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Aurophilicity in gold(I) thiosemicarbazone clusters†

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The reaction of the phosphine thiosemicarbazone ligands HLPH and HLPMe with Au(I) ions yields the gold complexes $[Au_3(HLPH)_2Cl_2]Cl{\cdot}2MeOH$ (**1**·2MeOH) and $[Au_2(HLPMe)Cl_2]$ (**2**). The structures determined by X Ray diffraction, $[Au_3(HLPH)_2Cl_2]Cl{\cdot}4MeOH$ (**1**·4MeOH) and $[Au_2(HLPMe)Cl_2]_2$ (**2**), are the first examples of gold(I) thiosemicarbazone clusters showing aurophilicity. The structure of the trinuclear cation **1** contains the Au(1) atom located in an inversion centre, being connected to another gold(I) atom, Au(2), through a phosphino thiosemicarbazone molecule which acts as a S,P-bridging ligand. Additionally, every gold(I) atom in the trinuclear cation **1** assembles into trinuclear linear cluster units by means of close gold–gold interactions, being connected through the crystal cell in a 2D zigzag mode. The crystal structure of $[Au_2(HLPMe)Cl_2]_2$ (**2**) contains one discrete molecule $[(AuCl)_2(HLPMe)]$ in the asymmetric unit, which is further assembled into tetranuclear $[(AuCl)_2(HLPMe)]_2$ units by means of close gold–gold interactions. Both clusters are highly luminescent in solution.

Introduction

Polynuclear gold(I) complexes have received much interest in recent decades mainly due to their intriguing structural dispositions,[1] their rich photoluminescent properties[2] or even their potential applications in very different fields such as pharmaceutics,[3] optical sensors,[4] chemosensing,[5] *etc.* Heteroleptic phosphine thiolato gold(I) complexes can be considered an important class of polynuclear compounds, because the presence of several P–Au–S structural units in their structures facilitates the formation of Au···Au interactions. These contacts, which are comparable in strength with hydrogen bonding,[6] have been recognized as a major motif for the design of functional molecular and supramolecular arrangements, both in the solid state and in solution.[7] While playing a significant role in the supramolecular aggregation pattern of gold(I) compounds, the existence of aurophilic interactions is not a requirement for luminescence, though they may influence the emission of phosphino gold(I) thiolates.[8]

The use of thiosemicarbazone ligands as thiolate scaffolds to stabilize gold(I) ions in the presence of phosphines is a quite recent event. Thus in 2006, Casas *et al.* published a [P,S]-monomer gold(I) compound derived from K_3 vitamin-thiosemicarbazone ligand and triphenylphosphine as co-ligand (Scheme 1a).[9] In 2006 Lobana *et al.* reported a S_2-monomer gold(I) complex exclusively derived from 3-nitrobenzaldehyde thiosemicarbazone, which was isolated as a homoleptic thiosemicarbazonate complex, despite its synthesis in the presence of triphenylphosphine (Scheme 1b).[10] More recently, another S_2-dimer gold(I) complex has been reported, $[Au(H_2Plhexim)]_2Cl_2{\cdot}S_8{\cdot}6H_2O$, but this complex was isolated after reduction of the expected gold(III) complex by the thiosemicarbazone thione group (Scheme 1c).[11]

Recently, we have started to use phosphino thiosemicarbazone ligands in order to achieve M(I) (M = Cu, Ag, Au) homoleptic calcogenide compounds. These ligands were previously employed to obtain Ni(II),[12] Au(III)[13] and Pt(II)[14] complexes only. Functionalization of a thiosemicarbazide skeleton with a phosphine head by means of a simple iminic condensation allowed us to isolate different Ag(I) clusters,[15] Cu(I) monomers,[16] and two Au(I) dinuclear complexes, the cation $[Au(HLPPh)]_2^{2+}$ (Scheme 1d),[17] and the chloro-cation $[Au_2(HLPEt)_4Cl]^+$ (Scheme 1e).[16] None of these gold(I) compounds exhibit aurophilicity,[6] since they do not display any Au–Au interaction.

Owing to the scantiness of reports on thiosemicarbazone Au(I) complexes and with the aim of exploring if the terminal substituents of the thiosemicarbazone branch play any role in the stoichiometry, the nuclearity and the photophysical properties of the resultant compounds, we decide to further explore the coordinative behaviour of phosphino thiosemicarbazone ligands towards gold(I) ions. In this occasion we have studied the interaction of the 4-N unsubstituted and 4-*N*-methyl substituted phosphino thiosemicarbazone ligands (Scheme 2). As a result of our studies, we report herein the first cases of Au(I) thiosemicarbazone cluster compounds showing aurophilicity.

Results and discussion

Chemistry

The ligands HLPH and HLPMe (Scheme 2) were synthesized by condensation of 2-diphenylphosphinebenzaldehyde with

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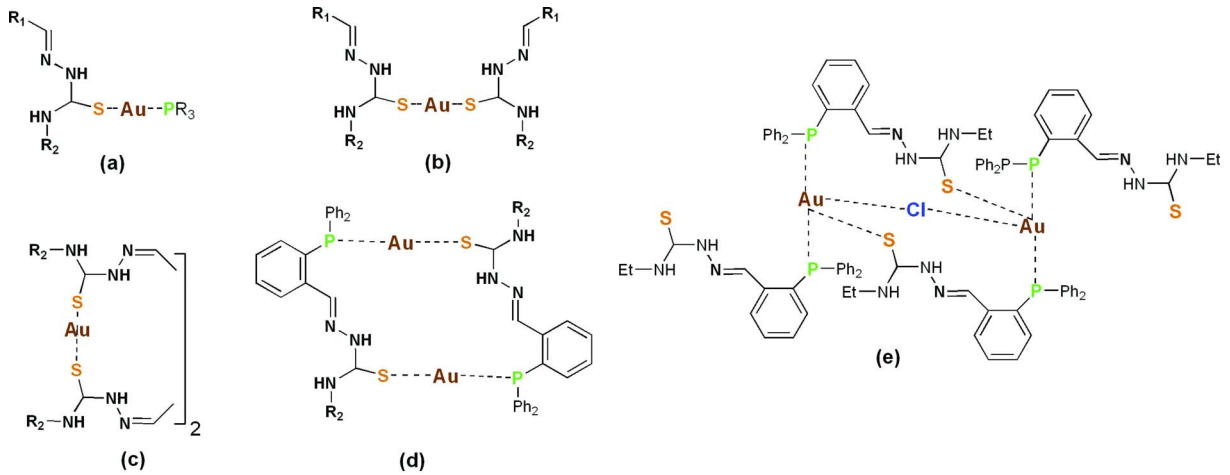
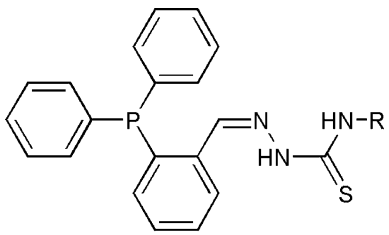


Scheme 1 Gold(I) complexes with thiosemicarbazone ligands.



HLPR (R= H, Me)

Scheme 2 Ligands HLPR (R = H, Me).

thiosemicarbazide and 4-*N*-methylthiosemicarbazide respectively, following the published procedure.[15–17] Crystallization of the ethanolic mother-liquors gave rise to good quality crystals of both phosphino thiosemicarbazone ligands.

The synthesis of the gold(I) complexes was performed by treatment of a solution of Au(tdg)Cl (tdg = thiodiglycol = 2,2′-thiobis(ethanol) with the ligands HLPH and HLPMe. The two complexes were readily characterized by elemental analysis, IR, mass spectrometry (ESI+), ^{1}H and ^{31}P NMR spectroscopy, the proposed formulae being $[Au_3(HLPH)_2Cl_2]Cl\cdot 2MeOH$ (**1**·2MeOH) and $[Au_2(HLPMe)Cl_2]$ (**2**). The complexes are air- and light-stable and soluble in common organic solvents. Partial evaporation of the solvent afforded the crystalline products $[Au_3(HLPH)_2Cl_2]Cl\cdot 4MeOH$ (**1**·4MeOH) and $[Au_2(HLPMe)Cl_2]$ (**2**).

The presence of ν(NH) bands in the range 3400–3200 cm^{-1} confirms the coordination of the neutral ligands HLPH and HLPMe to the Au(I) centres. The IR absorptions attributable to the C=S group have undergone low energy shifts with respect to the free ligands, this being indicative of the C=S bond weakening after coordination. We also have observed that the ν(C–N + C–C) bands have experienced some displacement in all complexes, probably due to the establishment of hydrogen-bond interactions, because coordination through the nitrogen atoms is unlikely.

