Structural diversity in silver(I) and gold(I) complexes with 2,5-bis(diphenylphosphinomethyl)thiophene

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Polynuclear silver(I) and gold(I) complexes with 2,5-bis(diphenylphosphinomethyl)thiophene (dpmt) [Ag$_2$(μ-dpmt)$_3$]-[BPh$_4$]$_2$·2MeCN **1**, [Ag$_2$Cl$_2$(μ-dpmt)] **2**, [Ag$_3$Br$_3$(μ-dpmt)$_2$] **3**, [Ag$_3$I$_3$(μ-dpmt)$_2$] **4**, [Au$_2$Cl$_2$(μ-dpmt)] **5**, [Au$_2$Cl$_2$-(μ-dpmt)$_2$] **6**, [Au$_2$Cl$_2$(μ-dpmt)$_3$] **7** and [(Au$_2$S)(μ-dpmt)] **8** were synthesised and **1**, **4**, **5** and **8** structurally characterised by X-ray crystallography. Complex **1** consists of a binuclear triple-helical [Ag$_2$(μ-dpmt)$_3$] cation with two three-co-ordinated Ag^I bridged by three dpmt ligands in a staggered-conformation with respect to the two AgP$_3$ moieties. Complex **4** has a 'three-runged ladder' Ag$_3$(μ$_3$-I)(μ-I)$_2$ unit which is bridged by two dpmt ligands above and below the trinuclear plane. Two of the Ag^I are tetrahedrally co-ordinated and one, in the middle of the structure unit, has trigonal co-ordination geometry. In **5**, a pair of AuCl is bridged by one dpmt in which both Au^I exhibit linear, two co-ordinated geometry. Complex **8** has a binuclear cyclic structure with a narrow Au–S–Au angle of 86.2(1)° and short Au$\cdots$Au distance of 3.131(1) Å indicating a certain amount of intra-molecular Au$\cdots$Au interaction.

Construction of small polynuclear complexes with phosphine-based ligands as backbones are of current interest because of the special structural, chemical and physical properties that such systems can display,[1] and a number of phosphine-based ligands has been examined in the synthesis of structurally diverse polynuclear silver(I)[2,4–11] and gold(I)[3,4,12–22] complexes. Bis(diphenylphosphinomethyl)phenylphosphine (dpmp), a linear tridentate ligand, supports the linear trinuclear silver(I) complex [Ag$_3$(NCMe)$_2$[ClO$_4$]$_2$(μ-dpmp)$_2$][ClO$_4$][2] and gold(I) complex [Au$_3$(μ-dpmp)$_2$Cl$_2$]Cl,[3] while tripodal tris(diphenyl-phosphino)methane is more suited for triangular arrangements of a Ag$_3$ centre in [Ag$_3${μ-(Ph$_2$P)$_3$CH}$_2$][ClO$_4$]$_3$ and a Au$_3$ centre in [Au$_3$Cl{μ-(Ph$_2$P)$_3$CH}$_2$][ClO$_4$]$_2$.[4] Both silver(I) and gold(I) can exhibit linear, triangular and tetrahedral geometries in their complexes with various bidentate phosphine ligands; the products obtained depend on factors such as the chain length, spatial arrangement and bulkiness of the ligands and prepar-ation conditions, as well as co-ordinating ability and properties of the counter ions. Such diversity in structural features with different metal to phosphorus ratios are exemplified by the silver(I)[6–10] and gold(I)[12–18] complexes with bis(diphenylphos-phino)methane (dppm) and 1,1′-bis(diphenylphosphino)-ferrocene (dppf). Moreover, weak Au$\cdots$Au interactions with contacts shorter than 3.5 Å are of much interest because of their important effects in determining molecular configurations/conformations and constructing supramolecular aggregations in gold(I) complexes.[19–23] In our efforts to examine the co-ordination properties of sulfur donor atoms in thiophene derivatives, we recently developed a novel potentially tridentate phosphine ligand: 2,5-bis(diphenylphosphinomethyl)thiophene (dpmt). With a suitable bridging length and spatial arrange-ment, dpmt is a good candidate in the preparation of poly-nuclear complexes. This was borne out in the reaction between dpmt and Cu^{I}X (X = Cl, Br or I) which gave trinuclear com-plexes [Cu$_3$(μ$_3$-X)(μ-X)$_2$(μ-dpmt)$_2$] with a 'three-runged ladder' framework in which the thiophene moiety just acts as a spacing unit.[24] We extend the reaction of dpmt to some silver(I) and gold(I) compounds and herein report the synthesis of [Ag$_2$(μ-dpmt)$_3$][BPh$_4$]$_2$·2MeCN **1**, [Ag$_2$Cl$_2$(μ-dpmt)] **2**, [Ag$_3$Br$_3$-(μ-dpmt)$_2$] **3**, [Ag$_3$I$_3$(μ-dpmt)$_2$] **4**, [Au$_2$Cl$_2$(μ-dpmt)] **5**, [Au$_2$Cl$_2$-(μ-dpmt)$_2$] **6**, [Au$_2$Cl$_2$(μ-dpmt)$_3$] **7** and [(Au$_2$S)(μ-dpmt)] **8**, and

