Heteropolynuclear Complexes with the Ligand Ph_2PCH_2SPh: Theoretical Evidence for Metallophilic Au–M Attractions

Eduardo J. Fernández,[b] José M. López-de-Luzuriaga,[b] Miguel Monge,[b] Miguel A. Rodríguez,*[b] Olga Crespo,[a] M. Concepción Gimeno,[a] Antonio Laguna,*[a] and Peter G. Jones[c]

Abstract: Addition of two equivalents of diphenylthiomethylphosphine (PPh_2CH_2SPh) to the starting materials $[Au(tht)_2]A$ (tht = tetrahydrothiophene), $AgCF_3SO_3$, or $[Cu(CH_3CN)_4]CF_3SO_3$ produces the mononuclear derivatives $[M(PPh_2CH_2SPh)_2]A$ (M = Au, A = CF_3SO_3 (**1a**); M = Au, A = ClO_4 (**1b**); M = Ag, A = CF_3SO_3 (**4**); M = Cu, A = CF_3SO_3 (**5**)) which are able to form the heterodinuclear complexes $[AuM'(PPh_2CH_2SPh)_2](CF_3SO_3)_2$ (M' = Ag (**2**), Cu (**3**)) with a P-Au-P environment. If the starting gold complex is $[Au(C_6F_5)(tht)]$, reaction with the phosphine produces $[Au(C_6F_5)(PPh_2CH_2SPh)]$ (**6**) from which, by reaction with $AgCF_3SO_3$ or $[Cu(CH_3CN)_4]CF_3SO_3$, the "snake"-type linear complexes $[Au_2M(C_6F_5)_2(PPh_2CH_2SPh)_2]CF_3SO_3$ (M = Ag (**7**), Cu (**8**)) are obtained. If the silver starting complex is $AgCF_3CO_2$, reaction in a 1:1 ratio gives the tetranuclear complex $[Au_2Ag_2(C_6F_5)_2(PPh_2CH_2SPh)_2(CF_3CO_2)_2]$ (**9**). When the molar ratio is 1:2 the trinuclear complex $[AuAg_2(C_6F_5)(CF_3CO_2)_2(PPh_2CH_2SPh)]$ (**10**) is obtained. According to ab initio calculations, the presence of only one gold atom is enough to induce metallophilic attractions in the group congeners, and this effect can be modulated depending on the gold ligand.

Keywords: ab initio · copper · gold · heteropolynuclear complexes · silver

Introduction

It is generally accepted that the elements of the third transition and 6p series frequently exhibit strong relativistic effects in their compounds.[1] The maximum effect, located at gold, has been recently summarized with theoretical and experimental evidence.[2] Nevertheless, our theoretical understanding of these interactions is in a highly preliminary state.[3]

For light elements, the effects of relativity are generally small, but there is no clear-cut watershed in the Periodic Table after which relativistic effects become important in determining the properties of elements and their compounds.

Recent studies carried out by Pyykkö[4, 5] and by us[6] developed a comparative approach for all three coinage metals, concluding that "metallophilic attraction is indeed present for all the coinage metals as a correlation effect and that it is strengthened by the relativistic effect for gold".[7–9] This conclusion was supported by the close agreement between theory and experimental data. The comparative studies were based on homometallic dimers, in which the presence of bridging ligands should facilitate intramolecular M^I-M^I contacts.[5, 6]

The question arises whether the presence of only one gold atom is enough to "promote" relativistic effects in the group congeners. Valid conclusions can be only reached if the theoretically predicted geometries show acceptable consistency with the experimental results.

Numerous gold derivatives that present gold–gold interactions have been reported to date; they are mononuclear (through associations), dinuclear or polynuclear species.[10] The great stability of these complexes, often explained by the presence of gold–gold interactions, renders difficult the preparation of heterometallic coinage compounds with appropriate geometry, and this seems to be the reason for the small number of such complexes reported to date. $Au\cdots Cu$ interactions are only found in heteronuclear cluster compounds[11] and no dinuclear derivative is known. $Au\cdots Ag$ interactions are more common but, again, they are found in

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[a] Prof. Dr. A. Laguna, Dr. O. Crespo, Dr. M. C. Gimeno
Departamento de Química Inorgánica-ICMA
Universidad de Zaragoza-CSIC
50009 Zaragoza (Spain)
Fax: (+34) 976-761187
E-mail: alaguna@posta.unizar.es

[b] Dr. M. A. Rodríguez, Dr. E. J. Fernández, Dr. J. M. López-de-Luzuriaga, M. Monge
Departamento de Química, Universidad de La Rioja
Grupo de Síntesis Química de La Rioja, UA-CSIC
Obispo Bustamante 3, 26001 Logroño, (Spain)

[c] Prof. Dr. P. G. Jones
Institut für Anorganische und Analytische Chemie
Technische Universität
Postfach 3329, 38023 Braunschweig (Germany)

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polynuclear species or cluster compounds;[11e, 11g, 12] the only dinuclear derivative with gold and silver atoms has been reported by Schmidbaur et al., $[AuAg(PPh_2py)_2](ClO_4)_2$.[13]

We considered that the use of an asymmetric bidentate ligand such as phenylthiomethylenediphenyphosphine could facilitate the synthesis of either homopolynuclear[6] or heteropolynuclear complexes of Group 11 metals, exploiting the different donor properties of phosphorus and sulfur atoms present in the ligand. Here we present the results of associated investigations.