The molar conductance value of 62.2 μS cm^{-1}, measured for the gold(I) complex **1**·2MeOH is in agreement with a 1 : 1 electrolyte compound. For complex **2**, the low value of conductance experimentally measured of 13.2 μS cm^{-1}, corresponds to a non-electrolyte.[18] The maintenance of the structure of the complexes in solution is further supported by ESI+ mass spectrometry. The mass spectrum of **1**·2MeOH exhibits the fragments $[Au(HLPH)]^+$, $[Au_2(HLPH)_2]^{2+}$ and $[Au_3(HLPH)_2]^{3+}$, thus confirming the proposed stoichiometry in solution. For **2** we have identified the $[Au(HLPMe)]^+$, $[Au_2(HLPMe)_2]^{2+}$ and $[Au_3(HLPH)_2]^{3+}$ fragments. The latter could correspond to species polymerized by means of Au···Au interactions.

The ^{1}H NMR spectra for the gold(I) complexes **1**·2MeOH and **2** show the characteristic NH thiosemicarbazone signals, but shifted downfield with respect to the free ligands, which points towards a neutral character of the ligands in these complexes. The displacement experienced by these signals (*ca.* 0.7 ppm in **1**·2MeOH and 0.2 ppm in **2**) could be attributed to the establishment of hydrogen-bond interactions in solution.[19] The imine signal hardly changes position in the spectra, which rules out the coordination of the imine nitrogen to the soft gold(I) centres. The ^{31}P spectra exhibit single signals at 29.7 (**1**·2MeOH) and 29.9 (**2**) ppm respectively, depicting the equivalence of the phosphine groups in these complexes. These signals are very significantly shifted downfield compared with the corresponding free ligands (~40 ppm), being indicative of coordination through to the phosphorus atom. These values compare well with those found in polynuclear gold(I) complexes having [PCl] linear kernels and showing aurophilic interactions.[20]

Structural studies

Crystal structures of HLPH and HLPMe. The molecular structures of the ligands HLPH and HLPMe are shown in Fig. 1 and 2 respectively, while selected geometric parameters are given in Table 2.

The ligands HLPH and HLPMe crystallize in the triclinic $P\bar{1}$ space group as two independent molecules in the asymmetric unit (denoted as **I** and **II** for each ligand). In both compounds all the molecules are *E* isomers in terms of the phosphorus-azomethine nitrogen positions, but in HLPH the two molecules have the same conformation, while in HLPMe they show opposite arrangements. In the molecule **I** these atoms are located *cis*, while in the molecule **II** they appear *trans* for the two molecules in HLPH.[21] These different orientations could be attributed to the

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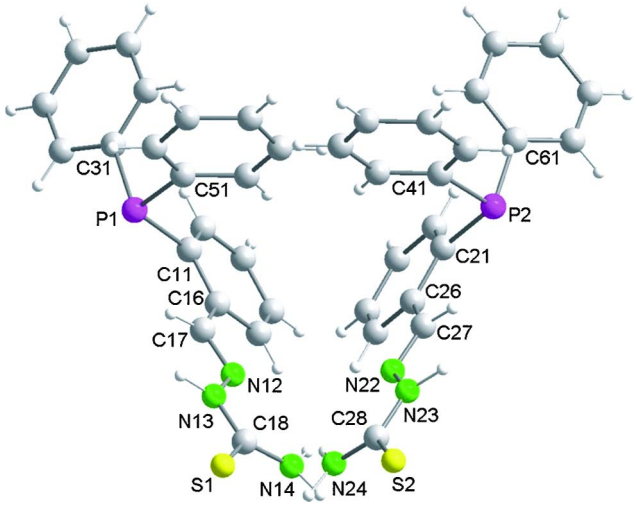

Fig. 1 Molecular structure and numbering scheme for the two independent molecules in the HPLH asymmetric unit.

packing resulting from different hydrogen-bond patterns and/or π-stacking interactions.

In HLPH, both molecules feature the typical intramolecular N–H···N hydrogen bond of thiosemicarbazone moeities, which involves the thioamide nitrogen [N(14), N(24)] and the imine nitrogen atom [N(12), N(22)] (Table S1, ESI†), together with a non-classical C–H···P interaction established between the imine carbon and the phosphorus atoms. Both conformers are linked in the asymmetric unit by an intermolecular hydrogen bond engaging the thioamide N(24)-hydrogen atom of **II** and the thioamide sulfur atom S(1) of **I** (Fig. S1, ESI†). In addition, molecule **I** features intermolecular N–H···S hydrogen bonds involving the hydrazide and the thiomide nitrogen atoms and the thioamide sulfur, while molecule **II** exhibits those involving the hydrazide nitrogen atom only. The arrangement of the molecules is additionally influenced by the existence of a weak C–H···π interaction [C(35)–H(35)···*Cg*{C(51)/C(56)}; H···*Cg* = 3.078 Å, $\alpha = 151.9°$ and $\beta = 15.0°$] (*Cg* = ring centroid).[22]

In HLPMe, molecule **II** displays a similar hydrogen bonding pattern than that in HLPH (Table S1, ESI†) while molecule **I** exhibits a different conformation, due to the absence of the intramolecular hydrogen bonds N(14)–H(14A)···N(12) and C(17)–H(17)···P(1) (Fig. S2, ESI†), together with the existence of weak π–π stacking [*Cg*{C(61)/C(66)}–*Cg*{C(61)/C(66)}, 2 − *x*, −*y*, 1 − *z*; 3.970 Å, $\alpha = 0.0°$][23] and π-ring interactions [2.951–3.182 Å for H···*Cg*, 131.0–161.0° for α and 14.1–15.6° for β].

All the bond distances and angles are in the usual range found for phosphine,[24] and thiosemicarbazone ligands,[19] and does not merit further analysis.

Crystal structure of $[Au_3(HLPH)_2Cl_2]Cl·4MeOH$ (1·4MeOH). The compound **1**·4MeOH crystallizes in the monoclinic space group $P2_1/c$ with half a molecule in the asymmetric unit. The gold(I) atom Au(1) is located in the inversion centre at a special position, being connected to another gold(I) atom, Au(2), through a phosphino thiosemicarbazone molecule, which acts as a S,P-bridging ligand. Consequently, the complex is composed of a trinuclear gold(I) cation (Fig. 3), a chloride anion with a 50% occupation and four methanol solvate molecules. Thus, every external Au(I) in the cation exhibits a distorted linear kernel by coordination to the phosphorus and the chloride atoms, with a P(1)–Au(2)–Cl(1) angle of 177.99(5)°. The deviation from linearity could be attributed to the establishment of short intermolecular Au···Au interactions (*vide infra*).[6,25] The central gold of the cation exhibits a perfect linear geometry (S–Au–S angle is 180°). This angle is notably higher than those in gold thiosemicarbazone complexes exhibiting an S–Au–S mode.[10]

The Au–P and Au–Cl bond lengths of 2.228(1) and 2.303(2) Å, respectively, are well within range reported for other Cl–Au–P complexes.[26] The Au(2)–S(1) bond lengths of 2.297(2) Å are shorter than that of 2.319(1) Å found in $[AuCl(HL)(PEt_3)]$ (HL = Vit K_3 thiosemicarbazone),[9] but within the range observed for gold(I) thiolate complexes (2.276–2.292 Å), as a result of the perfect S–Au–S alignment.[27]

Moreover the structure of **1**·4MeOH exhibits two short distances, Au1···H14B (2.88 Å) that could be considered weak agnostic interactions (Fig. 4).[28] The AuS_2H_2 skeleton is almost planar [the deviation of Au(1) from the least-squares plane is

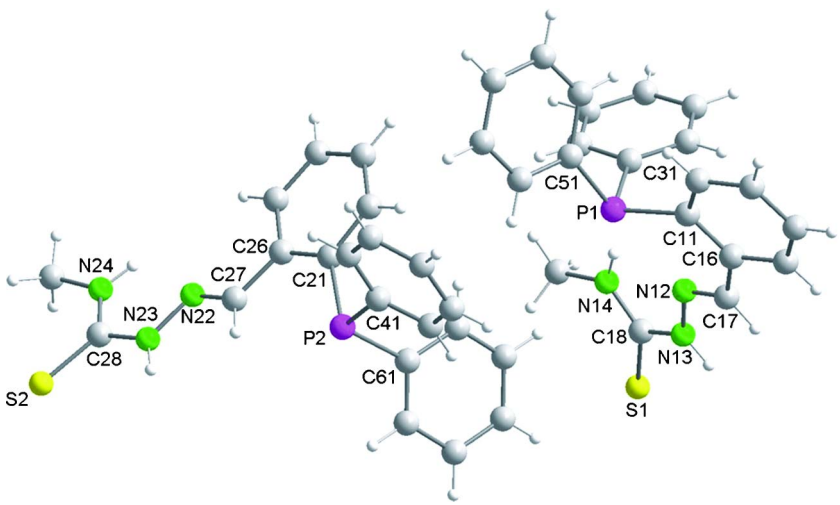

Fig. 2 Molecular structure and numbering scheme for the two independent molecules in the HPLMe asymmetric unit.