the crystal structures of **1**, **4**, **5** and **8** which present some inter-esting structural features in polynuclear silver(I)– and gold(I)–phosphine complexes.
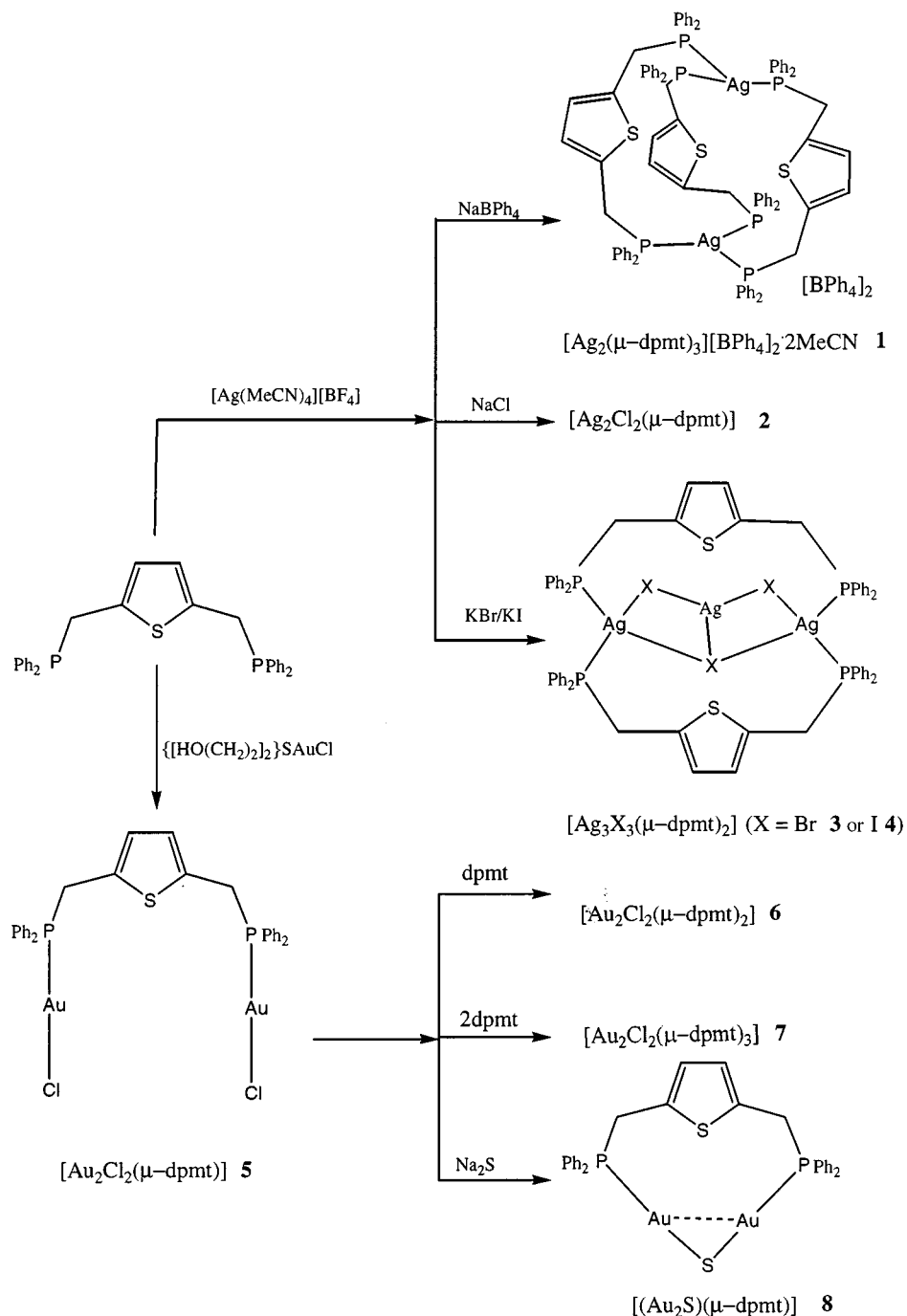
Results and discussion

The silver(I) and gold(I) complexes with 2,5-bis(diphenylphos-phinomethyl)thiophene (dpmt) reported here were synthesized according to the procedure shown in Scheme 1.

Silver(I) complexes with 2,5-bis(diphenylphosphinomethyl)-thiophene

Reaction of dpmt with an equimolar amount of [Ag(MeCN)$_4$]-[BF$_4$] in acetonitrile, followed by addition of NaBPh$_4$, NaCl, KBr or KI, afford the complexes **1**, **2**, **3** or **4** respectively. These complexes are colourless and air-stable, but crystals of **4** turn opaque when isolated from the mother-liquor. Complex **1** is soluble in acetonitrile but insoluble in dichloromethane and chloroform, while complexes **2**, **3** and **4** are soluble in dichloro-methane and chloroform but insoluble in methanol and acetonitrile. Solid samples and solutions of the complexes show no sensitivity to light. All the complexes were characterised by microanalysis, as well as by low temperature ^{1}H and ^{31}P-{^{1}H} NMR spectroscopy.

Complex **1** shows a characteristic ^{31}P-{^{1}H} NMR signal for silver(I) bound to three phosphorus atoms[25] at δ 13.4 [^1J(^{109}Ag–^{31}P) = 370.7, ^1J(^{107}Ag–^{31}P) = 320.6 Hz], consistent with its crystal structure. The molecular structure of **1** contains [Ag$_2$-(μ-dpmt)$_3$] cations, BPh$_4$ anions and acetonitrile solvate. It is of particular interest that the [Ag$_2$(μ-dpmt)$_3$] cation, consisting of a binuclear molecular unit with the two silver atoms bridged by three dpmt ligands with the two AgP$_3$ moieties in a staggered conformation, is a Δ- or Λ-triple-helicate as viewed along the Ag(1)$\cdots$Ag(1A) axis. Such helicates, due to their similiar structural features to some of the biological supramolecular structures such as the double helix of nucleic acids,[26] have been recently receiving considerable attention.[27] There are two Δ-[Ag$_2$(μ-dpmt)$_3$] and two Λ-[Ag$_2$(μ-dpmt)$_3$] in the unit cell and a perspective view of the structure of the Δ-[Ag$_2$(μ-dpmt)$_3$] cation is shown in Fig. 1. Selected bond distances and angles

Scheme 1

NaBPh$_4$

$[Ag_2(\mu\text{–}dpmt)_3][BPh_4]_2\cdot 2MeCN$ **1**

$[Ag(MeCN)_4][BF_4]$

NaCl

$[Ag_2Cl_2(\mu\text{–}dpmt)]$ **2**

KBr/KI

$[Ag_3X_3(\mu\text{–}dpmt)_2]$ (X = Br **3** or I **4**)

dpmt

$[Au_2Cl_2(\mu\text{–}dpmt)_2]$ **6**

2dpmt

$[Au_2Cl_2(\mu\text{–}dpmt)_3]$ **7**

$\{[HO(CH_2)_2]_2\}SAuCl$

Na$_2$S

$[(Au_2S)(\mu\text{–}dpmt)]$ **8**

$[Au_2Cl_2(\mu\text{–}dpmt)]$ **5**

are given in Table 1. The $[Ag_2(\mu\text{-}dpmt)_3]$ cation has a crystallographic C_2 symmetry axis passing through sulfur atom S(6) and bisecting the Ag(1)–Ag(1A) vector and an approximately C_3 symmetry axis passing through the Ag(1)–Ag(1A) vector. The silver atom is trigonally co-ordinated by three phosphorus atoms with a mean P–Ag–P angle of 120°. The AgP$_3$ unit is nearly planar with a mean deviation of 0.083 Å and the largest out-of-plane distance is 0.167 Å for Ag, towards the centre of the cation. The mean Ag–P distance of 2.529(1) Å in **1** is a little longer than the 2.482(4) Å in $[Ag_2(\mu\text{-}dppm)_3][NO_3]_2$[8b] and 2.486(7) Å in $[Ag_2(\mu\text{-}dppf)(dppf)_2][PF_6]_2$.[10b] Thiophene sulfur atoms S(5), S(5A) and S(6) are 3.482, 3.506 and 3.500 Å away from Ag(1) respectively, indicating there are no direct-bonded interactions between Ag(1) and the thiophene sulfurs. The Ag(1)···Ag(1A) separation is 5.782 Å. The two independent C–(C$_4$S)–C moieties are virtually planar and rigid with average deviations of 0.007 and 0.002 Å respectively from the mean planes.

