DOI: 10.1002/ejic.201100156

Synthesis and Structural Characterization of Copper(I), Silver(I) and Gold(I) Complexes with Pyrimidine-2-thionato Ligands and their Adducts with Phosphanes

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Keywords: Copper / Silver / Gold / N,S ligands / Phosphanes / Electrochemistry

Homoleptic copper and silver compounds of a series of pyrimidine-2-thionato derivatives (RpymS$^-$; R = 4,6-Me_2,5-Et; 4-CF_3; 4,6-CF_3,Ph) have been synthesized by electrochemical oxidation of anodic metal (copper or silver) in a cell containing an acetonitrile solution of the appropriate thione and a small amount of tetraethylammonium perchlorate as electrolytic carrier. Subsequent reaction of these pyrimidine-2-thionato compounds with triphenylphosphane or bis(diphenylphosphanyl)methane (dppm) in acetonitrile allowed the synthesis of the corresponding heteroleptic complexes. The reaction of [Au(PPh_3)Cl] with the corresponding pyrimidine-2-thione in ethanol in the presence of triethylamine gave [Au(4,6-Me_2,5-EtpymS)(PPh_3)] and [Au(4-CF_3pymS)(PPh_3)] in good yields. The compounds were characterized by microanalysis, IR spectroscopy, FAB-MS and, when sufficiently soluble, ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. Compounds [Cu_6(4,6-CF_3PhpymS)$_6$] (**1**), [Ag_6(4,6-Me_2,5-EtpymS)$_6$]·2MeOH·3H_2O (**2**), [Cu_2(4-CF_3pymS)$_2$(dppm)$_2$]·2CH_3CN (**3**), [Cu(4-CF_3pymS)(PPh_3)$_2$] (**4**) and [Au(4-CF_3pymS)(PPh_3)] (**5**) were also characterized by X-ray diffraction.

Introduction

Metal complexes with ligands such as S,N-heterocyclic thiones, amino acids and proteins have attracted a great deal of interest in recent decades because of the potential relevance of such compounds as models for active sites in metalloenzymes.[1] Blue copper proteins are electron carriers in biological systems[2] and X-ray diffraction studies have demonstrated that the copper active site has a distorted tetrahedral coordination environment in the oxidized form and involves two N atoms from imidazole groups (histidine residues) and two S atoms, one from a cysteine residue and the other from methionine.[3] Significant effort has been made in this field and a number of copper complexes with N,S donors have been prepared to model the active site of metalloproteins with Cu–N,S structures.[4]

S donor ligands are also interesting in terms of their silver chemistry. Silver(I), a soft acid, is suitable for the coordination of bases such as S- and unsaturated N-containing ligands and an interesting array of stereochemistry and geometric configurations can be produced.[5] Silver clusters have been extensively studied because of their role in catalytic processes, photography and their potential use in new electronic materials. The presence of sulfur in these silver clusters enhances their semiconducting properties due to the metal ionic/covalent bonding.[6] Ag^I complexes bearing simple neutral ligands such as pyridine- and pyrimidine-2-thione are usually monomeric species that exhibit the common trigonal planar or tetrahedral coordination around the metal centre,[7] although some silver polymers of neutral pyridinethiones have also been reported.[8] Oligomeric and polymeric Ag^I species have commonly been obtained[9] with the ligands in their anionic thionato form.

Gold complexes with S donor ligands have also been investigated and some thiolato gold species have been explored because of their potential luminescent properties.[10] The formation of aurophilic interactions, especially in phosphanyl gold(I) thiolatos, has been directly correlated to luminescence and, as a result, new analytical detection systems could be developed.[11,12] Thiolato gold derivatives are also useful in present and potential industrial applications[13] and they could also be used in chemical vapour deposition processes and pharmacology.[14] On the other hand, thiomalate[15] is an important anti-arthritic drug that contains linear S–Au–S groups and a wide range of phosphanyl gold thiolatos have also demonstrated their potential anti-cancer properties.[16]

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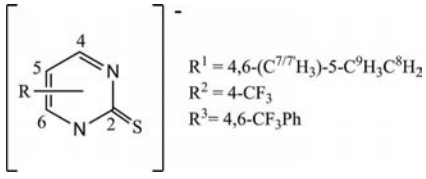
In addition, the chemistry of metal–sulfur complexes has attracted significant interest due to their ability to adopt geometries of variable nuclearity and great structural complexity. These latter features are a result of the tendency of S donor ligands to bridge metal centres to yield oligomeric or polymeric species, a situation that makes it difficult to obtain and isolate crystals suitable for X-ray diffraction studies. It has been shown[17–19] that the degree of association is very strongly dependent on both the reaction conditions and the nature of the S donor ligands. Moreover, these association phenomena can be limited by the incorporation of steric constraints through appropriate ligand design or the introduction of co-ligands to block a number of coordination sites around the metal. Recently, great effort has been made[20–26] to modify S donor ligands by introducing a solubilizing group or a bulky substituent that might modify the aggregation process.

As a part of our continued interest in the chemistry of sterically hindered S donor ligands,[27] we report herein the synthesis and characterization of copper(I), silver(I) and gold(I) complexes with several substituted pyrimidine-2-thionato ligands (Scheme 1).



Scheme 1.

The ligands have solubilizing and bulky groups that could modify the degree of aggregation as a result of steric constraints. In addition, this is one of the most versatile groups of sulfur ligands and a number of coordination modes have been reported: (a) a neutral monodentate ligand coordinated through the sulfur atom,[28] through one of the nitrogen atoms[29] and as a bridging ligand through sulfur[30] or as an N,S-chelating ligand[31,32] and (b) as an anionic ligand, in which case it can be monodentate through the sulfur atom,[33,34] an N,S-chelating ligand,[35–37] a binuclear bridging ligand through nitrogen and sulfur[9b,38] or sulfur only,[39] a binuclear triple bridging ligand through sulfur and one of the nitrogens[40] or the two nitrogen and sulfur atoms[41,42] and as a trinuclear triple bridging system.[43] To reduce their nuclearity, Cu^I and Ag^I complexes were treated with mono- and bidentate phosphanes to give the corresponding heteroleptic complexes.

Results and Discussion

Copper(I) and silver(I) complexes of general formula [M(RpymS)] (R = 4,6-Me_2,5-Et; 4-CF_3; 4,6-CF_3Ph) were prepared by a simple, one-step electrochemical procedure. The isolated compounds were usually recovered as solids at the bottom of the cell or, in some cases, after slow evaporation of the solvent. The products obtained were washed with cold acetonitrile and diethyl ether and then dried under vacuum.

The values for the electrochemical efficiency, defined as the amount of metal dissolved per unit of charge, were always close to 1.0 mol F^{-1}. This fact, together with the evolution of hydrogen at the cathode, leads us to propose the following mechanism:

Cathode: RpymSH + e^- → RpymS$^-$ + 1/2 H_2

Anode: M + RpymS$^-$ → [M(RpymS)] + e^-

(M = Cu, Ag).

Several of these homoleptic complexes are sparingly soluble in most common organic solvents as a result of their polymeric or oligomeric nature (see the structural characterization). This affected the study of these compounds in solution by NMR techniques and made it extremely difficult to obtain suitable crystals for X-ray diffraction studies. However, crystals of [Cu_6(4,6-CF_3PhpymS)$_6$] (**1**) and [Ag_6(4,6-Me_2,5-EtpymS)$_6$]·2MeOH·3H_2O (**2**) could be obtained for X-ray studies.

With the aim of reducing the level of polymerization, several heteroleptic complexes were prepared. Given the soft nature of Cu^I and Ag^I species, the chosen additional co-ligands were triphenylphosphane (PPh_3) and bis(diphenylphosphanyl)methane (dppm). The target complexes were synthesized by treatment of a suspension or solution of the homoleptic species in acetonitrile with the corresponding phosphane and the mixture was heated under reflux for several hours. The dissolution of the starting complex indicated that the reaction had taken place. Subsequent concentration at room temperature gave the corresponding solids and the analytical and spectroscopic data for these are consistent with the incorporation of the co-ligand in the coordination sphere of the metal. In the cases of [Cu_2(4-CF_3pymS)$_2$(dppm)$_2$]·2CH_3CN (**3**) and [Cu(4-CF_3pymS)(PPh_3)$_2$] (**4**), crystals suitable for X-ray diffraction studies were obtained (see below).