Results and Discussion

The use of a bidentate ligand such as Ph_2PCH_2SPh allows, as a first step, the selective coordination of the phosphorus atom to a metal centre, leaving the sulfur atom as a potentially coordinative heteroatom. Treatment of $[Au(tht)_2]X$ (tht = tetrahydrothiophene) with two equivalents of Ph_2PCH_2SPh involves the substitution of the tht ligands, giving rise to complexes of stoichiometry $[Au(Ph_2PCH_2SPh)_2]X$ ($X = ClO_4$ (**1a**), $X = CF_3SO_3$ (**1b**)) in which the phosphinothioether ligands are bonded to the gold centre through their phosphorus atoms.

Complexes **1a** and **1b** are air- and moisture-stable white solids. Their elemental analyses, physical and spectroscopic properties are in accordance with the proposed stoichiometry, and solutions of these complexes in acetone display conductivities typical of 1:1 electrolytes[14] ($\Lambda_M = 79.5$ (**1a**), 84.6 (**1b**) $\Omega^{-1}cm^2mol^{-1}$). Besides, their IR spectra show absorptions arising from the $CF_3SO_3^-$ ions at 1278 (vs, br), 1225 (s) and 1148 (s) cm^{-1} (**1a**) or from the ClO_4^- ions at 1104 (vs, br) and 623 (m) cm^{-1} (**1b**).

Abstract in Spanish: *La adición de dos equivalentes de difeniltiometilfosfina (PPh_2CH_2SPh) a los productos de partida $[Au(tht)_2]A$, $AgCF_3SO_3$ ó $[Cu(CH_3CN)_4]CF_3SO_3$ conduce a la formación de los compuestos mononucleares $[M(PPh_2CH_2SPh)_2]A$ ($M = Au$, $A = CF_3SO_3$ (**1a**); $M = Au$, $A = ClO_4$ (**1b**), $M = Ag$, $A = CF_3SO_3$ (**4**); $M = Cu$, $A = CF_3SO_3$ (**5**)) a partir de los cuales pueden obtenerse los complejos heterodinucleares $[AuM'(PPh_2CH_2SPh)_2](CF_3SO_3)_2$ ($M' = Ag$ (**2**), Cu (**3**)) que contienen un entorno P-Au-P. Si el producto de partida de oro es $[Au(C_6F_5)(tht)]$, la reacción con la fosfina da $[Au(C_6F_5)(PPh_2CH_2SPh)]$ (**6**), cuya reacción con $AgCF_3SO_3$ ó $[Cu(CH_3CN)_4]CF_3SO_3$, produce los complejos serpentiformes $[Au_2M(C_6F_5)_2(PPh_2CH_2SPh)_2]CF_3SO_3$ ($M = Ag$ (**7**); Cu (**8**)). Si se emplea $AgCF_3CO_2$ como producto de partida de plata, la reacción entre cantidades equimoleculares de los reactivos forma $[Au_2Ag_2(C_6F_5)_2(PPh_2CH_2SPh)_2(CF_3CO_2)_2]$ (**9**). Por el contrario, si la reacción se efectúa en proporción 1:2 se obtiene el complejo $[AuAg_2(C_6F_5)(CF_3CO_2)_2(PPh_2CH_2SPh)]$ (**10**). De acuerdo con los cálculos ab initio, podemos afirmar que la presencia de un único átomo de oro es suficiente para inducir atracciones metalofílicas en los otros elementos de su mismo grupo y que este efecto se puede modificar en función del ligando que soporta el oro.*

The $^{31}P\{^1H\}$ NMR spectra display singlets at $\delta = 39.7$ (**1a**) and $\delta = 39.9$ (**1b**), which are shifted to low-field compared with the signal of the free ligand ($\Delta\delta = -19$ ppm). Furthermore, in their ^1H NMR spectra a poorly resolved doublet at $\delta = 4.10$ (**1a**) and $\delta = 4.11$ (**1b**) is observed from the methylenic protons of the ligand. Finally, the molecular cations appear in their mass spectra (FAB+) at *m/z* 813 (100%, **1a** and **1b**) with an experimental isotopic distribution in agreement with calculation.