It is interesting to compare the structure of **1** with those of $[Ag_2(\mu\text{-}dppm)_3][NO_3]_2$[8b] and $[Ag_2(\mu\text{-}dppf)(dppf)_2][PF_6]_2$.[10b] A dinuclear silver(I) complex with three bridging/chelating bis(diphenylphosphine) ligands may have different possible structures as shown below. A triply-bridging skeleton is found for both **1** and $[Ag_2(\mu\text{-}dppm)_3][NO_3]_2$, but the arrangement of phosphorus atoms within the skeleton is different, showing staggered and eclipsed conformations respectively as shown in frameworks **I** and **II**.

The bulky backbone of dppf does not appear to favour a triply-bridging arrangement, and the preferred mode in $[Ag_2\text{-}(\mu\text{-}dppf)(dppf)_2][PF_6]_2$ is to have both chelating and bridging dppf (**III**). Co-ordination of dpmt in the chelating mode is possibly not favoured because of the rigidity of the C–(C$_4$S)–C moiety and the weak binding property of the thiophene sulfur.

Conductivity measurements in CH$_2$Cl$_2$ indicate that complexes **2**, **3** and **4** are non-electrolytes, suggesting all the halide anions are co-ordinated. Complex **2** exhibits ^{31}P-$\{^1H\}$ NMR

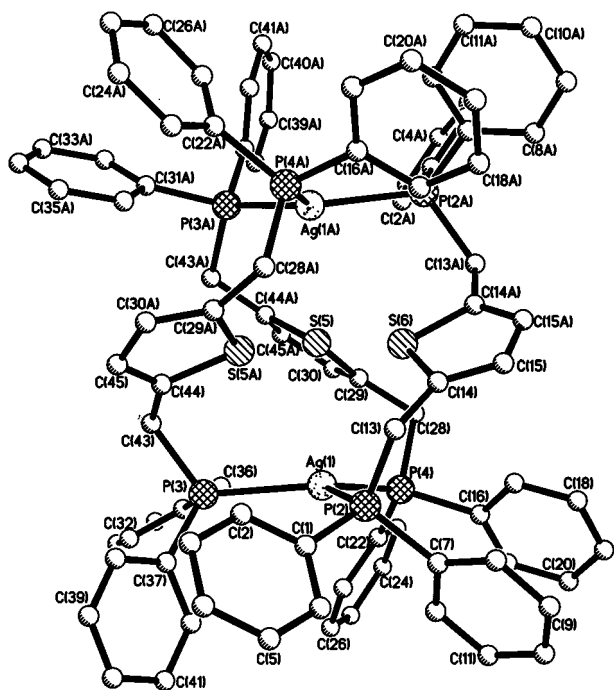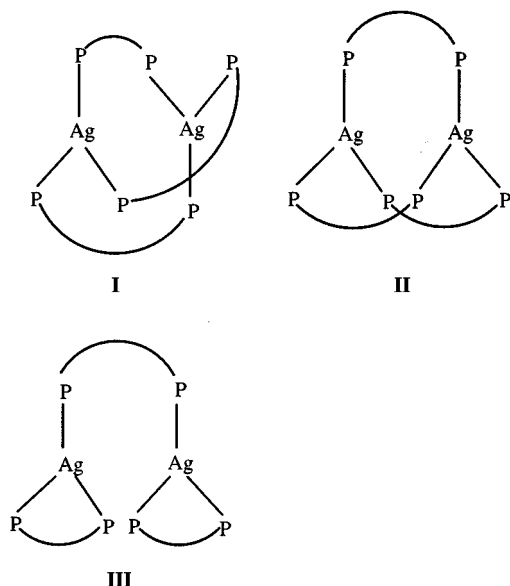**Fig. 1** Perspective view of the structure of the Δ-[Ag₂(μ-dpmt)₃] cation in **1** with atomic numbering scheme.

I   **II**

III

signals at δ 9.8 (298 K) and δ 10.3 (223 K) with characteristic $^1J(^{109}Ag-^{31}P)$ (700.7 Hz) and $^1J(^{107}Ag-^{31}P)$ (609.1 Hz) for Ag^I bound to one phosphorus atom.[25] Complex **3** shows $^{31}P-\{^1H\}$ NMR signals at δ 3.9 (298 K) and δ 0.5 [$^1J(^{109}Ag-^{31}P) = 499.5$, $^1J(^{107}Ag-^{31}P) = 432.9$ Hz] (223 K), characteristic for Ag^I bound to two phosphorus atoms[25] and may be attributed to trinuclear [Ag₃Br₃(μ-dpmt)₂]. There is also a very small amount of an unidentified isomer in the $^{31}P-\{^1H\}$ NMR spectrum at δ 5.8 [$^1J(^{109}Ag-^{31}P) = 649.7$, $^1J(^{107}Ag-^{31}P) = 564.1$ Hz] at 223 K. Complex **4** shows $^{31}P-\{^1H\}$ NMR signals at δ −5.5 at 298 K and δ −5.4 [$^1J(^{109}Ag-^{31}P) = 459.4$, $^1J(^{107}Ag-^{31}P) = 397.7$ Hz] at 223 K, which are typical for Ag^I bound to two phosphorus atoms[25] and consistent with the observed crystal structure of **4**.

The structure of complex **4** may be described as having a 'three-runged ladder' Ag₃(μ₃-I)(μ-I)₂ unit which is bridged by two dpmt ligands above and below the trinuclear plane. Fig. 2 shows the representative perspective drawing of the structure of complex **4**. Selected bond distances and angles are listed in Table 1. To the best of our knowledge, complex **4** represents the first example of trinuclear silver(ɪ) complexes with a 'three-
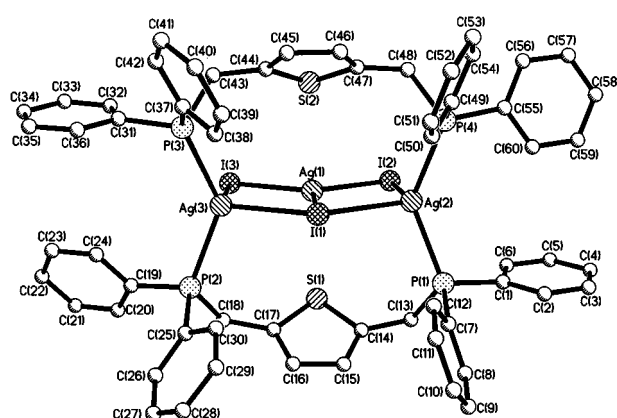