Heteroleptic gold(I) complexes of general formula [Au(RpymS)(PPh_3)] were also easily prepared by reaction between the corresponding thione and the precursor [AuCl(PPh_3)] in ethanol in the presence of triethylamine. In the case of [Au(4-CF_3pymS)(PPh_3)] (**5**), crystals suitable for X-ray diffraction were obtained.

Molecular Structures of [Cu_6(4,6-CF_3PhpymS)$_6$] (1) and [Ag_6(4,6-Me_2,5-EtpymS)$_6$]·2MeOH·3H_2O (2)

Perspective views of compounds **1** and **2** are shown in Figures 1 and 2, respectively, together with the atomic labelling used. Selected bond lengths and angles are given in Tables 1 and 2. Crystallographic data are reported in Table 7.

Complexes **1** and **2** consist of discrete neutral hexanuclear units formed by six metal atoms that describe a distorted octahedron (see Figure 3). All of the intermetallic bond lengths are substantially longer than those found in metallic copper[44] or silver,[45] which indicates that significant metal–metal interactions do not exist in these complexes.

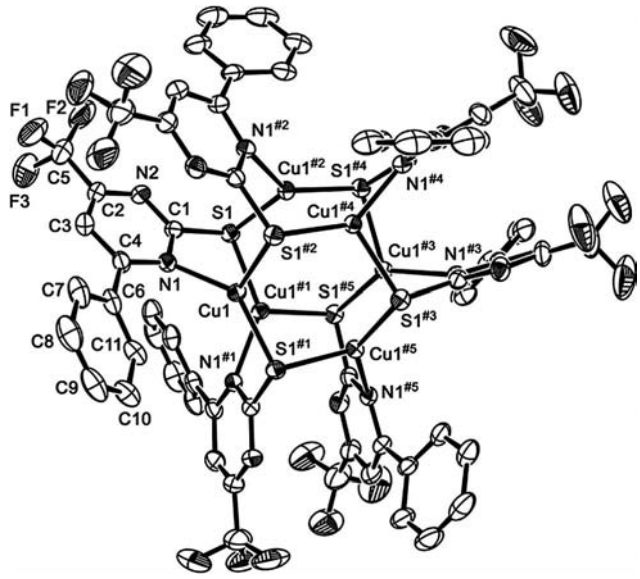


Figure 1. ORTEP diagram of the molecular structure of **1**.

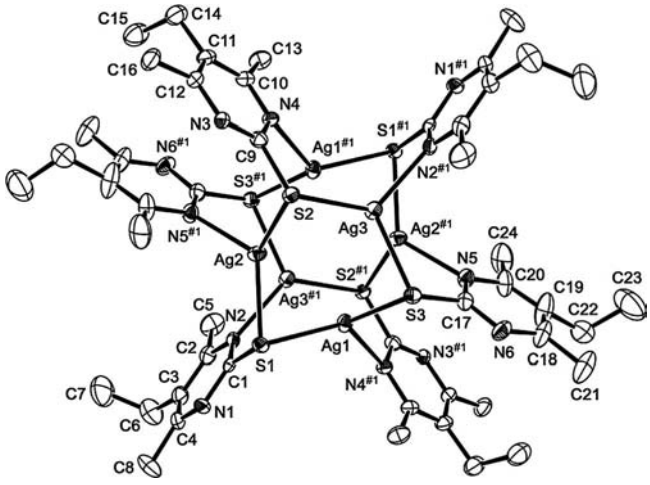


Figure 2. ORTEP diagram of the molecular structure of **2**.

Table 1. Selected bond lengths [Å] and angles [°] for **1**.[a]

Cu(1)–N(1)	2.0323(4)	Cu(1)–S(1)#1	2.21287(16)
Cu(1)–S(1)#2	2.2668(2)	S(1)–C(1)	1.7520(5)
N(1)–C(1)	1.3586(8)	N(2)–C(1)	1.3373(6)
N(1)–Cu(1)–S(1)#1	137.858(16)	N(1)–Cu(1)–S(1)#2	107.805(15)
S(1)#1–Cu(1)–S(1)#2	111.349(8)		

[a] Symmetry transformations used to generate equivalent atoms: #1: $x - y + 1/3, -y + 2/3, -z + 1/6$; #2: $y + 1/3, x - 1/3, -z + 1/6$.

In complexes **1** and **2** each metal is coordinated to one nitrogen atom from a thionato ligand and to two bridging sulfur atoms of two different ligands, which are bonded to two metal atoms. Therefore each thionato ligand behaves as a $\eta^1(N)\mu^2(S)$ ligand and is bonded to three metal atoms, which form one of the faces of the octahedron. The metal atoms are in a distorted trigonal environment [MS_2N] due to the non-equivalence of the donor atoms, a situation that causes the metal to move away from the plane described by the donors and the bond angles around the metal centre to deviate from the ideal values for a regular geometry.

Table 2. Selected bond lengths [Å] and angles [°] for **2**.[a]

Ag(1)–N(4)#1	2.331(4)	Ag(2)–S(2)	2.4996(13)
Ag(1)–S(1)	2.4514(14)	Ag(3)–N(2)#1	2.304(4)
Ag(1)–S(3)	2.4770(14)	Ag(3)–S(2)	2.4813(13)
Ag(2)–N(5)#1	2.319(5)	Ag(3)–S(3)	2.4951(13)
Ag(2)–S(1)	2.4604(13)	S(1)–C(1)	1.751(5)
S(2)–C(9)	1.757(5)	S(3)–C(17)	1.762(6)
N(1)–C(1)	1.348(6)	N(2)–C(1)	1.344(7)
N(3)–C(9)	1.338(6)	N(4)–C(9)	1.344(6)
N(5)–C(17)	1.345(7)	N(6)–C(17)	1.330(7)
N(4)#1–Ag(1)–S(1)	121.93(11)	S(1)–Ag(2)–S(2)	125.01(5)
N(4)#1–Ag(1)–S(3)	103.83(11)	N(2)#1–Ag(3)–S(2)	121.02(10)
S(1)–Ag(1)–S(3)	124.15(5)	N(2)#–Ag(3)–S(3)	114.50(10)
N(5)#1–Ag(2)–S(1)	121.52(12)	S(2)–Ag(3)–S(3)	117.13(5)
N(5)#1–Ag(2)–S(2)	105.05(12)		

[a] Symmetry transformations used to generate equivalent atoms: #1: $-x + 1, -y, -z + 1$.

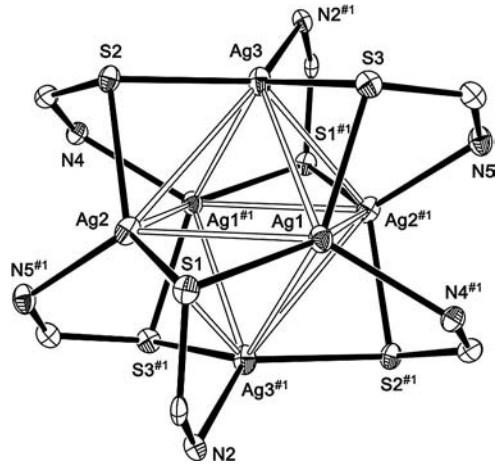


Figure 3. Octahedral metal core in complex **2**.

The Cu–S [2.21287(16) and 2.2668(2) Å] and Ag–S [2.4514(14)–2.4996(13) Å] bond lengths are in agreement with those found for other Cu^I [2.225(7)–2.2906(13) Å][46–48,50] or Ag^I [2.439(4)–2.529(4) Å][9a,47–50] hexanuclear complexes with heterocyclic thionato ligands in which the metal atoms are in a similar trigonal planar environment.

The M–N bond lengths [M = Cu: 2.0323(4) Å; M = Ag: 2.304(4)–2.331(4) Å] are also similar to those reported for Cu^I [1.978(4)–2.022(8) Å][43,50] or Ag^I [2.271(11)–2.363(11) Å][9a,47,48] complexes in which the metal atom is in a similar coordination environment.

In complexes **1** and **2** the pyrimidine rings are essentially planar with the sulfur atom almost in the same plane as the pyrimidine ring to which it is bound. The S–C and C–N bond lengths in the copper [1.7520(5) and an average value 1.3479(7) Å, respectively] and silver complexes [average values of 1.754(6) and 1.342(7) Å, respectively] are intermediate between those found in free ligands such as 4,6-dimethylpyrimidine-2-thione[51] [1.686(4) and 1.361(2) Å, respectively] or 1-phenyl-4,6-dimethylpyrimidine-2-thione[52] [1.686(4) and 1.376(2) Å, respectively] and those found in bis(4,6-dimethylpyrimidyl) 2,2′-disulfide[53] [1.782(3) and

1.323(5) Å, respectively]. This suggests that the ligand is in a form that is closer to the thionato than the thione form.