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Table 1 Crystal data and structure refinement for the compounds HLPH, HLPMe, **1**·4MeOH and **2**

	HLPH	HLPMe	**1**·4MeOH	**2**
Empirical formula	$C_{20}H_{18}N_3PS$	$C_{21}H_{20}N_3PS$	$C_{44}H_{52}Au_3Cl_3N_6O_4P_2S_2$	$C_{21}H_{20}Au_2Cl_2N_3PS$
M_r	363.40	377.43	1552.23	842.26
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a/Å	8.6649(6)	8.3820(9)	10.769(3)	9.1233(8)
b/Å	13.2989(10)	13.9983(15)	10.466(2)	10.3094(8)
c/Å	16.2517(11)	18.2378(18)	23.213(5)	13.3409(11)
α/°	84.183(4)	72.072(6)	90	100.296(4)
β/°	88.693(4)	82.970(5)	92.877(4)	105.008(4)
γ/°	89.976(4)	78.154(5)	90	96.479(4)
V/Å^3	1862.6(2)	1988.6(4)	2613.0(10)	1175.64(17)
Z	4	4	2	2
D_c/Mg m^{-3}	1.296	1.261	1.973	2.379
μ/mm^{-1}	0.267	0.252	8.741	12.863
F(000)	760	792	1480	780
Crystal size/mm	0.24 × 0.09 × 0.04	0.37 × 0.05 × 0.04	0.20 × 0.07 × 0.05	0.22 × 0.14 × 0.05
θ range/°	1.26–26.55	1.55–26.54	1.76–26.37	1.62–34.97
Limiting indices hkl	−10/10, −16/16, 0/20	−10/10, −16/17, 0/22	−13/13, 0/13, 0/29	−14/14, −16/16, 0/21
Refl. collect/unique	33453/7639	37195/8169	29302/5341	48953/10345
R_{int}	0.050	0.0739	0.0479	
Completeness θ/°	26.55 (98.6%)	26.54 (98.6%)	26.37 (100%)	34.97 (99.9%)
Max./min. transm.	0.9894/0.9388	0.9900/0.9124	0.6690/0.2738	0.5656/0.1641
Data/parameters	7639/451	8169/469	5341/279	10345/271
Goodness-of-fit on F^2	1.067	0.944	1.081	1.084
Final R indices	$R_1 = 0.0891$	$R_1 = 0.0734$	$R_1 = 0.0235$	$R_1 = 0.0263$
	$wR_2 = 0.2345$	$wR_2 = 0.1704$	$wR_2 = 0.0432$	$wR_2 = 0.0557$
R indices (all data)	$R_1 = 0.1387$	$R_1 = 0.1308$	$R_1 = 0.0626$	$R_1 = 0.0354$
	$wR_2 = 0.2598$	$wR_2 = 0.1935$	$wR_2 = 0.0988$	$wR_2 = 0.0581$
$\Delta\rho_{max/min}$/e Å^{-3}	2.691/−0.502	1.215/−0.688	3.395/−3.451	4.123/−2.774

Table 2 Selected bond lengths (Å) and angles (°) for HLPH and HLPMe

	HLPH-**I**	HLPMe-**I**		HLPH-**II**	HLPMe-**II**
S(1)–C(18)	1.682(5)	1.689(4)	S(2)–C(28)	1.688(5)	1.683(4)
C(18)–N(14)	1.331(6)	1.325(5)	C(28)–N(24)	1.314(6)	1.330(5)
N(13)–N(12)	1.383(5)	1.368(4)	N(23)–N(22)	1.383(5)	1.382(4)
N(12)–C(17)	1.280(6)	1.289(5)	N(22)–C(27)	1.270(6)	1.273(5)
S(1)–C(18)–N(14)	122.2(4)	124.7(3)	S(2)–C(28)–N(24)	122.4(4)	124.0(3)
S(1)–C(18)–N(13)	119.9(4)	119.5(3)	S(2)–C(28)–N(23)	119.6(4)	119.6(3)
N(14)–C(18)–N(13)	117.9(4)	115.8(4)	N(24)–C(28)–N(23)	118.0(4)	116.4(3)
C(18)–N(13)–N(12)	120.3(4)	119.7(3)	C(28)–N(23)–N(22)	119.8(4)	119.6(3)
N(13)–N(12)–C(17)	115.9(4)	115.2(3)	N(23)–N(22)–C(27)	115.6(4)	117.0(3)
N(12)–C(17)–C(16)	121.1(4)	122.1(4)	N(22)–C(27)–C(26)	120.5(4)	120.4(3)

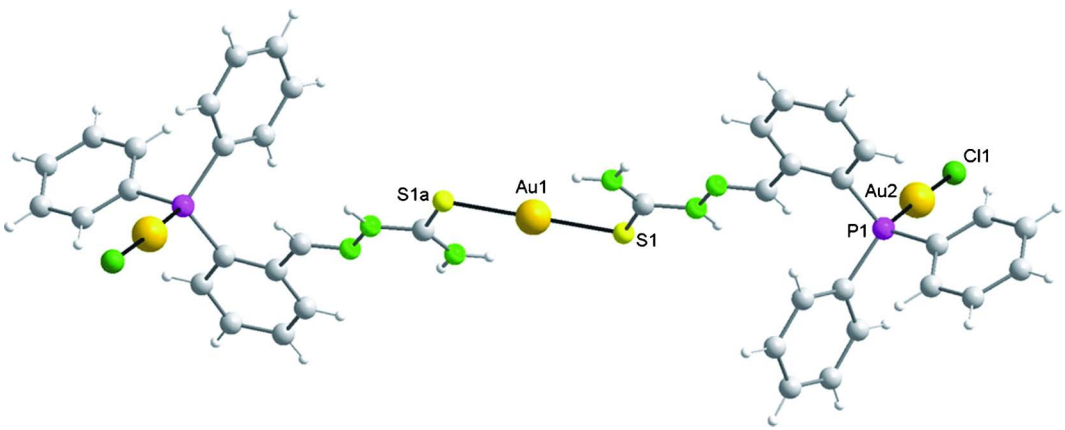

Fig. 3 View of the cation in **1**·4MeOH, showing the numbering scheme of the atoms in the molecule. Symmetry codes are given in Table 3.

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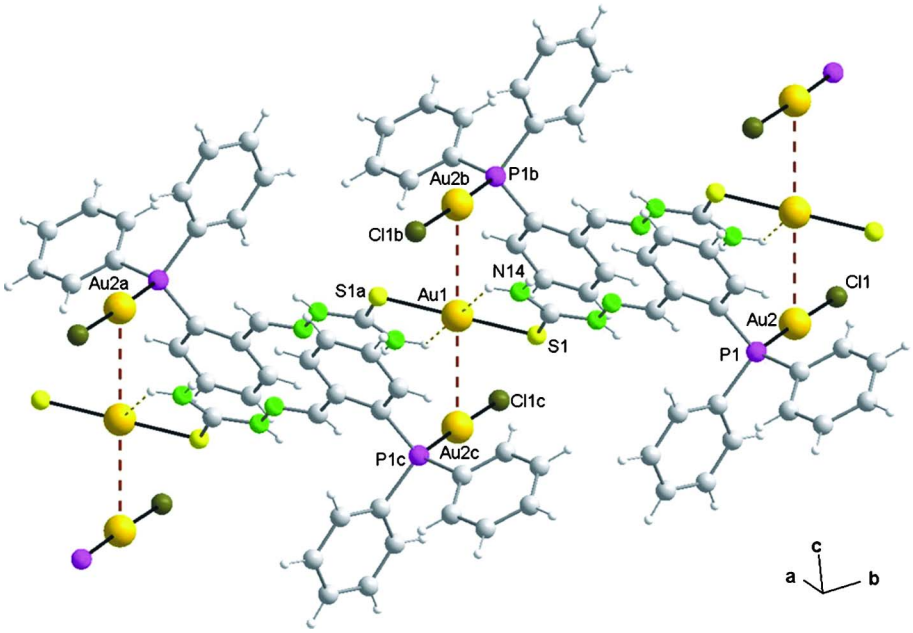

Fig. 4 View of the associated molecules of cation **1** as present in the crystal, showing the linear gold(I) trimers. The dotted lines indicate the aurophilic and weak agostic interactions.