Fig. 2 Perspective view of the structure of [Ag₃(μ₃-I)(μ-I)₂(μ-dpmt)₂] **4** with atomic numbering scheme.

runged ladder' structural framework constructed of one triple-bridging I atom [I(1)], two double-bridging I atoms [I(2) and I(3)], two tetrahedrally co-ordinated silver atoms [Ag(2) and Ag(3)] and one trigonally co-ordinated silver atom [Ag(1)], in the middle of the trinuclear structure unit. Atoms Ag(2) and Ag(3) are each co-ordinated to a phosphorus donor of two bridging dpmt molecules, one bridging I and one μ₃-bridging I. The structure of **4** bears some similarity to the chair Ag₄I₄(PPh₃)₄[11] as both of the structures have mixed tetrahedrally and trigonally co-ordinated silver(ɪ) and both triple- and double-bridging I, but differ from chair Ag₄I₄(PPh₃)₄ by the virtual planarity of the trinuclear Ag₃(μ₃-I)(μ-I)₂ frame.

The Ag–P bond distances [2.463(1) Å, average] are normal. The Ag–I bond distances for tetrahedrally co-ordinated Ag(2) and Ag(3) [2.959(1) Å, average] are longer than those for trigonally co-ordinated Ag(1) [2.791(1) Å, average]. Both of them are a little longer than those [2.893(2) and 2.765(2) Å, average] in chair Ag₄I₄(PPh₃)₄[11] for corresponding bonds. Atom Ag(1) is symmetrically tri-co-ordinated by three I with a mean I–Ag(1)–I angle of 120°. Co-ordination geometries around Ag(2) and Ag(3) deviate from ideal tetrahedral with bond angles ranging from 95.63(3) to 135.42(3)°. The Ag₃(μ₃-I)(μ-I)₂ moiety is virtually planar with a mean deviation of only 0.01 Å. The Ag(1)···Ag(2) [3.074(1) Å] and Ag(1)···Ag(3) [3.041(1) Å] distances, which are comparable with those in the range 2.866(2)–3.540(2) Å in some polynuclear silver(ɪ)–phosphine complexes,[2,4–11] are suggestive of either very weak or no Ag···Ag bonding interaction. The Ag(2)···Ag(3) separation is 5.300 Å, thus the three silver(ɪ) atoms form a nearly isosceles triangle. The Ag(1)···S(1) [3.174(1) Å] and Ag(1)···S(2) [3.111(1) Å] distances are comparable to those (2.92–3.32 Å) found in silver(ɪ) complexes with thiophene derivatives,[28] indicating there is no bonding interaction between Ag(1) and the thiophene sulfurs.

Trinuclear silver(ɪ) complexes are comparatively few and known structural frameworks (**IV–VII**) are summarised below. Linear tridentate bis(diphenylphosphinomethyl)phenylphosphine (dpmp) supports the linear Ag₃ framework **IV**,[2] while tripodal tris(diphenylphosphino)methane is more suited for triangular arrangements of Ag₃ (framework **V**).[3] Framework **VI** is stabilised by dppm together with anions such as Cl, Br, C≡CPh, C≡CC₆H₄NO₂-p.[7] In our reported isosceles arrangement of Ag₃ framework **VII**, dpmt is a good supporter together with suitable bridging anions Br and I. The fact that different phosphine-based ligands stabilise different trinuclear Ag₃ frameworks clearly indicates the crucial importance of the backbone in the ligand for the construction of diverse polynuclear metal complexes. It is to be noted that dpmt and m-pp (m-pp = 1,3-bis[(diphenylphosphino)methyl]benzene)[5] stabilised different structure frames in their polynuclear silver(ɪ) complexes. In silver(ɪ) complexes with m-pp acting as a bidentate bridging ligand, only binuclear Ag₂X₂(m-pp)₂

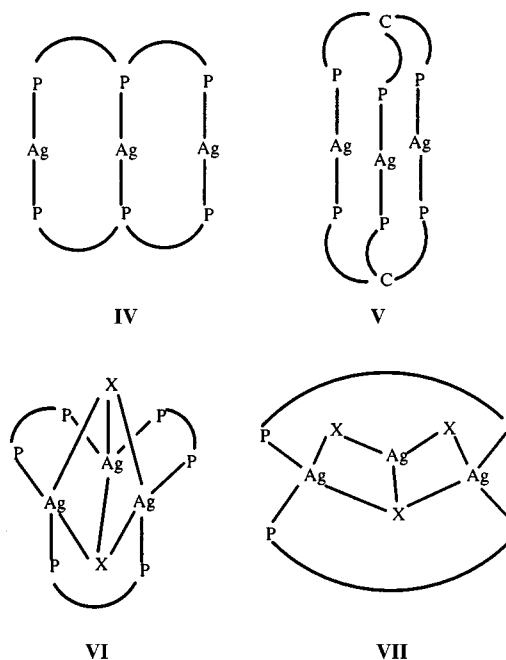**Table 1** Selected bond distances (Å), angles (°) and structural parameters for complexes **1** and **4**

$[Ag_2(\mu\text{-dpmt})_3][BPh_4]_2 \cdot 2MeCN$ **1**

Ag(1)–P(2)	2.533(1)	Ag(1)–P(3)	2.522(1)
Ag(1)–P(4)	2.531(1)	Ag(1)···Ag(1A)	5.782(6)
P(2)···P(2A)	7.10(1)	P(3)···P(4A)	7.16(1)
P(3)–Ag(1)–P(2)	117.52(3)	P(3)–Ag(1)–P(4)	123.24(2)
P(4)–Ag(1)–P(2)	116.94(3)	P(2)–C(13)–C(14)	114.3(2)
P(3)–C(43)–C(44)	116.5(2)	P(4)–C(28)–C(29)	113.9(2)
P(2)–C(13)–C(14)–S(6)	64.5(3)	P(3)–C(43)–C(44)–S(5A)	57.1(3)
P(4)–C(28)–C(29)–S(5)	73.0(3)		

$[Ag_3(\mu_3\text{-I})(\mu\text{-I})_2(\mu\text{-dmpt})_2]$ **4**$\cdot 0.25CH_2Cl_2 \cdot 0.25MeOH$