In complex **2** the asymmetric unit, which contains half a molecule of the hexameric species, has a molecule of methanol and one and a half molecules of water. These solvent molecules are involved in O–H···N hydrogen-bonding interactions with the nitrogen atoms of the pyrimidine rings that are not coordinated to the silver atom (Table 3). The hydrogen atoms of the water molecules could not be located because all of the residual electron density is around the silver atoms (see the Experimental Section). In any case, the existence of interactions involving hydrogen atoms can be deduced from the O···N distances, which are typical of classical hydrogen bonds. For this reason, these are the only hydrogen-bonding distances listed in Table 3 for this compound.

Table 3. Hydrogen bonds for **2**.[a]

D–H···A	*d*(D–H) [Å]	*d*(H···A) [Å]	*d*(D···A) [Å]	<(DHA) [°]
O(1S)–H(1S)···N(3)	0.84	2.08	2.892(7)	163.9
O(2S)···O(1S)#2	–	–	2.834(10)	–
O(2S)···N(6)#1	–	–	3.047(10)	–
O(3S)···N(1)	–	–	2.788(13)	–

[a] Symmetry transformations used to generate equivalent atoms: #1: $-x + 1, -y, -z + 1$; #2: $-x + 1/2, y - 1/2, -z + 3/2$.

Molecular Structure of $[Cu_2(4\text{-}CF_3pymS)_2dppm_2]\cdot 2CH_3CN$ (3)

The molecular structure of **3** is shown in Figure 4 together with the labelling scheme used. Selected bond lengths and angles are given in Table 4. Crystallographic data are reported in Table 7.

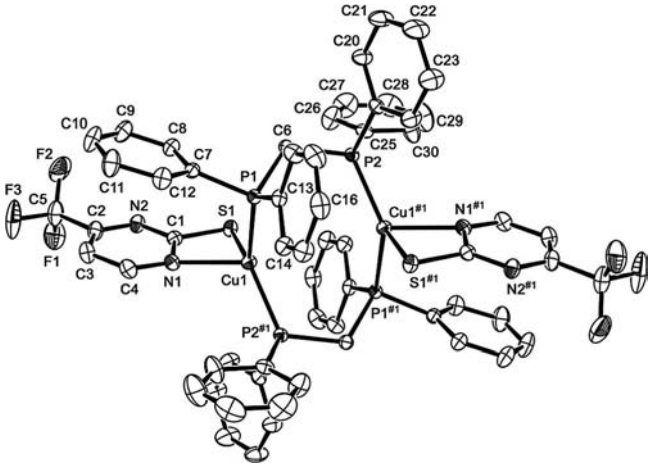


Figure 4. ORTEP diagram of the molecular structure of **3**.

Complex **3** consists of neutral dinuclear units in which the metal–metal distance [3.9043(5) Å] is somewhat longer than that found in the native metal, which indicates that copper–copper[44] interactions are not present in this compound.

Table 4. Selected bond lengths [Å] and angles [°] for **3**.[a]

Cu(1)–N(1)	2.1819(19)	Cu(1)–S(1)	2.4321(6)
Cu(1)–P(2)#1	2.2197(6)	Cu(1)–P(1)	2.2513(6)
S(1)–C(1)	1.727(2)		
N(1)–Cu(1)–P(2)#1	113.88(5)	N(1)–Cu(1)–S(1)	68.64(5)
N(1)–Cu(1)–P(1)	99.46(5)	P(2)#1–Cu(1)–S(1)	121.88(2)
P(2)#1–Cu(1)–P(1)	130.46(2)	P(1)–Cu(1)–S(1)	103.56(2)

[a] Symmetry transformations used to generate equivalent atoms: #1: $-x, -y + 1, -z$.

In complex **3** the metal atoms are linked to two phosphorus atoms from two bridging dppm ligands and to a sulfur and a nitrogen atom from a pyrimidine-2-thionato ligand, which indicates bidentate chelating behaviour. The result is a highly distorted $[CuP_2NS]$ tetrahedral conformation around the copper centre. The metal atoms are included in an eight-membered ring that has a chair conformation (see Figure 5).

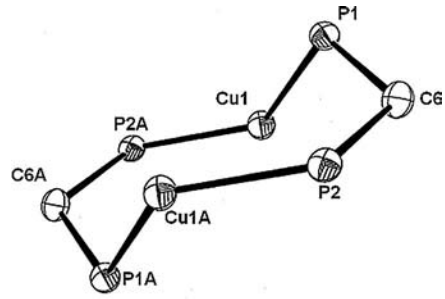


Figure 5. Chair conformation for **3**.

The structure of **3** differs from that found for $[Cu_2(6\text{-}t\text{BuMe}_2\text{SipyS})_2(dppm)_2]$,[54] which has a similar molecular formula but the two copper atoms are in a different environment and both dppm and the pyridine-2-thionato ligands show different coordination modes.

The Cu–S bond length [2.4321(6) Å] lies in the range of values reported for several complexes[48,54] containing copper(I) in a similar tetrahedral coordination environment. The Cu–N bond length of 2.1819(19) Å is also quite similar to those reported for several copper(I) complexes[4c,55–57] with a tetrahedral coordination environment for the metal atom. The two Cu–P bond lengths are slightly different to one another [2.2513(6) Å for Cu(1)–P(1) and 2.21976(6) Å for Cu(1)–P(2)#1]; both of these values are quite similar to those reported [2.1730(11)–2.3093(7) Å][48,54,58–60] for similar copper(I) complexes.

Complex **3** crystallizes with two acetonitrile molecules per dimeric copper unit (i.e., one acetonitrile molecule per asymmetric unit). These solvent molecules do not take part in coordination to the metal although non-classical C–H···N interactions with the complex are evident.

Molecular Structure of $[Cu(4\text{-}CF_3pymS)(PPh_3)_2]$ (4)

A perspective view of **4** is shown in Figure 6 together with the atomic labelling used. Selected bond lengths and angles are reported in Table 5 and crystallographic data are reported in Table 7.

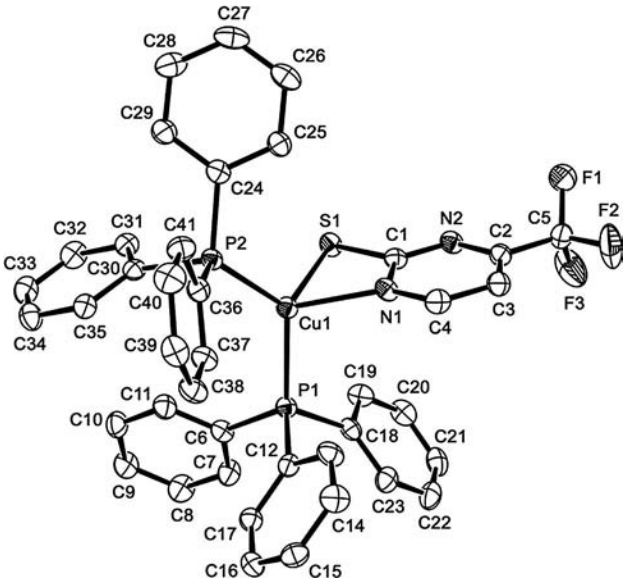


Figure 6. ORTEP diagram of the molecular structure of **4**.

Table 5. Selected bond lengths [Å] and angles [°] for **4**.

Cu(1)–N(1)	2.185(3)	Cu(1)–S(1)	2.3823(11)
Cu(1)–P(1)	2.2586(10)	Cu(1)–P(2)	2.2397(11)
S(1)–C(1)	1.705(4)		
N(1)–Cu(1)–P(2)	119.08(8)	N(1)–Cu(1)–S(1)	69.25(8)
N(1)–Cu(1)–P(1)	103.47(8)	P(2)–Cu(1)–S(1)	114.41(4)
P(2)–Cu(2)–P(1)	125.93(4)	P(1)–Cu(1)–S(1)	110.75(4)

Complex **4** consists of monomeric molecules with the copper in a highly distorted tetrahedral [$CuNSP_2$] environment with thionato ligands showing bidentate chelating behaviour through the exocyclic sulfur atom and one of the heterocyclic nitrogen atoms. The bond angles are far from those of a regular geometry with the smallest angle of 69.25(8)°, S(1)–Cu(1)–N(1), described by the thionato ligand.