Table 3 Selected bond lengths (Å) and angles (°) for **1**·4MeOH and **2**

1·4MeOH		**2**	
Au(1)–S(1)	2.2972(15)	Au(2)–S(1)	2.2659(8)
Au(1)–S(1)^{1}	2.2972(15)	Au(2)–Cl(2)	2.3020(8)
Au(1)–Au(2)^{2}	3.1480(5)	Au(1)–Au(2)^{1}	3.0492(3)
Au(1)–Au(2)^{3}	3.1480(5)	Au(1)–Cl(1)^{1}	3.5034(7)
Au(2)–P(1)	2.2278(13)	Au(1)–P(1)	2.2341(7)
Au(2)–Cl(1)	2.3026(16)	Au(1)–Cl(1)	2.3172(7)
Au(2)–Au(1)^{4}	3.1480(5)	Au(1)–Au(1)^{1}	4.5659(4)
S(1)^{1}–Au(1)–S(1)	180.00	S(1)–Au(2)–Cl(2)	169.80(3)
P(1)–Au(2)–Cl(1)	177.99(5)	P(1)–Au(1)–Cl(1)	173.01(3)
Au(2)^{2}–Au(1)–Au(2)^{3}	180.00	P(1)–Au(1)–Cl(1)^{1}	95.06(2)
		Cl(1)–Au(1)–Cl(1)^{1}	78.62(2)

Symmetry transformations: for **1**·4MeOH: 1: $-x, -y-1, -z+1$; 2: $-x, -y, -z+1$; 3: $x, y-1, z$; 4: $x, y+1, z$; for **2**: 1: $-x+1, -y+1, -z$.

0.792(3) Å] and forms a dihedral angle of 17.4(2)° with the thiosemicarbazone moiety.

More interestingly, every gold(I) atom in cation **1** assembles into trinuclear linear gold(I) units by means of close aurophililic interactions (Fig. 4), and therefore this complex is a cluster compound. Thus, every central S,S-coordinated Au(1) atoms occupies the central site of the cluster. The other two gold(I) atoms (Au(2)), which belong to different trimer complexes, are located at the sides of the aggregate. The Au(1)···Au(2) distances of 3.1480(5) Å fall within the aurophilic range, being indicative of a significant interaction between the two pairs of gold centres.[29,30]

Of particular interest is the perfect linear arrangement adopted by the trinuclear core in the $[Au_3(HPLH)_2Cl_2]^+$ cation, which arises from the Au(1) atom position in the inversion centre of the trimer. The S(1)–Au(1)–S(1^{a}) (a: $-x, -y-1, -z+1$), Cl(1^{b})–Au(2^{b})–P(1^{b}) (b: $-x, -y, -z+1$) and Cl(c)–Au(2^{c})–P(1^{c}) (c: $x, y-1, z$) vectors are not parallel, but are twisted by 77.20(5) and –91.2(1)°, respectively.

As a result of the establishment of the gold–gold interactions the different linear trimers are connected through the crystal cell in a 2D zigzag mode (Fig. S3, ESI†).

The existence of linearity in trinuclear Au(I) clusters is not frequent[31] and contrasts with most of the reported cases, for which bent[32] or triangular[33] arrangements have been observed. The bending degree in Au(I) cluster chains is closely related with the strength of the Au···Au interactions whiting the cluster. Thus, a larger bending angle has been attributed to strong Au···Au interactions, which could be enhanced by the coordination of halide ligands at the end of the chain.[34]

An additional point of interest in the structure of **1**·4MeOH lies in its crystal packing (Fig. S4, ESI†). As expected, the thioamide and the hydrazine hydrogen atoms of the thiosemicarbazone, together with the hydroxyl hydrogen atoms of methanol molecules are involved in hydrogen-bond formation (Table 4), with N(14), N(13), O(2) and O(3) acting as the H-donors and the chloride counter-anions, Cl(2), and the oxygen atoms of methanol molecules, O(2) and (O3), as acceptors. These interactions give rise to the rings Cl(2)/O(3), Cl(2)/O(3)/N(14) and Cl(2)/O(3)/N(14) of graph sets R^2_4 (4), R^2_3 (4), and R^4_6 (8), respectively.[35] The chloride ions Cl(2) and the oxygen atoms O(2) and O(3) establish further hydrogen bonds with the hydrogen atoms of methanol and the thioamide/hydrazide N–H groups, resulting in an alternating cation–methanol–anion–methanol–cation chain [N(13)/O(2)/C(l2)/O(3)/N(14)]. Within the chain, the hydrogen bonds combine to yield the graph set C^4_4 (8) (Table 4).

Crystal structure of $[Au_2(HLPMe)Cl_2]_2$ (2). compound **2** crystallizes in the triclinic space group $P\bar{1}$, with one discrete molecule [$(AuCl)_2$(HLPMe)] in the asymmetric unit (Fig. 5). Each phosphino thiosemicarbazone ligand is bound to two different gold(I) atoms, one of them, Au(1), through the phosphorus atom [Au(1)–P(1) = 2.2341(7) Å], whereas the second gold(I) ion, Au(2), is

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Table 4 Hydrogen bond parameters [Å, °] for **1**·4MeOH and **2**

D–H···A	D–H	H···A	D···A	∠DHA
1·4MeOH				
N(13)–H(13A)···O(2)[1]	0.88	1.88	2.749(11)	171.2
N(14)–H(14A)···O(3)[1]	0.88	2.14	2.89(2)	142.9
N(14)–H(14A)···Cl(2)[3]	0.88	2.67	3.379(9)	138.8
N(14)–H(14B)···Cl(1)[2]	0.88	2.55	3.328(8)	147.6
O(2)–H(2)···Cl(2)	0.84	2.05	2.862(9)	162.2
O(3)–H(3)···Cl(2)[4]	0.85	1.73	2.45(2)	141.5
O(3)–H(3)···Cl(2)[5]	0.85	2.44	3.08(3)	132.4
N(14)–H(14B)···Au(1)	0.88	2.89	3.421(7)	120.4
2				
N(13)–H(13A)···Cl(1)[1]	0.83	2.55	3.325(3)	158.0
N(14)–H(14A)···N(12)	0.76	2.18	2.606(3)	115.7
N(14)–H(14A)···Cl(2)[2]	0.76	2.83	3.393(3)	132.9
C(17)–H(17)···Cl(1)[1]	0.98	2.77	3.5464()	136.53
C(23)–H(23)···Cl(1)[3]	0.92	2.83	3.5854	140.73
N(13)–H(13A)···Au(2)	0.83	2.84	3.327(2)	119.4
C(17)–H(17)···Au(1)	0.98	2.86	3.389(3)	115.1

Symmetry transformations: for **1**·4MeOH: 1: $-x+1, -y+1, -z$; 2: $-x+1, -y, -z$; 3: $1+x, y, z$; for **2**: 1: $x+1/2, y-1/2, -z+1/2$; 2: $-x, -y, -z+1$; 3: $x-1/2, -y+1/2, z+1/2$; 4: $-x+1, -y+1, -z$; 5: $x-1, y, z$.

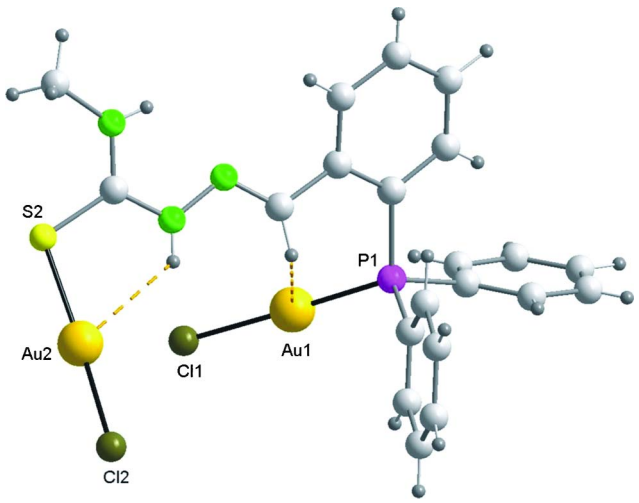

Fig. 5 Molecular structure of complex **2**.

coordinated to the thioamide sulfur atom [Au(2)–S(1) = 2.2659(8) Å]. The gold(I) atoms complete their coordination sphere with a chlorine atom [Au–Cl = av. 2.3096(8) Å], therefore generating distorted linear kernels [173.01(3)° for P(1)–Au(1)–Cl(1) and of 169.80(3)° for S(1)–Au(2)–Cl(2)]. The P–Au, S–Au and Cl–Au bond lengths fall within the range expected for linear phosphine gold(I)-chloride systems.[26]

The dinuclear gold monomer [$(AuCl)_2$(P,S-HLPMe)] is further assembled into tetranuclear [$(AuCl)_2$(HLPMe)]$_2$ units by means of close gold–gold interactions [Au(1)···Au(2[a])] (a: $-x+1, -y+1, -z$) of 3.0492(3) Å], therefore explaining the deviation from linearity. (Fig. 6). The dinuclear units show torsion angles Cl(1)–Au(1)–Au(2)–Cl(2) of −81.53°, which are close to the value of 90° estimated for X(1)–Au(1)–Au(2)–X(2) torsion angles in those cases where the gold–gold separation falls in the range 3.00–3.25 Å.[32c]