Ag(1)–I(1)	2.8254(5)	Ag(1)–I(2)	2.7669(4)
Ag(1)–I(3)	2.7821(5)	Ag(2)–I(1)	2.9967(4)
Ag(1)–I(2)	2.9223(4)	Ag(2)–P(1)	2.464(1)
Ag(2)–P(4)	2.467(1)	Ag(3)–I(1)	2.9064(4)
Ag(3)–I(3)	3.0097(5)	Ag(3)–P(2)	2.459(1)
Ag(3)–P(3)	2.462(1)	Ag(1)···Ag(2)	3.074(1)
Ag(1)···Ag(3)	3.041(1)	Ag(2)···Ag(3)	5.300(1)
P(1)···P(2)	7.08(1)	P(3)···P(4)	7.16(1)
I(3)–Ag(1)–I(2)	118.00(2)	I(3)–Ag(1)–I(1)	121.30(2)
I(2)–Ag(1)–I(1)	120.64(2)	P(4)–Ag(2)–P(1)	135.42(3)
P(4)–Ag(2)–I(1)	105.73(2)	P(4)–Ag(2)–I(2)	98.67(2)
P(1)–Ag(2)–I(1)	103.40(2)	P(1)–Ag(2)–I(2)	101.94(2)
I(1)–Ag(2)–I(2)	110.34(1)	P(3)–Ag(3)–P(2)	132.85(4)
P(3)–Ag(3)–I(3)	99.50(3)	P(2)–Ag(3)–I(3)	95.63(3)
P(3)–Ag(3)–I(1)	108.01(3)	P(2)–Ag(3)–I(1)	107.31(3)
I(3)–Ag(3)–I(1)	111.41(1)	Ag(1)–I(1)–Ag(2)	63.65(1)
Ag(1)–I(1)–Ag(3)	64.07(1)	Ag(2)–I(1)–Ag(3)	127.72(1)
Ag(1)–I(2)–Ag(2)	65.34(1)	Ag(1)–I(3)–Ag(3)	63.20(1)
P(2)–C(18)–C(17)	113.6(3)	P(1)–C(13)–C(14)	112.8(2)
P(3)–C(43)–C(44)	112.6(3)	P(4)–C(48)–C(47)	113.2(3)
P(2)–C(18)–C(17)–S(1)	−106.3(5)	P(1)–C(13)–C(14)–S(1)	101.0(5)
P(3)–C(43)–C(44)–S(2)	111.6(5)	P(4)–C(48)–C(47)–S(2)	−111.1(5)

(X = Cl, Br, I or NO_3) was established. Such a difference is likely to be due to the different bridging length between the two terminal diphenylphosphine groups. The bridging length of the rigid C–(C_4S)–C moiety in dpmt is about 5.40 Å, while that of C–(C_6)–C is about 5.05 Å in m-pp. Such a difference makes the P···P separation in dpmt longer than that in m-pp. The P···P separation in $Ag_2X_2(\text{m-pp})_2$ is about 6.15 Å, shorter than those (7.08–7.16 Å) in complexes **1** and **4**.

Gold(I) complexes with 2,5-bis(diphenylphosphinomethyl)-thiophene

Complex **5** was synthesised by the addition of a stoichiometric amount of dpmt to a water–acetone (1:1) solution of freshly prepared chloro(thiodiethanol)gold, ${[HO(CH_2)_2]_2S}AuCl$, generated *in situ* by the reduction of $Na[AuCl_4] \cdot 2H_2O$ with excess 2,2′-thiodiethanol at room temperature. The resulting $[Au_2Cl_2(\mu\text{-dpmt})]$ **5** precipitates from the reaction medium as it is formed and is easily isolated by filtration. Addition of one and two equivalents of dpmt to $[Au_2Cl_2(\mu\text{-dpmt})]$ **5** in dichloromethane lead to the formation of $[Au_2Cl_2(\mu\text{-dpmt})_2]$ **6** and $[Au_2Cl_2(\mu\text{-dpmt})_3]$ **7** respectively. Complex **5** is soluble in dichloromethane and chloroform, and insoluble in methanol, acetonitrile and acetone. Complexes **6** and **7** are soluble in a number of solvents such as dichloromethane, chloroform, methanol, acetonitrile and acetone. Molar conductivities and $^{31}P-\{^1H\}$ signals at δ 32.8, 37.9 and 36.2 respectively, for complexes **5**, **6** and **7**, are comparable with those found in other gold(I) complexes with bidentate diphenylphosphines.[13]

The structure of **5** consists of a pair of AuCl bridged by one dpmt ligand as shown in Fig. 3. Such binuclear gold(I) complexes are commonly found with bidentate phosphine ligands.[12,19,21] Selected bond distances and angles are given in Table 2. The Au–P and Au–Cl bond distances are comparable


IV

V

VI

VII

to those found in related binuclear gold(I) complexes. The P–Au–Cl units are nearly linear with angles of 177.6(2)° and 177.9(2)°. The intramolecular Au···Au separation is 5.145 Å and the shortest intermolecular Au···Au separation is 7.255 Å, indicating there is no Au–Au interaction in complex **5**. The C–(C_4S)–C moiety is planar and the absence of any distortion indicates a strain-free situation.

Treatment of complex **5** in dichloromethane with sodium sulfide hydrate $Na_2S(aq)$ at room temperature gave quantitative

Table 2 Selected bond distances (Å), angles (°) and structural parameters for complexes **5** and **8**

[Au₂Cl₂(μ-dmpt)] 5

Au(1)–P(1)	2.224(4)	Au(1)–Cl(1)	2.278(4)
Au(2)–P(2)	2.230(4)	Au(2)–Cl(2)	2.282(4)
Au(1)⋯Au(2)	5.15(5)	P(1)⋯P(2)	6.59(3)
P(1)–Au(1)–Cl(1)	177.64(14)	P(2)–Au(2)–Cl(2)	177.9(2)
P(1)–C(13)–C(14)	110.1(8)	P(2)–C(18)–C(17)	112.8(9)
P(1)–C(13)–C(14)–S(1)	−98.9(5)	P(2)–C(18)–C(17)–S(1)	66.0(5)