The Cu–S bond length is 2.3823(11) Å, which is longer than that found in **1** and slightly shorter than that found in **3**. The value obtained for complex **4** is in the usual range previously reported for tetrahedral copper(I) complexes[48,54] with sulfur ligands: 2.3164(7)–2.435(3) Å. The Cu–N bond length is 2.185(3) Å, which is longer than that found in **1** and quite similar to that found in **3**. However, all of these distances are in the same range as those [2.054(2)–2.188(7) Å] found in several tetracoordinate copper(I) complexes[4c,55–57] with N donors and phosphane ligands around the metal atom. Complex **4** shows two different values for the Cu–P bond lengths, 2.2397(11) and 2.2586(10) Å, and these are not markedly different to those found in **3**. These values are quite similar to those reported for other tetracoordinate copper(I) complexes: 2.1730(11)–2.3562(6) Å.[48,58–60]

Molecular Structure of [Au(4-CF_3pymS)(PPh_3)] (5)

The molecular structure of **5** is shown in Figure 7 together with the labelling scheme used. Selected crystal data are given in Table 6.

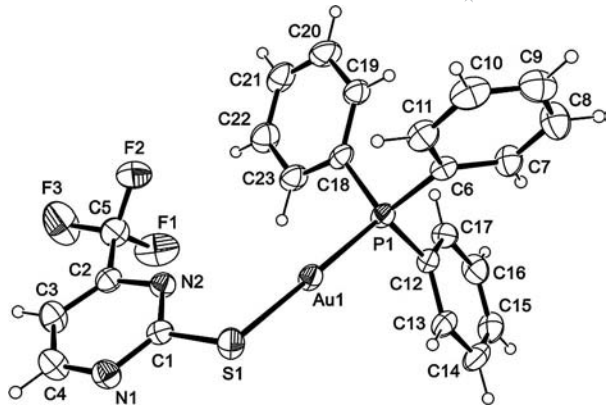


Figure 7. ORTEP diagram of the molecular structure of **5**.

Table 6. Selected bond lengths [Å] and angles [°] for **5**.

Au(1)–P(1)	2.2532(14)	Au(1)–S(1)	2.3018(14)
S(1)–C(1)	1.742(6)	N(1)–C(1)	1.344(7)
N(2)–C(1)	1.344(6)		
P(1)–Au(1)–S(1)	179.33(5)		

The structure has two independent monomeric molecules in the unit cell. For each monomer, the Au atom is coordinated in a linear fashion to a sulfur atom from the thionato ligand and a phosphorus atom of PPh_3. The S–Au–P group is linear with a bond angle of 179.33(5)°.

The Au–S bond length is 2.3018(14) Å and this is in the range 2.2975(19)–2.3274(9) Å reported for several phosphane gold(I) thiolato complexes.[61] These bond lengths are also quite similar to those reported for several triphenylphosphane gold(I) complexes[62] with 2-mercaptobenzamides: 2.3095(14)–2.319(4) Å.

The Au–Au distance [5.1392(4) Å] is much longer than those found in similar complexes in which intermetallic interactions exist; for instance, the complexes [AuCl{($HOCH_2CH_2$)dmit}][63a] [dmit = 4,5-bis(2-hydroxyethylthio)-1,3-dithiole-2-thione] and [AuCl($C_3H_4S_3$)][63b] ($C_3H_4S_3$ = ethylenetrithiocarbonate) also show this kind of interaction with Au–Au distances of 3.078(6) and 3.366 Å, respectively. This kind of interaction has also been observed in gold macrocycles.[63c]

An intramolecular interaction between the Au and N(2) atoms could be considered. The value of 3.102(5) Å is too large for a normal Au–N bond but is slightly shorter than the sum of their van der Waals radii[64] (3.25 Å), so we can propose the existence of a weak interaction between the metal centre and one of the non-coordinated heteroatoms. This kind of interaction has been observed previously in related systems, for example, [Ph_3PAuSC(=NCN)N(H)-Me],[65a] with a value for the Au···N bond length of 3.331(6) Å, that is, longer than that reported for complex **5**. A similar Au···N distance (3.10 Å) has been observed for a pyridine-2-thionato gold complex.[65b] In this compound and in **5**, the Au–C–S bond angles are quite similar (102.39 and 101.1°, respectively), and this is consistent with the presence of a weak Au···N interaction. This situation could

also explain the unexpected absence of aurophilic interactions in **5**, given the tendency of gold(I) thiolate complexes to exhibit this kind of phenomenon.[65c,65d]

The pyrimidinic group is planar with a deviation from planarity of 0.0037 Å. The S–C and N–C bond lengths [average values of 1.742(6) and 1.344(7) Å, respectively] are similar to those found in other pyrimidine-2-thionato complexes, which suggests thionato behaviour for the ligand.

Spectroscopic Data

In the IR spectra of the complexes (see the Experimental Section) the bands due to the NH group, which in the free ligands appear at about 3200 cm^{-1}, are absent. This indicates that the deprotonation of this group occurred during the synthesis of the complexes and therefore the ligands are coordinated in the thionato form. This conclusion is supported by the shift to lower wavenumbers of the strong bands due to ν(C=C) and ν(C=N), which in the free ligands appear at around 1590–1650 and 1525–1570 cm^{-1}, respectively. In addition, bands attributable to the ring breathing vibration at around 1000 and 630 cm^{-1} confirm that the nitrogen is also coordinated to the metal centre.[66]

Complexes with diphosphanes also show bands at around 1470, 1130, 1025, 785, 725 and 700 cm^{-1}, which are typical for coordinated dppm.[67] Copper and gold complexes containing PPh_3 show bands attributable to this coordinated phosphane.

Most of the homoleptic complexes have low solubility and this made it difficult to study their behaviour in solution by NMR spectroscopy. However, the signal that appears in the ^1H NMR spectra of the free ligands at around 14 ppm due to the –NH group is absent from the spectra of the complexes. This finding confirms that the ligands are deprotonated and that they act in the thionato form. The ^1H NMR spectra of the complexes show signals attributable to pyrimidinic hydrogen atoms and the signals for the methyl, ethyl or phenyl groups appear slightly displaced relative to their positions in the spectra of the free ligands. The ^1H NMR spectra for the heteroleptic complexes containing a methylene group contain, together with signals attributable to the thionato and phenyl protons, a broad singlet in the range 2.90–4.02 ppm. This signal is assigned to the methylene protons.

The most important point to note in the ^{13}C NMR spectra (when registered) is the displacement of the signal for C-2 to a lower chemical shift; this is probably due to the reduction of the C–S bond strength, which confirms once again that the ligands are in the thionato form. The corresponding ^{13}C NMR spectra show signals in the aromatic region (118.2–135.2 ppm) and one more signal at 24.8–30.7 ppm, which has been assigned to methylenic carbons. The ^{31}P NMR spectra of the heteroleptic complexes containing dppm as a bridging ligand show a signal in the range 23.0–44.9 ppm: This signal appears at δ = –23.6 ppm for the free ligand and the downfield shift is a consequence of the coordination of the phosphorus atom to the metal. In a similar way, the complexes that contain coordinated PPh_3 show positive displacements in chemical shifts as a consequence of coordination to the metal.

Most of the complexes were also characterized by mass spectrometry using the positive ion FAB technique with 3-nitrobenzyl alcohol (NBA) as matrix. The FAB spectra of [Au(4,6-Me_2,5-EtpymS)(PPh_3)] and [Au(4-CF_3pymS)(PPh_3)] (**5**) show the molecular ion with the appropriate isotopic distribution as well as peaks due to molecular rearrangements. A number of spectra also show the peak attributable to $[M(dppm)]^+$ with M = Cu, Ag.

Conclusions

The work described in this paper concerns the electrochemical synthesis and structural characterization of homoleptic copper and silver compounds with pyrimidine-2-thionato ligands containing different substituents on the heterocyclic ring. In addition, a number of heteroleptic copper and silver complexes containing triphenylphosphane or bis(diphenylphosphanyl)methane as co-ligand was prepared by direct reaction between the homoleptic derivative and the co-ligand in acetonitrile.

The homoleptic complexes under investigation have a hexanuclear structure regardless of the nature and position of the substituent on the heterocyclic ring and the metal is in a trigonal environment. The presence of an additional ligand reduces the nuclearity of the compound; the bis(diphenylphosphanyl)methane derivatives are dimeric with the dppm ligand acting as a [μ^2P,P] system. The compound that contains triphenylphosphane as a co-ligand is monomeric. In both the dimeric and monomeric complexes the metal is in a distorted tetrahedral [NSP_2] environment.