The phosphino thiosemicarbazone strands are disposed with an *anti* arrangement in complex **2** probably to avoid unfavourable

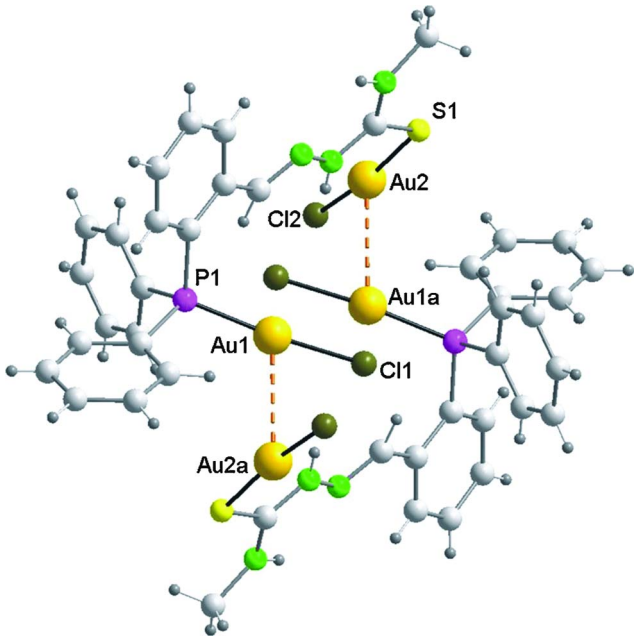

Fig. 6 Intermolecular association of **2** through aurophilic interactions (symmetry operation, a: $-x+1, -y+1, -z$).

steric interactions of the bulky phosphine that could prevent the dimerization of the complex through Au···Au interactions.[36]

The establishment of aurophilic contacts permits the formation of a twenty-membered metallacycle, which features a couple of Au···Au pairs (Fig. 7). The central part of the metallacycle ring is essentially a parallelogram with sides of 4.318(1) Å for P(1)···Cl(1[a]) (a: $-x+1, -y+1, -z$) and 4.543(1) Å for P(1)···Cl(1), and an angle of 129.290(2)°. The thiosemicarbazone moieties are twisted by 85.65(5)° as a result of the need to bring the two gold atoms into close proximity and maximize the aurophilic attractions. The conformation of the auromacrocycle is achieved

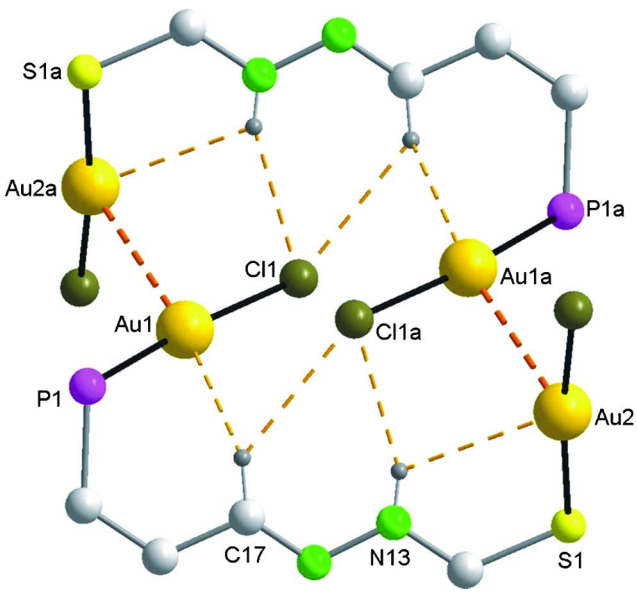

Fig. 7 Perspective view of the $Au_4S_2P_2$ central core in **2**, illustrating the metallacycle structure and the endocycle weak interactions (symmetry operation, a: $-x+1, -y+1, -z$).

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by means of weak agostic interactions between Au(2) and one proton of the hydrazine nitrogen atom [H(13A)···Au(2), 2.84 Å; N(13)···Au(2), 3.327(2) Å] and also between Au(1) and a proton of a methyl carbon atom [H(17)···Au(1), 2.86 Å; C(17)···Au(1), 3.389(3) Å] (Table 4).[28] It is noteworthy that there are also classical and non-classical hydrogen-bonding interactions within the ring. Specifically, the metallacycle exhibits two hydrogen bonds, N(13) and C(17) acting as proton donors and Cl(1) as acceptor. The metallo-ring, with approximate dimensions of the 8.20 × 8.01 Å, features a distorted square cavity through the crystal cell, the chloride ions Cl1 and Cl1a being oriented *ca.* 1.6 Å above and below the cavity, respectively (Fig. 7).

In the crystal packing two-dimensional layers run approximately parallel to the plane (111) (Fig. S5, ESI†) This assembly arises from new inter- and intramolecular hydrogen bonds involving the thioamide nitrogen atom N(14) and the C(23) atom acting as proton donors, and the imine nitrogen atom, N(12), and the chlorine atoms of neighbouring tetramers as acceptors (Table 4).

Photophysical studies

Electronic absorption spectroscopy. The electronic absorption spectra of the ligands HLPH and HLPMe are very similar (Fig. 8), showing high-energy absorption shoulders at *ca.* 232 and 272 nm and a strong low-energy absorption band at *ca.* 320 nm. The close resemblance of their UV-visible absorption spectra is understandable since a variation in the size of the substituents located at the terminal 4-N position of the thiosemicarbazone should have very little influence on the spectroscopic properties of the ligands. However, the absorption spectra of the crystalline gold(I) complexes **1**·4MeOH and **2** are notably different. Thus, UV spectrum of complex **1**·4MeOH shows a notable displacement on the high energy absorptions with respect to the corresponding ligand HLPH, with bands appearing at 267, 338 and 373 nm. The spectrum of complex **2** is similar to its precursor ligand HLPMe, but the low energy absorption band (~320 nm) is split in three bands at 313, 325 and 340 nm. In these complexes the absorptions

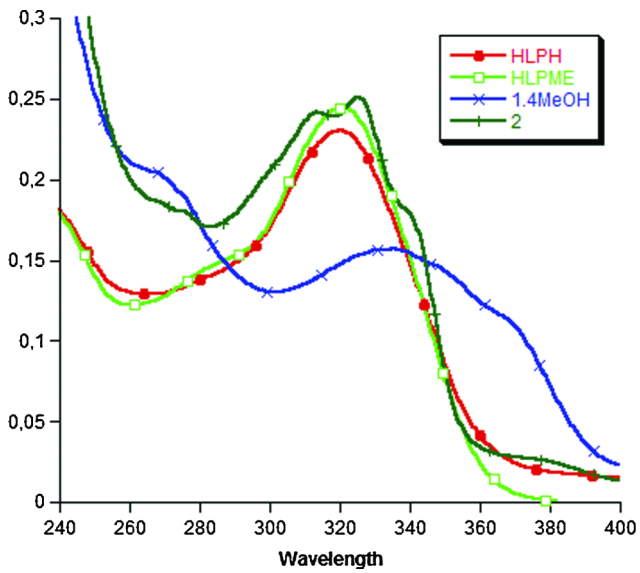

Fig. 8 Absorption spectra of the ligands HLPH and HLPMe and the Au(I) complexes **1**·4MeOH and **2** in methanol (1 × 10^{-5} M).

below 300 nm could be attributed to intraligand (IL) transitions of the phosphino thiosemicarbazone moieties, while the lowest energy bands are characteristic of thiolato gold(I) phosphine systems.[37]

The emission spectra of the ligands HLPH and HLPMe and their corresponding Au(I) complexes **1**·4MeOH and **2** were recorded at room temperature in methanol (Fig. 9). These spectra exhibit intense bands, with maxima at *ca.* 359 (HLPH), 353 (HLPMe), 415 (**1**·4MeOH) and 378 (**2**) nm (excitation at 320 (HLPH, HLPMe) or 340 nm (**1**·4MeOH and **2**). As it can be seen from the data, the emissions in the complexes are slightly red-shifted by 56 (**1**·4MeOH) and 38 (**2**) cm^{-1}, respectively, compared with the emissions in the parent ligands. It has been reported that the luminescence properties in most phosphine gold(I) thiolates are determined mainly by the nature of the thiolate ligand. Although the phosphine ligand often contains a chromophore, the optical processes predominantly occur *via* the excitation of sulfur with subsequent charge transfer to gold.[1f] Another factor to be considered in halo phosphine Au(I) complexes is the contribution of halide ligands to the energy levels.[20a] Whereas the existence of Au–Au interactions, either intermolecularly or intramolecularly, is not mandatory for emission in thiolates, if present, they could influence the emission energy and the excitation maxima of the metal complexes.[2,8b,c]