[(Au₂S)(μ-dmpt)] 8

Au(1)–P(1)	2.261(1)	Au(1)–S(2)	2.289(1)
Au(2)–P(2)	2.267(1)	Au(2)–S(2)	2.292(1)
Au(1)⋯Au(2)	3.131(1)	P(1)⋯P(2)	6.20(1)
Au(1)–S(2)–Au(2)	86.22(5)	P(1)–Au(1)–S(2)	175.77(5)
P(2)–Au(2)–S(2)	178.59(5)	P(1)–C(13)–C(14)	110.8(4)
P(2)–C(18)–C(17)	110.0(4)		
P(2)–C(18)–C(17)–S(1)	83.6(2)	P(1)–C(13)–C(14)–S(1)	−81.7(2)
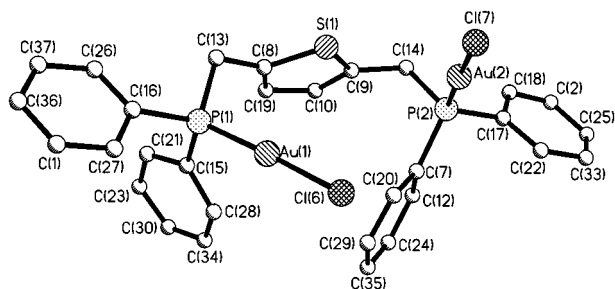
Fig. 3 Perspective view of the structure of [Au₂Cl₂(μ-dmpt)] **5** with atomic numbering scheme.
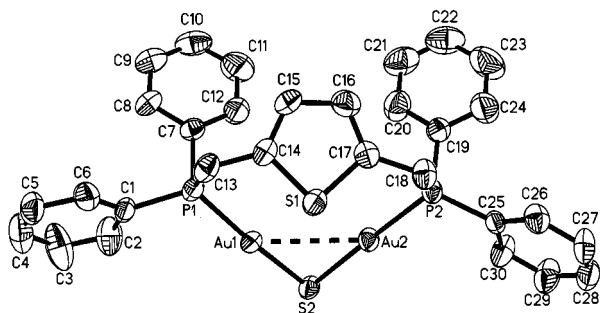
Fig. 4 Perspective view of the structure of [(Au₂S)(μ-dmpt)] **8** with atomic numbering scheme.

yields of the binuclear cyclic complex [(Au₂S)(μ-dpmt)] **8**. Complex **8** is soluble in dichloromethane and chloroform, and insoluble in methanol, acetonitrile and acetone. Conductivity measurements indicate that complex **8** is a non-electrolyte. The room temperature NMR spectrum has a singlet ³¹P-{¹H} resonance at δ 33.6 and one set of ¹H signals for thiophene and methylene protons at δ 5.81 and 3.90 respectively for a symmetrically disposed bidentate ligand.

The structure of **8** is a binuclear cyclic complex consisting of digold sulfide (Au₂S) bridged by one dpmt as shown in Fig. 4. Selected bond distances and angles are given in Table 2. The macrocycle has a narrow Au–S–Au angle of only 86.2(1)°, associated with a short intramolecular Au⋯Au distance of 3.131(1) Å. The S–Au–P linkages deviate very little from linearity with angles of 175.8(1) and 178.6(1)°, respectively, and the slight bending is such that the two gold atoms approach each other. The Au–P bond distance [2.264(2) Å, average] is a little longer than that [2.227(4) Å, average] in complex **5**, and

comparable to 2.260(2) Å (average) in Au₂S{1,4-(Ph₂PCH₂)₂-C₆H₄}.[22] Thiophene sulfur atom S(1) is 3.527 and 3.516 Å away from Au(1) and Au(2) respectively, indicating there is no bonding interaction between gold(I) and the thiophene sulfur. As in the structure of Au₂S{1,4-(Ph₂PCH₂)₂C₆H₄} in which distortion of the bridging p-xylene unit has been found, the geometry of the bridging C(13)–C₄S–C(18) moiety is also indicative of some ring strain as shown in the deviation of C(14), C(17), C(13) and C(18) from the S(1)–C(15)–C(16) plane with distances of 0.03, 0.03, 0.13 and 0.19 Å respectively, towards the co-ordination centres. Schmidbaur et al.[22] ascribed the distortion of the bridging p-xylene unit in the structure of Au₂S{1,4-(Ph₂PCH₂)₂-C₆H₄} to the effects of Au⋯Au interactions on the molecular configurations and conformations; probably Au⋯Au interactions are, to some extent, also responsible for the distortion of the bridging C(13)–C₄S–C(18) moiety in the structure of complex **8**. Meanwhile, the backbones of the phosphine ligands also affect the strength of Au⋯Au interactions as shown in the different Au⋯Au contacts of 2.882(1) Å in [(Au₂S)-(dppf)],[18a] 3.018(1) Å in [S(AuPPh₃)₂],[23] 3.131(1) Å in complex **8** and 3.147(1) Å in Au₂S{1,4-(Ph₂PCH₂)₂C₆H₄}.[22] The flexible dppf apparently favours strong Au⋯Au interactions in [(Au₂S)-(dppf)], while the rigid dmpt and {1,4-(Ph₂PCH₂)₂C₆H₄} are comparatively less able to induce Au⋯Au interactions to the same extent in complex **8** and Au₂S{1,4-(Ph₂PCH₂)₂C₆H₄} respectively.

All the dpmt molecules in our reported copper(I), silver(I) and gold(I) complexes are bridging bidentate ligands in which the thiophene moiety acts as a spacing unit. They are characterised by the planarity and rigidity of the C–(C₄S)–C bridge of about 5.4 Å. Adjusting the P–C–C–S torsion angle [rotation with the planar and rigid C–(C₄S)–C moiety] and P–C–C(S) angle may change the P⋯P separation to a certain extent, in order to incorporate dpmt in different structural frameworks as shown in [Cu₃(μ₃-X)(μ-X)₂(μ-dpmt)₂] (X = Cl, Br or I),[24] [Ag₂-(μ-dpmt)₃][BPh₄]₂·2MeCN **1**, [Ag₃I₃(μ-dpmt)₂] **4** and [Au₂Cl₂-(μ-dpmt)] **5** with P⋯P and M⋯M separations in the range 6.59–7.16 and 4.65–5.78 Å respectively. In the binuclear cyclic complex [(Au₂S)(μ-dpmt)] **8** the C–(C₄S)–C moiety was distorted due to ring constraint and Au⋯Au interaction, having a short P⋯P separation of 6.20 Å and Au⋯Au contact distance of 3.131(1) Å. The results also show that the structures of the copper(I) and silver(I) complexes are dependent on the nature and the size of the supporting anions. This evidence is in the different structural frameworks of copper(I) halide complexes in solution[24] and silver(I) halide complexes in which chlorine co-supports the apparently dinuclear [Ag₂Cl₂(μ-dpmt)] **2**, while bromine and iodine stabilise the trinuclear [Ag₃(μ₃-X)-(μ-X)₂(μ-dpmt)₂] frame (X = Br, **3** or I, **4**). More interestingly, without co-supporting bridging anions, self-assembly of three dpmt molecules with two silver(I) readily forms the binuclear triple-helical [Ag₂(μ-dpmt)₃][BPh₄]₂·2MeCN. We are currently exploring the deployment of dpmt in other polynuclear metal complexes.