The reaction between [Au(PPh_3)Cl] and the corresponding pyrimidine-2-thione in ethanol in the presence of triethylamine also gave a monomeric compound in which the Au atom is coordinated in a linear fashion to a sulfur atom from the thionato ligand and a phosphorus atom from PPh_3.

Experimental Section

General: Thiourea, 3-ethyl-2,4-pentanedione, benzaldehyde, 1,1,1-trifluoroacetone, 4-trifluoromethylpyrimidine-2-thione, triphenylphosphane, bis(diphenylphosphanyl)methane and triphenylphosphane gold(I) chloride are all commercial products and were used as supplied. Copper and silver were used as foils and were washed with an acid solution and brushed prior to use. 4-Trifluoromethyl-6-phenylpyrimidine-2-thione and 4,6-dimethyl-5-ethylpyrimidine-2-thione were obtained as reported previously.[34,68]

Elemental analyses were performed with a Carlo–Erba EA microanalyser. IR spectra were recorded as KBr mulls with a Bruker IFS-66V spectrophotometer. ^1H and ^{13}C NMR spectra were recorded with a Bruker AMX 300 MHz instrument with $CDCl_3$ or [D_6]DMSO as solvent. Chemical shifts are given relative to TMS as the internal standard. Mass spectra (FAB) were recorded with a Micromass Autospec spectrometer with 3-nitrobenzyl alcohol as the matrix material.

Electrochemical Synthesis: The cell consisted of a copper or silver foil (anode) and a platinum wire (cathode) in contact with the thione solution in acetonitrile. A small amount of tetraethylammonium perchlorate acted as the electrolyte. (**Caution:** Although no problem was encountered in this work, all perchlorate compounds are potentially explosive and should be handled in small quantities and with great care!). The cell can be summarized as $M_{(+)}/CH_3CN$ + RpymSH/$Pt_{(-)}$. All of the syntheses were carried out at room temperature and the current was kept at 10 mA. In all of the reactions hydrogen evolved at the cathode and the yellow or orange solutions changed colour. At the end of the reactions the solids were isolated by filtration, washed with acetonitrile and diethyl ether and dried under vacuum.

[Cu(4,6-Me_2,5-EtpymS)]: Electrochemical oxidation of a copper anode in a solution of 4,6-Me_2,5-EtpymSH (0.100 g, 0.59 mmol) in acetonitrile (50 mL) at 10 mA over 1.5 h caused 35.2 mg of copper to be dissolved (E_f = 0.99). During the electrolysis the initial yellow solution became brown and at the end of the reaction a pale-brown solid was obtained. Analytical data confirmed that this was not the desired product. The solid was washed with acetonitrile and diethyl ether, dried under vacuum and characterized as [Cu(4,6-Me_2,5-EtpymS)$_2$]. Yield: 82 mg; 60.3%. IR (KBr): $\tilde{\nu}$ = 3500 (m, br), 2950 (m), 1570 (m, br), 1420 (w), 1380 (w), 1335 (m), 1260 (s), 1150 (m), 1060 (w) cm^{-1}. $C_8H_{11}CuN_2S$ (230.54): calcd. C 41.64, N 12.14, H 4.77, S 13.88; found C 41.07, N 11.89, H 4.92, S 13.45. This compound is sparingly soluble in the usual solvents and NMR spectra were not recorded. The mass spectrum did not contain any identifiable peaks.

[Cu(4-CF_3pymS)]: A solution of 4-CF_3pymSH (0.100 g, 0.55 mmol) in acetonitrile (50 mL) was electrolysed at 10 mA over 1.5 h and 34.8 mg of copper were dissolved from the anode (E_f = 0.98). At the end of the reaction an insoluble dusty orange solid was obtained. This was washed with diethyl ether, dried and identified as [Cu(4-CF_3pymS)]. Yield: 121 mg, 90.7%. IR (KBr): $\tilde{\nu}$ = 3040 (m), 1590 (s, br), 1420 (m), 1330 (s), 1195 (s), 1135 (w), 1110 (m), 830 (m), 725 (m), 670 (m) cm^{-1}. MS (FAB): *m*/*z* = 484 [Cu_2(4-CF_3pymS)$_2$]$^+$, 307 [Cu_2(4-CF_3pymS)]$^+$, 242 [Cu(4-CF_3pymS)]$^+$, 179 [4-CF_3pymS]$^+$. $C_5H_2CuF_3N_2S$ (242.54): calcd. C 24.73, N 11.54, H 0.82, S 13.19; found C 24.76, N 11.51, H 0.80, S 13.12. The complex is insoluble in the usual solvents and NMR spectra were not recorded.

[Cu(4,6-CF_3PhpymS)]: A solution of the ligand (0.100 g, 0.39 mmol) in acetonitrile (50 mL) was electrolysed for 1 h and 23.4 mg of copper were dissolved from the anode (E_f = 0.99). At the end of the electrolysis a solid was not obtained. The solvent was partially removed and a dark-green dusty solid was obtained. The solid was washed with acetonitrile and diethyl ether, dried under vacuum and identified as [Cu(4,6-CF_3PhpymS)]. Yield: 101 mg, 81.3%. IR (KBr): $\tilde{\nu}$ = 1640 (m), 1565 (s), 1540 (m), 1460 (m, br), 1435 (m), 1370 (s), 1330 (w), 1280 (w), 1250 (s), 1180 (s, br), 1135 (s), 990 (m), 860 (w), 830 (m), 760 (s), 710 (m), 700 (w), 680 (m), 640 (m), 625 (w) cm^{-1}. ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 8.39 (s, 1 H, 5-H), 7.47–8.09 (broad and complex signals) ppm. ^{13}C NMR (300 MHz, [D_6]DMSO): δ = 203.5 (C-2), 168.5 (C-4), 166.6 (C-6), 133.6–129.8 (Ph-C), 128.0 (q, CF_3), 110.0 (C-5) ppm. MS (FAB): *m*/*z* = 634 [Cu_2(4,6-CF_3PhpymS)$_2$]$^+$, 381 [Cu_2(4,6-CF_3-PhpymS)]$^+$, 317 [Cu(4,6-CF_3PhpymS)]$^+$, 255 [4,6-CF_3PhpymS]$^+$. $C_{11}H_6CuF_3N_2S$ (318.78): calcd. C 41.45, N 8.79, H 1.90, S 10.06; found C 41.44, N 9.18, H 1.95, S 9.87. Crystals of [Cu_6(4,6-CF_3PhpymS)$_6$] (**1**) suitable for X-ray diffraction were obtained by crystallization from MeOH/DMF.

[Ag(4,6-Me_2-5-EtpymS)]: A solution of the ligand (0.100 g, 0.59 mmol) in acetonitrile (50 mL) was electrolysed at 10 mA for 1.5 h and 59.7 mg of silver were dissolved from the anode (E_f = 0.99). A pale-green dusty solid was deposited at the bottom of the cell. This solid was washed with diethyl ether and dried. Yield: 117 mg, 72.2%. IR (KBr): $\tilde{\nu}$ = 2950 (m), 1620 (w), 1585 (s), 1440 (w), 1420 (w), 1380 (w), 1350 (m), 1255 (s), 1150 (m), 1060 (w), 980 (w), 910 (w), 770 (w), 560 (w) cm^{-1}. MS (FAB): *m*/*z* = 382 [Ag_2(4,6-Me_2,5-EtpymS)]$^+$, 275 [Ag(4,6-Me_2,5-EtpymS)]$^+$. $C_8H_{11}AgN_2S$ (274.87): calcd. C 34.92, N 10.18, H 4.00, S 11.64; found C 34.68, N 10.31, H 4.07, S 11.41. The complex is scarcely soluble in the usual solvents and NMR spectra were not recorded. Crystals of [Ag_6(4,6-Me_2,5-EtpymS)$_6$]·2MeOH·3H_2O (**2**) suitable for X-ray diffraction were obtained by crystallization from MeOH/DMSO.

