically (except for $[CuL^{3a}]PF_6$ where the data: parameter ratio only permitted the Cu, S, P and F atoms to be refined anisotropically), H atoms were placed in fixed, calculated positions.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/226.

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[*] $C_{30}H_{36}AgBF_4O_2P_2S_2Se_2$, M = 906.27, trigonal, space group $R\bar{3}(h)$, a = 35.23(3), c = 14.15(4) Å, U = 15 206 Å^3, Z = 18, D_c = 1.783 g cm^{-3}, T = 150 K, colourless column, 0.35 × 0.15 × 0.10 mm, μ = 30.18 cm^{-1}, $F(000)$ = 8100. ω–2θ scans, 5358 unique reflections measured ($2\theta_{max}$ = 50°), 1558 with $I > 2\sigma(I)$ used in all calculations. The structure was solved by heavy-atom methods[24] and refined using iterative cycles of full-matrix least squares.[25] During refinement the O atoms of two fully occupied water molecules were identified per silver(I) cation. At isotropic convergence the data were corrected for absorption using DIFABS (maximum, minimum transmission factors, 1.000, 0.559);[26] and the Ag, Se, P and S atoms were then refined anisotropically and H atoms included in fixed, calculated positions. Since the H atoms associated with the H_2O solvent molecules were not located in the difference map they were not included in the final structure-factor calculation. This model refined to R, R' = 0.092, 0.081 respectively and S = 2.73 for 212 parameters and the final Fourier-difference map showed residual electron-density peaks of 1.15 and −1.40 e Å^{-3}.

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