Experimental

Materials and methods

Table 3 Crystal data and refinement details for complexes **1**, **4**, **5** and **8**

Compound	**1·2MeCN**	**4·0.25CH₂Cl₂·0.25CH₃OH**	**5**	**8**
Formula	$C_{142}H_{124}Ag_2B_2N_2P_6S_3$	$C_{60.5}H_{53.5}Ag_3Cl_{0.5}I_3O_{0.25}P_4S_2$	$C_{30}H_{26}Au_2Cl_2P_2S$	$C_{30}H_{26}Au_2P_2S_2$
M	2377.79	1694.57	945.34	906.50
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$C2/c$	$C2/c$	$P\bar{1}$	$P\bar{1}$
$a/\text{Å}$	37.999(4)	55.989(1)	9.546(12)	9.206(1)
$b/\text{Å}$	14.528(2)	9.807(1)	12.302(14)	11.075(1)
$c/\text{Å}$	28.107(3)	23.334(1)	13.757(12)	14.537(1)
$\alpha/°$			100.74(4)	104.15(1)
$\beta/°$	127.97(1)	91.27(1)	102.20(4)	94.14(1)
$\gamma/°$			97.85(4)	91.44(1)
$U/\text{Å}^3$, Z	12231(2), 4	12842(1), 8	1525(3), 2	1432(1), 2
$D_c/\text{mg cm}^{-3}$	1.247	1.758	2.059	2.102
μ/mm^{-1}	0.502	2.576	9.976	10.509
$F(000)$	4928	6552	888	852
Crystal size/mm	$0.38 \times 0.28 \times 0.23$	$0.48 \times 0.30 \times 0.10$	$0.35 \times 0.25 \times 0.08$	$0.28 \times 0.12 \times 0.10$
hkl Index ranges	−45 to 45, −16 to 17, −33 to 32	−69 to 58, −12 to 12, −28 to 29	−11 to 11, −7 to 14, −16 to 13	−9 to 11, −13 to 13, −18 to 17
Independent reflections	11175	12846	5459	5599
No. parameters refined	693	691	335	325
Min. and max. transmission factors	0.786, 0.935	0.670, 0.928	0.096, 0.942	0.486, 0.894
Largest difference peak and hole/e Å⁻³	0.57, −0.60	0.75, −0.72	3.60, −3.00	0.95, −1.50
$R1$,[a] $wR2$[b]	0.0365, 0.0869	0.0323, 0.0790	0.0652, 0.2048	0.0293, 0.0681
Goodness of fit on F^2	1.057	1.084	1.083	0.969

[a] $R1 = \Sigma w|F_o - F_c|/\Sigma(F_o)$. [b] $wR2 = \{\Sigma w[(F_o{}^2 - F_c{}^2)^2]/\Sigma w F_o{}^4\}^{\frac{1}{2}}$.

Preparations

[Ag₂(μ-dpmt)₃][BPh₄]₂·2MeCN 1. The dpmt ligand (144 mg, 0.30 mmol) was added to a stirred solution of [Ag(Me-CN)₄][BF₄] (108 mg, 0.30 mmol) in acetonitrile (15 cm³). After 2 h, acetonitrile (10 cm³) containing NaBPh₄ (0.90 mmol) was added and stirred for 1 h. After standing for several days, colourless crystals were formed and collected as **1** (196 mg, yield 55%). $\delta(^{31}P)$ (CD₃CN) 11.6 [d, ^1J(Ag–P) = 354.3] at 298 K and 13.4 [dd, $^1J(^{109}$Ag–P) = 370.7, $^1J(^{107}$Ag–P) = 320.6 Hz] at 223 K. $\delta(^1H)$ (CD₃CN) 7.29–6.80 (m, 106 H), 4.71 (s, 12 H) (298 K); 7.38–6.70 (m, 100 H), 6.14 (s, 6 H), 4.35 (d, 6 H), 3.54 (s, 3 H), 3.35 (s, 3 H) (223 K) (Found: C, 71.08; H, 5.36; N, 1.02; S, 4.06. Calc. for $C_{142}H_{124}Ag_2B_2N_2P_6S_3$: C, 71.72; H, 5.21; N, 1.18; S, 4.49%).

[Ag₂Cl₂(μ-dpmt)] 2. The dpmt ligand (144 mg, 0.30 mmol) was added to a stirred solution of [Ag(MeCN)₄][BF₄] (108 mg, 0.30 mmol) in acetonitrile (15 cm³). After 2 h, an aqueous solution (10 cm³) containing NaCl (0.90 mmol) was added and stirred for 1 h. After the acetonitrile was removed *in vacuo*, CH₂Cl₂ (30 cm³) was added to the residue. The CH₂Cl₂ phase was washed with water (2 × 20 cm³) and evaporated to give crude complex **2**. Recrystallisation of the crude product from CH₂Cl₂–MeOH gave **2** (48 mg, yield 42%). $\delta(^{31}P)$ (CD₃Cl) 9.8 (s, br) at 298 K and 10.3 [dd, $^1J(^{109}$Ag–P) = 700.7, $^1J(^{107}$Ag–P) = 609.1 Hz] at 223 K, $\delta(^1H)$ (CD₃Cl) 7.70–7.30 (m, 20 H), 5.99 (s, 2 H), 3.77 [d, 4 H, ^2J(PH) = 7.0 Hz] (298 K); 7.78–7.42 (m, 20 H), 5.95 (s, 2 H), 3.78 (br, 4 H) (223 K). $\Lambda_M = 0.5$ cm² Ω⁻¹ mol⁻¹ (CH₂Cl₂) (Found: C, 46.42; H, 3.56; S, 3.77. Calc. for $C_{30}H_{26}Ag_2Cl_2P_2S$: C, 46.95; H, 3.39; S, 4.18%).

[Ag₃X₃(μ-dpmt)₂] (X = Br 3 or I 4). The dpmt ligand (144 mg, 0.30 mmol) was added to a stirred solution of [Ag(Me-CN)₄][BF₄] (108 mg, 0.30 mmol) in acetonitrile (15 cm³). After 2 h, methanol (10 cm³) containing KX (0.90 mmol) was added and stirred for 1 h. The precipitated white powder was collected and recrystallised from CH₂Cl₂–MeOH to give **3** (79 mg, yield 52%) or **4** (93 mg, yield 56%) respectively. **3**: $\delta(^{31}P)$ (CD₃Cl) 3.9 (s, br) at 298 K, 0.5 [dd, $^1J(^{109}$Ag–P) = 499.5, $^1J(^{107}$Ag–P) = 432.9 Hz] at 223 K(s). $\delta(^1H)$ (CD₃Cl) 7.58–7.33 (m, 20 H), 5.87 (s, 2 H), 3.84 (s, 4 H) (298 K); 7.75–7.06 (m, 20 H), 5.34 (s, 2 H), 4.10 [d, 2 H, ^2J(HH) = 13.8], 3.69 [d, 2 H, ^2J(HH) = 13.8 Hz]. $\Lambda_M = 0.4$ cm² Ω⁻¹ mol⁻¹ (CH₂Cl₂) (Found: C, 46.58; H, 3.06; S,