[Ag(4-CF_3pymS)]: Electrolysis of a solution of the thione (100 mg, 0.55 mmol) in acetonitrile (50 mL) at 10 mA for 1.5 h caused the oxidation of 59.1 mg of silver from the anode (E_f = 0.98). A pale-yellow dusty solid was obtained. Yield: 147 mg, 93.2%. IR (KBr): $\tilde{\nu}$ = 1550 (s), 1420 (m), 1350 (s), 1330 (s), 1210 (m), 1195 (s), 1175 (m), 1130 (m), 1110 (s), 835 (m) 730 (m), 670 (m) cm^{-1}. $C_5H_2AgF_3N_2S$ (286.87): calcd. C 20.91, N 9.76, H 0.07, S 11.15; found C 20.87, N 9.79, H 0.09, S 10.97. Once again, NMR and FAB-MS spectra were not recorded because of the poor solubility of the complex.

[Ag(4,6-CF_3PhpymS)]: A solution of the ligand (100 mg, 0.39 mmol) in acetonitrile (50 mL) was electrolysed at 10 mA for 1 h and 39.4 mg of silver were dissolved from the anode (E_f = 0.98). A solid was not obtained in the cell and the solvent was removed by slow evaporation at room temperature. A grey dusty solid was obtained, washed with diethyl ether and dried. Yield: 82 mg, 57.9%. IR (KBr): $\tilde{\nu}$ = 3040 (m), 1590–1570 (s, br), 1430 (s), 1390 (s), 1360 (s), 1300 (m), 1280 (s), 1240 (s), 1180 (s), 1130 (s), 1065 (m), 1020 (m), 1005 (s), 910 (w), 835 (m), 810 (s), 790 (m), 760 (s), 710 (s), 690 (s), 650 (w), 640 (m), 620 (m), 590 (w) cm^{-1}. ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 8.34 (s, 1 H, 5-H), 7.39–8.09 (Ph-H) ppm. ^{13}C NMR (300 MHz [D_6]DMSO): δ = 127.5–131.9 (Ph-C) ppm. MS (FAB): *m*/*z* (%) = 1561 [Ag_5(4,6-CF_3PhpymS)$_4$]$^+$, 1196 [Ag_4(4,6-CF_3PhpymS)$_3$]$^+$, 834 [Ag_3(4,6-CF_3PhpymS)$_2$]$^+$, 471 [Ag_2(4,6-CF_3PhpymS)]$^+$, 363 [Ag(4,6-CF_3PhpymS)]$^+$, 255 [4,6-CF_3PhpymS]$^+$. $C_{11}H_6AgF_3N_2S$ (362.87): calcd. C 36.39, N 7.71, H 1.57, S 8.83; found C 36.32, N 7.79, H 1.62, S 8.24.

Synthesis of Copper and Silver Heteroleptic Complexes: For the synthesis of copper and silver heteroleptic complexes, a suspension of the homoleptic compound and the phosphane was heated under reflux in acetonitrile for several hours and the hot solutions/suspensions were filtered. When a solid was obtained it was washed with diethyl ether and dried. In cases in which a solid was not obtained directly, the solvent was removed by slow evaporation at room temperature.

[Cu(4,6-Me_2,5-EtpymS)(dppm)]: The initial yellow suspension of the homoleptic complex (150 mg, 0.62 mmol) in acetonitrile became a solution when dppm (370 mg, 0.96 mmol) was added. After filtration, the solvent was partially removed by slow evaporation at room temperature and a pale-yellow dusty solid was obtained. The solid was filtered off, washed with diethyl ether and dried. Yield: 369 mg, 92%. IR (KBr): $\tilde{\nu}$ = 3050 (m), 2950 (m), 1520 (s, br), 1470 (m), 1420 (m), 1380 (m), 1350 (s), 1260 (s), 1150 (s), 1090 (s), 1060 (m), 1020 (w), 990 (m), 910 (m), 770 (s), 750 (s), 690 (s), 510 (m) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.80 (t, $^3J_{9H,8H}$ = 7.33 Hz, 3 H, 9-H), 2.12 (s, 6 H, 7-H/7′-H), 2.45 (q, 2 H, 8-H), 3.31 (s, CH_2), 7.31–7.77 (m, Ph-H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 162.5 (C-4, C-6), 127.6–132.6 (broad and complex, Ph-C), 25.6 (CH_2), 20.8, 20.7 (C-7/C-7′), 19.9 (C-8), 12.8 (C-9) ppm. ^{31}P NMR (300 MHz, $CDCl_3$): δ = 44.9 (s) ppm. MS

(FAB): *m/z* = 677 [Cu_2(4,6-Me_2,5-EtpymS)(dppm)]$^+$, 614 [Cu(4,6-Me_2,5-EtpymS)(dppm)]$^+$, 447 [Cu(dppm)]$^+$, 167 [4,6-Me_2,5-EtpymS]$^+$. $C_{33}H_{33}CuN_2P_2S$ (613.54): calcd. C 64.54, N 4.56, H 5.37, S 5.21; found C 64.62, N 4.61, H 5.52, S 5.12.

[Cu(4-CF_3pymS)(dppm)]: dppm (350 mg, 0.91 mmol) was added to a suspension of the homoleptic copper complex (0.150 g, 0.61 mmol) in acetonitrile. The mixture was heated under reflux for 2 h and the resulting solution was filtered (a solid was not obtained). The solvent was partially removed by slow evaporation at room temperature and a yellow solid was obtained. Yield: 108 mg, 28%. IR (KBr): $\tilde{\nu}$ = 3040 (m), 1575 (w), 1550 (s), 1470 (m), 1425 (s), 1400 (m), 1350 (w), 1320 (s), 1180 (s), 1130 (s), 1100 (s), 1090 (m), 1060 (m), 1020 (m), 990 (w), 960 (m), 900 (w), 820 (m), 800 (m), 760 (s), 735 (s), 725 (s), 690 (s), 660 (s), 500 (s), 480 (m), 460 (m) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.90 (br. s, 2 H, CH_2), 6.70 (d, $^3J_{6H,5H}$ = 4.89 Hz, 1 H, 6-H), 6.90–7.50 (Ph-H), 8.10 (d, 1 H, 5-H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 181.2 (C-2), 157.2 (C-6), 154.1 (q, C-4), 134.4–118.2 (Ph-C), 128.6 (q, CF_3), 108.0 (C-5), 25.6 (CH_2) ppm. ^{31}P NMR (300 MHz, $CDCl_3$): δ = 23.0 (s) ppm. MS (FAB): *m/z* = 688 [Cu_2(4-CF_3pymS)(dppm)]$^+$, 447 [Cu(dppm)]$^+$. $C_{30}H_{24}CuF_3N_2P_2S$ (626.50): calcd. C 57.46, N 4.47, H 3.86, S 5.11; found C 57.54, N 4.27, H 4.02, S 5.75. Yellow crystals of [Cu_2(4-CF_3pymS)$_2$(dppm)$_2$]·2CH_3CN (**3**) suitable for X-ray diffraction studies were obtained from the mother liquor.

[Cu(4,6-CF_3PhpymS)(dppm)]: dppm (0.184 g, 0.47 mmol) was added to a green solution of the initial copper complex in acetonitrile (102 mg, 0.32 mmol). The colour immediately changed to yellow. The mixture was heated under reflux for 2 h and the hot solution was filtered. A solid was not obtained. Slow evaporation of the solvent at room temperature gave a dusty dark-yellow solid. Yield: 113 mg, 39%. IR (KBr): $\tilde{\nu}$ = 3040 (m), 1680 (m), 1575 (m, br), 1520 (m), 1475 (m), 1430 (s), 1380 (s), 1305 (w), 1285 (w), 1240 (s), 1180 (s), 1140 (w), 1115 (w), 1095 (w), 1020 (m), 995 (m), 840 (m), 825 (w), 775 (s), 735 (s), 715 (w), 690 (s), 535 (w), 510 (m), 500 (s), 470 (m) cm^{-1}. ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 4.02 (br. s, 2 H, CH_2), 6.97–7.79 (Ar-H) ppm. ^{13}C NMR (300 MHz, [D_6]DMSO): δ = 30.7 (CH_2), 128.0–135.2 (Ph-C) ppm. ^{31}P NMR (300 MHz, [D_6]DMSO): δ = 41.2 (s) ppm. MS (FAB): *m/z* = 767 [Cu_2(4,6-CF_3PhpymS)(dppm)]$^+$, 702 [Cu(4,6-CF_3PhpymS)(dppm)]$^+$, 447 [Cu(dppm)]$^+$. $C_{36}H_{28}CuF_3N_2P_2S$ (702.54): calcd. C 61.49, N 3.98, H 3.98, S 4.55; found C 61.42, N 3.98, H 3.81, S 4.67.