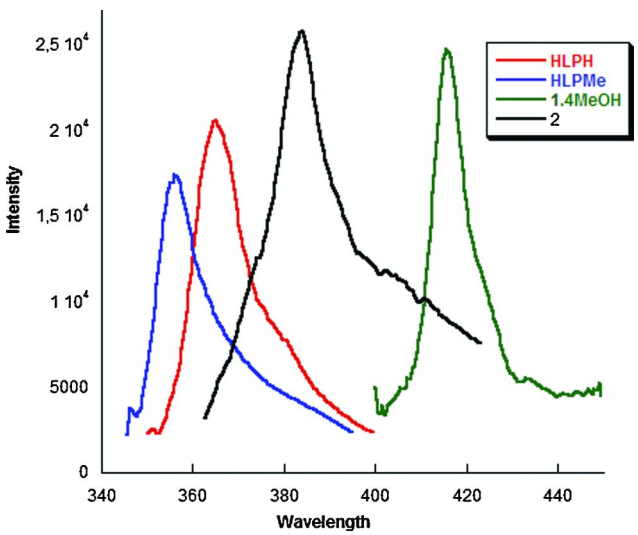

Fig. 9 Emission spectra of the ligands HLPH and HLPMe and the Au(I) complexes **1**·4MeOH and **2** in methanol (1 × 10^{-5} M).

The fact that the ligands HLPH and HLPMe and its corresponding Au(I) complexes **1**·4MeOH and **2** exhibit bands at similar energy values suggests that the emissions probably arise from the same electronic states, and therefore they could be assignable to intraligand (IL) or S-to-Au LMCT transitions. However some influence from aurophilic contacts and a certain degree of charge transfer from chloride to gold can not be discounted.[38]

The introduction of different substituents in the 4-N-terminal position of the thiosemicarbazone chain affects mainly the structure of the complexes,[16,17] but does not significantly their emission properties. Thus, we must indicate that all Au(I) complexes of the series HLPR (R = H, Me, Et, Ph) exhibit different structures despite that they were synthesised by using the same

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chemical procedure and crystallised under similar conditions. Previous works covering the structural chemistry of different N-substituted ligands indicated that the 4-N-terminal group of the thiosemicarbazones does not exert a great influence in the structure of the assembled complex. The Au(I) HLPR (R = H, Me, Et, Ph) collection of complexes breaks that prediction: the ethyl and phenyl derivates are Au(I) dimers with metal–metal interactions (Schemes 1d and e),[16,17] while the herein presented unsubstituted and methyl derived Au(I) complexes are trinuclear and dinuclear complexes, further assembled by means of aurophilic interactions (*vide supra*). Regarding the emissive properties, the ethyl and phenyl derived complexes displayed enhanced luminescence, but at similar wavelengths as their precursor ligands.[16,17] In the herein studied unsubstituted and the methyl substituted gold(I) derivatives the emission is slightly red-shifted with respect to the corresponding ligands. Hence, in these cases the presence of gold–gold contacts could be a factor influencing the slight displacement of the emission maxima.

Conclusions

In summary, tuning a thiosemicarbazone ligand with a phosphine group not only allows the isolation of homoleptic Au(I) thiosemicarbazone complexes, but also leads to the first cases of thiosemicarbazone clusters showing aurophilicity. These clusters are luminescent at room temperature with the emission maxima possibly influenced by the presence of multiple aurophilic contacts. These clusters perfectly exemplify that the synergistic combination of the attractive forces from hydrogen bonds and Au···Au interactions contributes to the stabilization of gold(I) polymeric arrays.

Experimental section

Materials

All solvents, thiosemicarbazide, 4-*N*-methylthiosemicarbazide and 2-diphenylphosphinobenzaldehyde are commercially available and were used without further purification. Commercial $H[AuCl_4]$ was reduced with 2,2′-thio-bis(ethanol) in a 1 : 1 methanol : water mixture.

Methods

Elemental analysis of C, H, N and S were performed on a FISONS EA 1108 analyzer. ^{1}H, ^{13}C and ^{31}P NMR studies (H_3PO_4 was used as internal reference) in a VARIAN MERCURY 300 spectrometer. Infrared spectra were measured from KBr pellets on a BRUKER IFS-66V spectrophotometer in the ranges 4000–100 or 500–100 cm^{-1}. Electrospray ionisation (ESI) mass spectra were recorded on an API4000 Applied Biosystems mass spectrometer with Triple Cuadrupole analyser. Conductivity was measured at 25 °C from 10^{-3} M solutions in DMF on a Crison Micro CM 2200 conductivimeter. UV-vis spectra were measured in a Hewlett Packard 8452A spectrophotometer using 1×10^{-5} M solutions in methanol. Luminescence was recorded at room temperature in a Jovin Yvon-Spex Fluoromax-2 spectrophotometer using 1×10^{-5} M solutions in methanol.

Synthesis of the ligands

The ligands 2-(2-(diphenylphosphino)benzylidene) thiosemicarbazone (HLPH) and 2-(2-(diphenylphosphino)benzylidene)-*N*-methylthiosemicarbazone (HLPMe) were prepared following the procedure reported before,[15–17] which is detailed in ESI†. In both cases good quality crystals were obtained from ethanol solutions (*vide supra*).

Synthesis of the complexes

The Au(I) complexes were synthesized by reaction of reduced $H[AuCl_4]$ with the ligands HLPH and HLPMe, respectively. The experimental procedures and the characterization data are summarized below.

$[Au_3(HLPH)_2Cl_2]Cl·2MeOH$ (1·2MeOH). 46.55 mg (0.381 mmol) of 2,2′-thiodiethanol were added to 50.29 mg (0.127 mmol) of $H[AuCl_4]$ previously dissolved in water (~2 mL). The colourless solution formed was added to 50 mg of the ligand HLPH (0.127 mmol) dissolved in methanol (30 mL). The clear solution was refluxed for 2 h and then left stirring overnight at room temperature. After that, the solution was concentrated to a small volume (15 mL) and allowed to crystallize at room temperature for 24 h. After that time the crystalline solid obtained was filtered off and finally dried *in vacuo*. Yield: 0.15 g (79%); mp >221 °C; $C_{42}H_{44}Au_3Cl_3N_6O_2P_2S_2$ (1488.18): calc.: C, 33.9; H, 3.0; N, 5.6; S, 4.3; found: C, 33.7; H, 3.1; N, 5.6; S, 4.4%; ESI(+) 560.1 $[Au(HLPH)]^+$; 757.6 $[Au_2(HLPH)]^{2+}$, 1119.2 $[Au_2(HLPH)_2]^{2+}$, 1315.1 $[Au_3(HLPH)_2]^{3+}$; ^{1}H NMR (DMSO-d_6, ppm): δ 6.77 (m, 1H), 7.48–7.69 (m, 12H), 8.43 (m, 2H), 8.82 (s, 1H), 8.79 (s, 1H), 12.28 (s, 1H); ^{31}P NMR (DMSO-d_6, ppm): δ 29.7; IR (KBr, cm^{-1}): 3485, 3332 ν(OH) + ν(NH), 1553–1436 ν(C═N) + ν(C–N), 1080 ν(N–N), 751 ν(C═S); 370, 308 ν(Au–Cl); UV/Vis (MeOH): λ_{max} = 267, 338, 373 nm. Λ_M = 62.2 μS cm^{-1}. Well-shaped colourless needles of **1**·4MeOH were studied by X-ray diffraction. The same complex **1**·2MeOH was obtained by using a 3 : 2 metal : ligand ratio in the reaction.

$[Au_2(HLPMe)Cl_2]$ 2. 93.11 mg (0.762 mmol) of 2,2′-thiodiethanol were added to 92.27 mg (0.254 mmol) of $H[AuCl_4]$ previously dissolved in water (~2 mL). The colourless solution formed was added to 100 mg of the ligand HLPMe (0.254 mmol) dissolved in methanol (30 mL). The white suspension formed was refluxed for 2 h and then left stirring overnight at room temperature. After that, the suspended white solid was filtered off and finally dried under *vacuo*. Yield 71% (0.15 g); mp >245 °C; $C_{21}H_{20}Au_2Cl_2N_3P_1S_1$ (842.28): calc.: C, 29.9; H, 2.4; N, 5.0; S, 3.8; found: C, 29.8; H, 2.2; N, 5.1; S, 3.9%; ESI(+) 574.1 $[Au(HLPMe)]^+$; 1147.1 $[Au_2(HLPMe)_2]^{2+}$; 1343.1 $[Au_3(HLPMe)_2]^{3+}$; ^{1}H NMR (DMSO-d_6, ppm): δ 2.98 (d, 3H), 6.75 (m, 1H), 7.70–7.43 (m, 9H), 8.39 (m, 4H), 8.69 (m, 2H), 11.88 (s, 1H); ^{31}P NMR (DMSO-d_6, ppm): δ 29.93; IR (KBr, cm^{-1}): 3334 ν(NH), 1574–1436 ν(C═N) + ν(C–N), 1098 ν(N–N), 749 ν(C═S) 408, 335 ν(Au–Cl); UV/Vis (MeOH): λ_{max} = 267, 313, 325, 340 nm. Λ_M = 13.2 μS cm^{-1}. Recrystallization of solid **2** in methanol at room temperature yielded the same compound as colourless prismatic crystals.