3.76. Calc. for $C_{60}H_{52}Ag_3Br_3P_4S_2$: C, 47.26; H, 3.41; S, 4.21%). **4**: $\delta(^{31}P)$ (CD₃Cl) −5.5 [dd, br, ^1J(Ag–P) = 412.3] at 298 K, −5.4 [dd, $^1J(^{109}$Ag–P) = 459.4, $^1J(^{107}$Ag–P) = 397.7 Hz] at 223 K. $\delta(^1H)$ (CD₃Cl) 7.56–7.33 (m, 20 H), 5.73 (s, 2 H), 3.87 (s, 4 H) (298 K); 7.85–7.08 (m, 20 H), 5.50 (s, 2 H), 4.05 [d, 2 H, ^2J(HH) = 14.1], 3.75 [d, 2 H, ^2J(HH) = 14.1 Hz] (223 K). $\Lambda_M = 0.5$ cm² Ω⁻¹ mol⁻¹ (CH₂Cl₂) (Found: C, 42.92; H, 2.96; S, 3.85. Calc. for $C_{60}H_{52}Ag_3I_3P_4S_2$: C, 43.25; H, 3.12; S, 3.85%).

[Au₂Cl₂(μ-dpmt)] 5. Thiodiethanol (0.20 cm³) was first added to a stirring water–acetone (1 : 1) solution (10 cm³) containing Na[AuCl₄]·2H₂O (200 mg, 0.50 mmol). When the solution became colourless, dpmt (121mg, 0.25 mmol) was added. After 1 h, the formed white precipitate was filtered off, washed with water, dried and recrystallised from dichloromethane–methanol as white crystals **5** (180 mg, yield 76%). $\delta(^{31}P)$ (CD₃Cl, 298 K) 32.8. $\delta(^1H)$ (CD₃Cl, 298 K) 7.65–7.45 (m, 20 H), 6.49 (s, 2 H), 3.94 [d, 4H, ^2J(PH) = 9.5 Hz]. $\Lambda_M = 0.2$ cm² Ω⁻¹ mol⁻¹ (CH₂Cl₂) (Found: C, 38.35; H, 2.46; S, 3.25. Calc. for $C_{30}H_{26}Au_2Cl_2P_2S$: C, 38.08; H, 2.75; S, 3.39%).

[(Au₂Cl₂(μ-dpmt)]₂ 6. To a dichloromethane (10 cm³) solution containing **5** (94 mg, 0.10 mmol), dpmt (48 mg, 0.10 mmol) was added. The resulting mixture was stirred for 1 h and then concentrated *in vacuo*. Addition of diethyl ether to the residue gave a solid **6** (121 mg, yield 85%). $\delta(^{31}P)$ (CD₃Cl, 298 K) 37.9. $\delta(^1H)$ (CD₃Cl, 298 K) 7.72–7.42 (m, 20 H), 6.51 (s, 2 H), 3.88 [d, 4 H, ^2J(PH) = 8.6 Hz]. $\Lambda_M = 42.5$ cm² Ω⁻¹ mol⁻¹ (CH₂Cl₂) and 52.7 cm² Ω⁻¹ mol⁻¹ (CH₃COCH₃) (Found: C, 50.26; H, 3.47; S, 4.18. Calc. for $C_{60}H_{52}Au_2Cl_2P_4S_2$: C, 50.53; H, 3.65; S, 4.50%).

[(Au₂Cl₂(μ-dpmt)₃] 7. To a dichloromethane (10 cm³) solution containing **5** (94 mg, 0.10 mmol), dpmt (96 mg, 0.20 mmol) was added. The resulting mixture was stirred for 1 h and then concentrated *in vacuo*. Addition of diethyl ether to the residue gave a white solid **7** (149 mg, yield 78%). $\delta(^{31}P)$ (CD₃Cl, 298 K) 36.2. $\delta(^1H)$ (CD₃Cl, 298 K) 7.66–7.40 (m, 20 H), 7.08 (s, 2 H), 4.09 (d, 4 H). $\Lambda_M = 68.3$ cm² Ω⁻¹ mol⁻¹ (CH₂Cl₂) and 103.2 cm² Ω⁻¹ mol⁻¹ (CH₃COCH₃) (Found: C, 55.93; H, 3.76; S, 4.84. Calc. for $C_{90}H_{78}Au_2Cl_2P_6S_3$: C, 56.69; H, 4.09; S, 5.04%).

[(Au₂S)(μ-dpmt)] 8. Complex **5** (190 mg, 0.2 mmol) was dissolved in dichloromethane (15 cm³) and an aqueous (8 cm³)

solution of $Na_2S \cdot 2H_2O$ (68 mg, 0.6 mmol) was added. The resulting two-phase system was stirred vigorously for 2 h. The aqueous layer was separated from the organic layer and washed with dichloromethane (2×5 cm^3). The combined organic solution was dried with Na_2SO_4 and the solvents evaporated *in vacuo*. Recrystallisation of the residue in CH_2Cl_2–MeOH gave **8** (186 mg, yield 85%). $\delta(^{31}P)$ (CD$_3$Cl, 298 K) 33.6. $\delta(^1H)$ (CD$_3$Cl, 298 K) 7.79–7.40 (m, 20 H), 5.81 [d, 2 H, ^4J(PH) = 2.6], 3.90 [d, 4 H, ^2J(PH) = 8.8 Hz]. $\Lambda_M = 0.2$ cm^2 Ω^{-1} mol^{-1} (CH$_2$Cl$_2$) (Found: C, 39.31; H, 2.47; S, 6.78. Calc. for $C_{30}H_{26}$-$Au_2P_2S_2$: C, 39.74; H, 2.87; S, 7.07%).

Crystallography

A single crystal of **1** (**5** or **8**) was mounted on a glass fiber, while a crystal of **4** was sealed into a glass capillary with the mother-liquor. Crystal data for **1, 4, 5** and **8** and a summary of the crystallographic analyses are given in Table 3. The data were collected at 295 K on a Siemens CCD diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Structures were solved by the Patterson (**1** and **5**) or direct (**4** and **8**) methods. All non-hydrogen atoms were refined anisotropically. Refinement was by full-matrix least-squares based on F^2 using SHELXL 93.[29] Hydrogen atoms were placed in assigned positions and their isotropic thermal parameters were on a riding mode of the parent carbon atoms.

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See http://www.rsc.org/suppdata/dt/1998/4035/ for crystallographic files in .cif format.

Acknowledgements

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