[Ag(4,6-Me_2,5-EtpymS)(dppm)]: The initial suspension of the single silver complex (112 mg, 0.41 mmol) in acetonitrile became a solution when dppm (250 mg, 0.65 mmol) was added and the mixture was heated under reflux for 2 h. The hot solution was filtered and a solid was not obtained. Slow evaporation of the solvent at room temperature led to the formation of a dusty pale-yellow solid. Yield: 265 mg, 49%. IR (KBr): $\tilde{\nu}$ = 3040 (m), 2950 (m), 1535 (m), 1470 (w), 1430 (s), 1380 (w), 1350 (m), 1255 (s), 1175 (m), 1145 (w), 1115 (w), 1095 (w), 1020 (w), 995 (w), 810 (w), 775 (m), 735 (s), 715 (w), 690 (s), 535 (m), 510 (m), 500 (m), 470 (w) cm^{-1}. ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 1.05 (t, $^3J_{9H,8H}$ = 1.94 Hz, 3 H, 9-H), 2.00 (s, 6 H, 7-H/7′-H), 2.45 (q, 2 H, 8-H), 3.99 (br. s, 2 H, CH_2), 7.00–7.79 (Ph-H) ppm. ^{13}C NMR (300 MHz, [D_6]DMSO): δ = 13.0 (C-9), 20.1 and 20.9 (C-7/C-7′), 28.8 (CH_2), 162.8 (C-4, C-6) ppm. ^{31}P NMR (300 MHz, [D_6]DMSO): δ = 41.2 (s) ppm. MS (FAB): *m/z* = 1319 [Ag_2(4,6-Me_2,5-EtpymS)$_2$(dppm)$_2$]$^+$, 933 [Ag_2(4,6-Me_2,5-EtpymS)$_2$(dppm)]$^+$, 767 [Ag_2(4,6-Me_2,5-EtpymS)(dppm)]$^+$, 659 [Ag(4,6-Me_2,5-EtpymS)(dppm)]$^+$, 493 [Ag(dppm)]$^+$, 275 [Ag(4,6-Me_2,5-EtpymS)]$^+$. $C_{33}H_{33}AgN_2P_2S$ (659.51): calcd. C 60.10, N 4.25, H 5.04, S 4.86; found C 61.79, N 4.37, H 5.66, S 5.01.

[Ag(4-CF_3pymS)(dppm)]: The initial suspension of the single complex (149 mg, 0.52 mmol) in acetonitrile became a yellow solution when dppm (200 mg, 0.52 mmol) was added. The mixture was heated under reflux for 2 h and then filtered. A solid was not obtained. Slow evaporation of the solvent at room temperature gave a dusty yellow solid. Yield: 289 mg, 83%. IR (KBr): $\tilde{\nu}$ = 2990 (m), 1545 (w), 1520 (s), 1440 (m), 1395 (s), 1380 (s), 1285 (s), 1150 (s), 1110 (s), 1075 (s), 990 (w), 960 (w), 935 (w), 790 (s), 735 (s), 700 (s), 680 (w), 655 (s), 630 (m), 500 (w), 475 (s), 435 (m), 400 (w) cm^{-1}. ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 3.65 (br. s, 2 H, CH_2), 7.01–7.28 (Ph-H), 7.44 (d, $^3J_{6H,5H}$ = 4.85 Hz, 1 H, 6-H), 7.79 (d, 1 H, 5-H) ppm. ^{13}C NMR (300 MHz, [D_6]DMSO): δ = 24.8 (CH_2), 108.9 (C-5), 119.1–132.7 (Ph-C), 157.3 (C-4), 158.3 (C-6) ppm. ^{31}P NMR (300 MHz, [D_6]DMSO): δ = 41.1 (s) ppm. MS (FAB): *m/z* = 779 [Ag_2(4-CF_3pymS)(dppm)]$^+$, 491 [Ag(dppm)]$^+$. $C_{30}H_{24}AgF_3N_2P_2S$ (670.80): calcd. C 53.67, N 4.17, H 3.60, S 4.78; found C 53.55, N 4.36, H 3.65, S 4.73.

[Ag(4,6-CF_3PhpymS)(dppm)]: dppm (0.106 g, 0.27 mmol) was added to the initial suspension of the homoleptic complex (0.100 g, 0.27 mmol) in acetonitrile. The mixture was heated under reflux for 2 h and the hot solution was filtered. A solid was not obtained. Slow evaporation of the solvent at room temperature gave a dusty grey solid. Yield: 179 mg, 89%. IR (KBr): $\tilde{\nu}$ = 3060 (m), 1685 (m), 1585 (m), 1555 (s), 1480 (m), 1430 (s), 1370 (s), 1310 (w), 1290 (w), 1255 (s), 1190 (s), 1140 (s), 1100 (m), 1030 (w), 1000 (m), 840 (w), 820 (w), 770 (m), 740 (s), 720 (m), 695 (s), 645 (w), 510 (m), 475 (w) cm^{-1}. ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 3.77 (br. s, 2 H, CH_2), 7.03–7.95 (Ar-H) ppm. ^{13}C NMR (300 MHz, [D_6]DMSO): δ = 126.1–133.0 (Ar-C) ppm. ^{31}P NMR (300 MHz, [D_6]DMSO): δ = 43.7 (s) ppm. MS (FAB): *m/z* = 855 [Ag_2(4,6-CF_3PhpymS)-(dppm)]$^+$, 491 [Ag(dppm)]$^+$. $C_{36}H_{28}AgF_3N_2P_2S$ (747.47): calcd. C 57.85, N 3.78, H 3.75, S 4.29; found C 57.42, N 3.49, H 3.87, S 4.13.

[Cu(4-CF_3pymS)(PPh_3)$_2$]: The homoleptic complex precursor (0.150 mg, 0.61 mmol) was suspended in acetonitrile and heated. Triphenylphosphane was added (0.356 mg, 1.36 mmol) and the mixture was stirred and heated under reflux for 3 h. The initial orange suspension became a yellow solution and this was filtered. A solid was not obtained. Slow partial evaporation at room temperature gave a crystalline orange solid Yield: 314 mg, 67.2%. IR (KBr): $\tilde{\nu}$ = 3440 (w), 3070 (m), 3060 (m), 1580 (m), 1560 (s), 1480 (s), 1435 (s), 1415 (m), 1405 (w), 1325 (s), 1310 (m), 1190 (s), 1160 (s), 1145 (s), 1110 (s), 1090 (s), 1070 (m), 1025 (m), 985 (m), 977 (s), 920 (w), 835 (m), 810 (s), 745 (s), 730 (m), 695 (s), 673 (m), 525 (m), 515 (s), 505 (s), 475 (w), 440 (w), 425 (w) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88 (d, $^3J_{6H,5H}$ = 4.93 Hz, 1 H, 6-H), 7.54–7.81 (Ph-H), 9.08 (d, 1 H, 5-H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 134.0–138.1 (Ph-C), 168.0 (C-6) ppm. ^{31}P NMR (300 MHz, $CDCl_3$): δ = 26.4 (s) ppm. MS (FAB): *m/z* = 764 [Cu(4-CF_3pymS)(PPh_3)$_2$]$^+$, 587 [Cu(PPh_3)$_2$]$^+$, 505 [Cu(4-CF_3pymS)(PPh_3)]$^+$, 325 [Cu(PPh_3)]$^+$, 242 [Cu(4-CF_3pymS)]$^+$. $C_{41}H_{32}CuF_3N_2P_2S$ (763.23): calcd. C 64.18, N 3.65, H 4.17, S 4.17; found C 64.31, N 3.67, H 4.21, S 4.00. Crystals of [Cu(4-CF_3pymS)(PPh_3)$_2$] (**4**) suitable for X-ray diffraction were obtained by slow concentration of the mother liquor.