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Crystal structure determinations

Colourless crystals of HLPH and HLPMe, $[Au_3(HLPH)_2Cl_2]$-Cl·4MeOH (**1**·4MeOH) and $[Au(HLPMe)_2Cl]_2$ **2** were mounted on glass fibers and used for data collection. Crystal data were collected at 100.0(1) K (HLPLH, **2**) or 110(2) K (HLPMe) using a Bruker X8 Kappa APEXII diffractometer or at 110(2) K using a Bruker Smart CCD 1000 diffractometer (**1**·4MeOH). Graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) was used throughout. The data for HLPH, HLPMe and **2** were processed with APEX2[39] or SAINT (**1**·4MeOH) and corrected for absorption using SADABS.[40] The structures were solved by direct methods using SHELXS-97[41] and refined by full-matrix least-squares techniques against F^2 using SHELXL-97.[41] Positional and anisotropic atomic displacement parameters were refined for all non-hydrogen atoms. Hydrogen atoms for HLPH and **1**·4MeOH were included in geometrically idealized positions and for HLPMe and **2** were located in difference maps. The N–H hydrogen atoms were located unambiguously from difference Fourier maps for all compounds. In all compounds, the hydrogen atoms were included in refinement as fixed contributions riding on attached atoms with isotropic displacement parameters constrained to $1.2U_{eq}$ of their carrier atoms. The lowest and highest peaks in the final difference Fourier map were located close to the phosphorus atoms in the ligands and close to the gold atoms in complex. Criteria of a satisfactory complete analysis were the ratios of rms shift to standard deviation less than 0.001 and no significant features in final difference maps. Atomic scattering factors were obtained from International Tables for Crystallography.[42] Molecular graphics were prepared with ORTEP, implemented in PLATON,[43] and with DIAMOND.[44] A summary of the crystal data, experimental details and refinement results are listed in Table 1.

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References

1 (*a*) M. C. Gimeno and A. Laguna, *Silver and Gold. Comprehensive Coordination Chemistry II*, ed, J. A. MacCleverty and T. J. Meyer, Elsevier, Pergamon, New York, 2003, vol. 6, p. 911; (*b*) *Modern Supramolecular Gold Chemistry*, ed. A. Laguna, Wiley-WCH, 2008; (*c*) H. E. Abdou, A. A. Mohamed, J. P. Fackler Jr, *Gold Chemistry: Applications and Future Directions in the Life Sciences*, ed. F. Mohr, Wiley-WCH, 2009; (*d*) R. J. Puddephatt, *Chem. Soc. Rev.*, 2008, **37**, 2012; (*e*) M. C. Gimeno and A. Laguna, *Chem. Soc. Rev.*, 2008, **37**, 1952; (*f*) E. R. T. Tiekink and J.-G. Kang, *Coord. Chem. Rev.*, 2009, **253**, 1627; (*g*) T. N. Hooper, M. Green and C. A. Russell, *Chem. Commun.*, 2010, **46**, 2313; (*h*) A. Himmelspach, M. Finze and S. Raub, *Angew. Chem., Int. Ed.*, 2011, **50**, 2628; (*i*) I. O. Koshevoy, M. Haukka, S. I. Selivanov, S. P. Tunik and T. A. Pakkanen, *Chem. Commun.*, 2010, **46**, 8926.

2 (*a*) J. M. Forward, D. Bohmann, J. P. R. Fackler Jr. and J. Staples, *Inorg. Chem.*, 1995, **34**, 6330; (*b*) V. W.-W. Yam and K. K.-W. Lo, *Chem. Soc. Rev.*, 1999, **28**, 323; (*c*) V. W.-W. Yam, E. C. C. Cheng and Z. Y. Zhou, *Angew. Chem., Int. Ed.*, 2000, **39**, 1683; (*d*) Y. Lee and R. Eisenberg, *J. Am. Chem. Soc.*, 2003, **125**, 7778; (*e*) A. Pintado-Alba, H. De la Riva, M. Niewenhuyzen, D. Bautista, P. R. Raithby, H. A. Sparkes, S. J. Teat, J. M. López-de-Luzuriaga and M. C. Lagunas, *Dalton Trans.*, 2004, 3459; (*f*) S.-K. Yip, E. C.-C. Cheng, L.-H. Yuan, N. Zhu and V. W.-W. Yam, *Angew. Chem., Int. Ed.*, 2004, **43**, 4954; (*g*) J. Chen, A. A. Mohamed, H. E. Abdou, J. A. Krause Bauer, J. P. Fackler Jr., A. E. Bruce and M. R. M. Bruce, *Chem. Commun.*, 2005, 1575; (*h*) M. Bardají, M. J. Calhorda, P. J. Costa, P. G. Jones, A. Laguna, M. R. Pérez and M. D. Villacampa, *Inorg. Chem.*, 2006, **45**, 1059; (*i*) S.-Y. Yu, Q.-F. Sun, T. K.-M. Lee, E. C.-C. Cheng, Y.-Z. Li and V. W.-W. Yam, *Angew. Chem., Int. Ed.*, 2008, **47**, 4551; (*j*) T. K.-Ming Lee, N. Zhu and V. W.-W Yam, *J. Am. Chem. Soc.*, 2010, **132**, 17646; (*k*) I. O. Koshevoy, C.-L. Lin, A. J. Karttunen, M. Haukka, C.-W. Shih, P.-T. Chou, S. P. Tunik and T. A. Pakkanen, *Chem. Commun.*, 2011, **47**, 5533.

3 S. Y. Ho, E. R. T. Tiekink, in *Metallotherapeutic Drugs and Metal-Based Diagnostic Agents: The Use of Metals in Medicine*, ed. M. Gielen and E. R. T. Tiekink, John Wiley & Sons Ltd, Chichester, UK, 2005, ch. 26, p. 507.

4 M. A. Mansour, W. B. Connick, R. J. Lachicotte, H. J. Gysling and R. Eisenberg, *J. Am. Chem. Soc.*, 1998, **120**, 1329.

5 (*a*) V. W.-W. Yam, C. K. Li and C. L. Chan, *Angew. Chem., Int. Ed.*, 1998, **37**, 2857; (*b*) V. W.-W. Yam, C. L. Chan, C. K. Li and K. M. C. Wong, *Coord. Chem. Rev.*, 2001, **216–217**, 173; (*c*) X. He, F. Herranz, E. C.-C. Cheng, R. Vilar and V. W.-W. Yam, *Chem.–Eur. J.*, 2010, **16**, 9123.

6 (*a*) F. Scherbaum, A. Grohmann, B. Huber, C. Kruger and H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1544; (*b*) H. Schmidbaur, S. Cronje, B. Djordjevic and O. Schuster, *Chem. Phys.*, 2005, **311**, 151; (*c*) H. Schmidbaur, A. Grohmann and M. E. Olmos, *Gold: Progress in Chemistry Biochemistry and Technology*, ed. H. Schmidbaur, Wiley, Chichester, 1999, p. 648; (*d*) W. Schneider, A. Bauer and H. Schmidbaur, *Organometallics*, 1996, **15**, 5445; (*e*) C. Hollatz, A. Schier and H. Schmidbaur, *J. Am. Chem. Soc.*, 1997, **119**, 8115; (*f*) H. Schmidbaur, *Gold Bull.*, 2000, **33**, 3; (*g*) H. Schmidbaur and A. Schier, *Chem. Soc. Rev.*, 2008, **37**, 1931.

7 (*a*) D. Braga, F. Grepioni and G. R. Desiraju, *Chem. Rev.*, 1998, **98**, 1375; (*b*) S. R. Pathaneni and G. R. Desiraju, *J. Chem. Soc., Dalton Trans.*, 1993, 319; (*c*) M. A. Bennett, L. L. Welling and A. C. Willis, *Inorg. Chem.*, 1997, **36**, 5670; (*d*) P. M. Van Calcar, M. M. Olmstead and A. L. Balch, *J. Chem. Soc., Chem. Commun.*, 1995, 1773; (*e*) P. M. Van Calcar, M. M. Olmstead and A. L. Balch, *Inorg. Chem.*, 1997, **36**, 5231; (*f*) D. M. P. Mingos, J. Yau, S. Menzer and D. J. Williams, *Angew. Chem.*, 1995, **107**, 2045; (*g*) C. P. McArdle, M. J. Irwin, M. C. Jennings and R. J. Puddephatt, *Angew. Chem.*, 1999, **111**, 3571; (*h*) B.-Chiau Tzeng, A. Schier and H. Schmidbaur, *Inorg. Chem.*, 1999, **38**, 3978.

8 (*a*) V. W.-W. Yam and E. C.-C. Cheng, *Gold Bull.*, 2001, **34**, 20; (*b*) S. Y. Ho, E. C.-Chin Cheng, E. R. T. Tiekink and V. W.-W. Yam, *Inorg. Chem.*, 2006, **45**, 8165; (*c*) I. O. Koshevoy, E. S. Smirnova, M. Haukka, A. Laguna, J. C. Chueca, T. A Pakkanen, S. P. Tunik, I. Ospino and O. Crespo, *Dalton Trans.*, 2011, **40**, 7412.

9 J. S. Casas, E. E. Castellano, M. D. Couce, J. Ellena, A. Sánchez, J. Sordo and C. Taboada, *J. Inorg. Biochem.*, 2006, **100**, 1858.

10 T. S. Lobana, S. Khanna and R. J. Butcher, *Inorg. Chem. Commun.*, 2008, **11**, 1433.

11 A. Castiñeiras, S. Dehnen, A. Fuchs, I. García-Santos and P. Sevillano, *Dalton Trans.*, 2009, 2731.

12 V. M. Leovac, B. Ribár, G. Argay, A. Kálmán and I. Brčeski, *J. Coord. Chem.*, 1996, **39**, 11.

13 U. Abram, K. Ortner, R. Gust and K. Sommer, *J. Chem. Soc., Dalton Trans.*, 2000, 735.

14 D. You, S. O. Kang, J. Ko and M. Choi, *Bull. Korean Chem. Soc.*, 1997, **18**, 305.

15 (*a*) A. Castiñeiras and R. Pedrido, *Inorg. Chem.*, 2008, **47**, 5534; (*b*) A. Castiñeiras and R. Pedrido, *Inorg. Chem.*, 2009, **48**, 4847.

16 A. Castiñeiras and R. Pedrido, *Dalton Trans.*, 2010, **39**, 3572.

17 A. Castiñeiras, R. Pedrido and G. Pérez-Alonso, *Eur. J. Inorg. Chem.*, 2008, 5106.

18 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.

19 R. Pedrido, A. M. González-Noya, M. J. Romero, M. Martínez-Calvo, M. Vázquez López, E. Gómez-Fórneas, G. Zaragoza and M. R. Bermejo, *Dalton Trans.*, 2008, 6776.

20 (*a*) D. Fernández, M. I. García-Seijo, M. Bardají, A. Laguna and M. E. García-Fernández, *Dalton Trans.*, 2008, 2633; (*b*) U. Monkowius, M. Zabel and H. Yersin, *Inorg. Chem. Commun.*, 2008, **11**, 409.

21 (*a*) J. Easmon, G. Heinisch and W. Holzer, *Heterocycles*, 1989, **29**, 1399; (*b*) D. X. West, C. S. Carlson, K. J. Bouck and A. E. Liberta, *Transition Met. Chem.*, 1991, **16**, 271; (*c*) D. X. West, B. L. Mokijewski, H. Gebremedhin and T. J. Romack, *Transition Met. Chem.*, 1992, **17**, 384.

22 G. A. Bogdamonic, A. Spasojević-de Biré and S. D. Zaric, *Eur. J. Inorg. Chem.*, 2002, 1599.

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23 C. Janiak, *J. Chem. Soc., Dalton Trans.*, 2000, 3885.
24 I. Schranz, G. R. Lief, S. J. Midstokke and L. Stahl, *Inorg. Chem.*, 2002, **41**, 6919.
25 M. B. Smith, S. H. Dale, S. J. Coles, T. Gelbrich, M. B. Hursthouse and M. E. Light, *CrystEngComm*, 2006, **8**, 140.
26 (*a*) M. R. J. Elsegood, M. B. Smith and S. H. Dale, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2006, **62**, m1850; (*b*) R. C. Bott, P. C. Healy and G. Smith, *Polyhedron*, 2007, **26**, 2803.
27 (*a*) K. Nunokawa, S. Onaka, Y. Mizuno, K. Okazaki, T. Sunahara, M. Ito, M. Yaguchi, H. Imai, K. Inoue, T. Ozeki, H. Chiba and T. J. Yoshida, *J. Organomet. Chem.*, 2005, **690**, 48; (*b*) S. Onaka, M. Yaguchi, R. Yamauchi, T. Ozeki, M. Ito, T. Sunahara, Y. Sugiura, M. Shiotsuka, K. Nunokawa, M. Horibe, K. Okazaki, A. Iida, H. Chiba, K. Inoue, H. Imai and K. Sako, *J. Organomet. Chem.*, 2005, **690**, 57, and references therein.
28 (*a*) M. J. Calhorda, *Chem. Commun.*, 2000, 801; (*b*) G. R. Desiraju, *J. Chem. Soc., Dalton Trans.*, 2000, 3745; (*c*) M. Lein, *Coord. Chem. Rev.*, 2009, **253**, 625.
29 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.
30 H. Schmidbauer, *Gold Bull.*, 1990, **23**, 11.
31 (*a*) W. Schuh, H. Kopacka, K. Wurst and P. Peringer, *Chem. Commun.*, 2001, 2186; (*b*) S. D. Hanna, S. I. Khan and J. I. Zink, *Inorg. Chem.*, 1996, **35**, 5813.
32 (*a*) D. Li, C.-M. Che, S.-M. Peng, S.-T. Liu, Z.-Y. Zhou and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*, 1993, 189; (*b*) H. Xiao, Y.-X. Weng, W.-T. Wong, T. C. W. Mak and C.-M. Che, *J. Chem. Soc., Dalton Trans.*, 1997, 221; (*c*) D. V. Toronto, B. Weissbart, D. S. Tinti and A. L. Balch, *Inorg. Chem.*, 1996, **35**, 2484; (*d*) A. Hamel, N. W. Mitzel and H. Schmidbaur, *J. Am. Chem. Soc.*, 2001, **123**, 5106; (*e*) T.-L. Zhang, Y. Qina and X.-G. Meng, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2005, **61**, m2588.
33 (*a*) E. C. Constable, C. E. Housecroft, M. Mneuburger, S. Schaffner and E. J. Shardlow;, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2007, **63**, m1698; (*b*) C.-M. Che, H.-K. Yip, V. W.-W. Yam, P.-Y. Cheung, T.-F. Lai, S.-J. Shieh and S.-M. Peng, *J. Chem. Soc., Dalton Trans.*, 1992, 427.
34 P. Pyykkö, J. Li and N. Runeberg, *Chem. Phys. Lett.*, 1994, **218**, 133.
35 J. Bernstein, R. E. Davis, L. Shimoni and N.-L. Chang, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1555.
36 K. Angermaier, E. Zeller and H. Schmidbaur, *J. Organomet. Chem.*, 1994, **472**, 371.
37 C.-K. Li, X.-X. Lu, K. M.-C. Wong, C.-L. Chan, N. Zhu and V. W.-W. Yam, *Inorg. Chem.*, 2004, **43**, 7421.
38 (*a*) E. J. Fernández, A. Laguna, J. M. López-de-Luzuriaga, M. Monge, M. Montiel, M. E. Olmos, R. C. Puelles and E. Sánchez- Forcada, *Eur. J. Inorg. Chem.*, 2007, 4001; (*b*) Y. Zhou, W. Chen and D. Wang, *Dalton Trans.*, 2008, 1444; (*c*) M. Bardají, M. J. Calhorda, P. J. Costa, E. J. Fernández, A. Laguna, J. M. López-de-Luzuriaga, M. Monge and E. Sánchez-Forcada, *Dalton Trans.*, 2011, **40**, 3287.
39 *Bruker APEX2 Software*, Bruker AXS Inc V2.0-1, Madison, WI, USA, 2005.
40 G. M. Sheldrick, *SADABS. Program, for Empirical Absorption Correction of Area Detector Data*, University of Gottingen, Germany, 1997.
41 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2007, **64**, 112.
42 A. J. C. Wilson, *International Tables for Crystallography*, Vol. C, Kluwer Academic Publishers, Dordrecht, 1992.
43 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.
44 K. Brandenburg, *DIAMOND*, ver. 3.2; Crystal Impact GbR, Bonn, Germany, 2009.

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