Synthesis of Triphenylphosphane Gold(I) Complexes

[Au(4,6-Me_2,5-EtpymS)(PPh_3)]: The thione (150 mg, 0.89 mmol) was dissolved in ethanol and treated with triethylamine (1.1 equiv., 99 mg, 0.97 mmol, 91.0 μL). The mixture was stirred at room temperature for 30 min and the initial dark-yellow solution became pale yellow. The solution was heated and [Au(PPh_3)Cl] (430 mg, 0.93 mmol) was added. This mixture was heated under reflux for

3 h and the hot solution was filtered (a solid was not obtained). Slow evaporation of the solvent at room temperature gave a crystalline solid. Yield: 228 mg, 41%. IR (KBr): $\tilde{\nu}$ = 3040 (m), 2950 (m), 1520 (s), 1465 (m), 1420 (s), 1380 (m), 1350 (s), 1260 (s), 1170 (m), 1140 (m), 1095 (s), 1065 (w), 1020 (w), 990 (m), 975 (m), 905 (m), 840 (m), 770 (w), 750 (m), 740 (s), 705 (s), 690 (s), 550 (w), 535 (s), 500 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.06 (t, $^3J_{9H,8H}$ = 7.53 Hz, 3 H, 9-H), 2.3 (s, 6 H, 7-H/7′-H), 2.5 (q, 2 H, 8-H), 7.42–7.60 (Ph-H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 13.2 (C-9), 21.0 (C-7/C-7′), 23.9 (C-8), 114.6 (C-5), 163.7 and 165.8 (C-4 and C-6) ppm. ^{31}P NMR (300 MHz, $CDCl_3$): δ = 38.16 (s) ppm. MS (FAB): *m*/*z* = 626 [Au(4,6-Me_2,5-EtpymS)(PPh_3)]$^+$, 459 [Au(PPh_3)]$^+$, 365 [Au(4,6-Me_2,5-EtpymS)]$^+$. $C_{26}H_{26}AuN_2PS$ (625.96): calcd. C 49.85, N 4.47, H 4.98, S 4.18; found C 49.77, N 4.36, H 4.18, S 5.12.

[Au(4-CF_3pymS)(PPh_3)]: An ethanolic solution of the thione (59 mg, 0.32 mmol) was treated with Et_3N (1.1 equiv., 35 mg, 0.35 mmol, 54.3 μL) and stirred at room temperature for 30 min. The colour changed from orange to pale yellow. This solution was heated and [Au(PPh_3)Cl] (150 mg, 0.32 mmol) was added. The mixture was then heated under reflux for 3 h and the solution became colourless. The hot solution was filtered (a solid was not obtained). Slow evaporation of the solvent at room temperature gave a colourless solid. Yield: 118 mg, 56%. IR (KBr): $\tilde{\nu}$ = 3100 (m), 1550 (s), 1470 (s), 1425 (s), 1410 (s), 1390 (w), 1320 (s), 1190 (s), 1175 (w), 1160 (s), 1140 (s), 1115 (s), 1095 (s), 1075 (m), 1020 (m), 990 (m), 970 (m), 920 (w), 830 (s), 750 (s), 740 (m), 705 (m), 690 (s), 660 (m), 535 (s), 495 (s), 470 (w), 445 (w), 430 (w) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.11 (d, $^3J_{5H,6H}$ = 4.90 Hz, 1 H, 6-H), 7.44–7.63 (Ph-H), 8.57 (d, 1 H, 5-H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 110.4 (C-5), 119.0–134.1 (Ph-C), 154 (q, $^3J_{C,F}$ = 106.2 Hz, C-4, 158.2 (C-6), 182.1 (C-2) ppm. ^{31}P NMR (300 MHz, $CDCl_3$): δ = 38.0 (s) ppm. MS (FAB): *m*/*z* = 639 [Au(4-CF_3pymS)(PPh_3)]$^+$, 459 [Au(PPh_3)]$^+$. $C_{23}H_{17}AuF_3N_2PS$ (638.38): calcd. C 43.27, N 4.39, H 2.68, S 5.02; found C 43.44, N 4.10, H 2.76, S 5.26. Crystals of [Au(4-CF_3pymS)(PPh_3)] (**5**) suitable for X-ray diffraction were obtained by slow concentration of the mother liquor.

X-ray Crystallography: Intensity data for compound **1** were collected by using a Smart-CCD-1000 Bruker diffractometer (Cu-K_α radiation, λ = 1.54184 Å) equipped with a graphite monochromator. Intensity data sets for compounds **2**–**5** were collected by using a Smart-CCD-1000 Bruker diffractometer (Mo-K_α radiation, λ = 0.71073 Å) equipped with a graphite monochromator. The ω scan technique was employed to measure the intensities for all crystals. Compounds **1**, **3** and **5** were studied at 293 K, compound **2** was studied at 125 K and compound **4** at 100 K. Decomposition of the crystals was not detected during data collection. The intensities of all data sets were corrected for Lorentzian and polarization effects. Absorption effects in all compounds were corrected using the SADABS program.[69] The crystal structures of all compounds were solved by direct methods. Crystallographic programs used for structure solution and refinement were those in SHELX97.[70] Scattering factors were provided with the SHELX program system. Missing atoms were located in the difference Fourier map and included in subsequent refinement cycles. The structures were refined by full-matrix least-squares refinement on F^2. Hydrogen atoms were placed geometrically and refined by using a riding model with U_{iso} constrained at 1.2 (for non-methyl groups) and 1.5 (for methyl groups) times U_{eq} of the carrier C atom. For all structures, non-hydrogen atoms were anisotropically refined and in the last cycles of refinement a weighting scheme was used with weights calculated by using the formula $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ with $P = (F_o^2 + 2F_c^2)/3$.

In compound **1** the trifluoromethyl group was found to be disordered over two positions with 50:50 occupancy. In compound **2** one of the ethyl groups (C22, C23) was also disordered over two positions with 50:50 occupancy. Disorder was typically handled by introducing split positions for the affected group into the refinement of the respective occupancies. Compound **2** presents one half of the hexamer complex, one molecule of methanol and one molecule and a half of water per asymmetric unit. The hydrogen atoms of the water molecules could not be located from the difference map because most of the residual density is gathered around the three silver atoms.

Table 7. Crystal data and structure refinement for complexes **1**–**5**.

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_{66}H_{36}Cu_6F_{18}N_{12}S_6$	$C_{50}H_{74}Ag_6N_{12}O_5S_6$	$C_{64}H_{54}Cu_2F_6N_6P_4S_2$	$C_{41}H_{32}CuF_3N_2P_2S$	$C_{23}H_{17}AuF_3N_2PS$
Formula mass	1912.67	1762.79	1336.21	767.23	638.38
Crystal system	Trigonal	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$R\bar{3}c$	$P2(1)/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	14.651(14)	12.6774(16)	10.4677(2)	10.288(3)	8.9145(2)
b [Å]	14.651(14)	18.724(2)	12.7841(2)	12.844(3)	11.2632(2)
c [Å]	58.838(11)	14.1396(18)	13.60430(10)	14.382(4)	11.9104(2)
α [°]	90	90	67.0010(10)	89.527(4)	99.5496(7)
β [°]	90	107.691(2)	74.079(10)	72.584(4)	104.4529(4)
γ [°]	120	90	69.7980(10)	79.298(4)	94.9418(6)
Volume [Å^3]	10937(2)	3197.6(7)	1552.12(4)	1779.5(8)	1131.75(4)
Z	6	2	1	2	2
D_c [Mg m^{-3}]	1.742	1.831	1430	1.432	1.873
μ(Mo-K_α) [mm^{-1}]	4.369	2.052	0.919	0.811	6.700
F(000)	5688	1752	684	788	612
Crystal size [mm]	0.24 × 0.20 × 0.20	0.62 × 0.21 × 0.17	0.60 × 0.60 × 0.40	0.46 × 0.34 × 0.24	0.40 × 0.25 × 0.10
T [K]	293(2)	125(2)	293(2)	100	293(2)
Reflections collected	17085	28873	10811	22396	7532
Independent reflections	1768 [*R*(int) = 0.0559]	6537 [*R*(int) = 0.0570]	7417 [*R*(int) = 0.0306]	8487 [*R*(int) = 0.0570]	5361 [*R*(int) = 0.0352]
Goodness of fit on F^2	1.164	1.002	0.980	1.051	1.000
$R1$[a]	0.0431	0.0344	0.0467	0.0597	0.0385
$wR2$[b]	0.1109	0.0786	0.1244	0.1589	0.0866

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

Pertinent details of the data collections and structure refinements are summarized in Table 7. ORTEP3 drawings[71] with the numbering schemes used are shown in Figures 1, 2, 4, 6 and 7.

CCDC-812221 (for **1**), -812222 (for **2**), -812223 (for **3**), -812224 (for **4**) and -812225 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

This work was supported by the Xunta de Galicia (Spain) (grant no. PGIDIT07PXIB203038PR) and by the Ministerio de Ciencia yTecnología (Spain) (grant no. CTQ2006-05298BQU).

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Received: February 16, 2011
Published Online: June 29, 2011