The proposed structure was unequivocally confirmed by X-ray diffraction studies of complex **1a**. The cation is shown in Figure 1, with a selection of bond lengths and angles in Table 1. The geometry around the gold atom is almost perfectly linear with a P-Au-P angle of 178.16(8) Å. The Au–P distances are 2.306(2) and 2.308(2) Å and are of the same order as those found in bis(phosphine) gold compounds such as $[Au(PR_3)_2]^+$ ($PR_3 = PPh_2Me$, 2.316(4) Å; PCy_3, 2.321(2) Å).[15, 16] The sulfur atoms are located at 3.786 and 3.747 Å from the gold atom but this distance is too long to consider any bonding interaction.

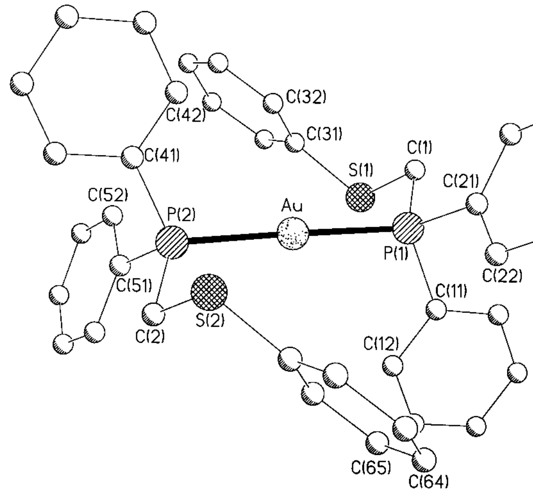


Figure 1. The structure of the cation of complex **1a** in the crystal. The H atoms are omitted for clarity.

The structure displays several weak contacts, such as intramolecular H···Au contacts of 2.91–2.97 Å. Rather stronger secondary interactions are indicated by six C–H···O contacts < 2.5 Å, the shortest of which are

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

Au–P(1)	2.306(2)	Au–P(2)	2.308(2)
S(1)–C(31)	1.771(8)	S–C(1)	1.806(8)
S(2)–C(61)	1.748(7)	S(2)–C(2)	1.807(8)
P(1)-Au-P(2)	178.16(8)	C(21)-P(1)-C(1)	107.9(1)
C(31)-P(1)-C(1)	102.9(3)	C(21)-P(1)-Au	115.6(2)
C(11)-P(1)-Au	112.3(2)	C(1)-P(1)-Au	111.8(2)
C(41)-P(2)-C(2)	103.7(3)	C(51)-P(2)-C(2)	107.3(3)
C(41)-P(2)-Au	113.2(2)	C(51)-P(2)-Au	113.8(2)
C(2)-P(2)-Au	111.4(2)	C(31)-S(1)-C(1)	105.4(4)
C(61)-S(2)-C(2)	104.7(4)	S(1)-C(1)-P(1)	109.2(4)
S(2)-C(2)-P(2)	108.6(4)	C(22)-C(21)-P(1)	118.8(6)
C(26)-C(21)-P(1)	122.3(6)	C(36)-C(31)-S(1)	115.6(6)
C(32)-C(31)-S(1)	124.3(5)		

O1 ⋯ H32 (0.5 − *x*,*y*, − 0.5+*z*) and H2b ⋯ O2, 2.40 and 2.41 Å, respectively. All these contacts are of acceptable linearity (≥144°) to be classed as hydrogen bonds.

In order to investigate the coordinative ability of the free sulfur atoms present in complex **1b**, we have tested its reactivity towards $AgCF_3SO_3$ and $[Cu(CH_3CN)_4]CF_3SO_3$ and obtained the heterobinuclear complexes $[AuM(Ph_2PCH_2SPh)_2](CF_3SO_3)_2$ (M = Ag (**2**), M = Cu (**3**)) in which the new metallic fragments are expected to be coordinated through the previously free sulfur atoms.

Complexes **2** and **3** are air- and moisture-stable white solids at room temperature, soluble in chlorinated solvents and acetone and insoluble in diethyl ether and hexane. Their analytical and spectroscopic data are in accordance with the proposed stoichiometry. In the $^{31}P\{^1H\}$ NMR spectra a singlet at $\delta = 43.1$ (**2**) or $\delta = 42.3$ (**3**) is observed. This is in agreement with the expected coordination, in which both phosphorus atoms remain coordinated at gold centres, consistent with the close similarity of these values to those of the starting material, and of the lack of P−Ag^{107},Ag^{109} coupling in **2**. Their mass spectra (FAB +) display the peak corresponding to $[M+CF_3SO_3]^+$ at *m*/*z* 1070 (10 %, **2**) and 1025 (3 %, **3**).

The structure of complex **2** in the solid state has been confirmed by an X-ray diffraction study and the cation is shown in Figure 2, with a selection of bond lengths and angles in Table 2. Complex **2** crystallizes together with one molecule of diethyl ether. The lattice is composed of dinuclear mixed metal dications associated with two trifluromethanesulfonate anions, one of which is coordinated to the silver centre through one of the oxygen atoms. The gold atom is bonded to both phosphorus atoms, whereas the silver centre is bonded to the two sulfur atoms of the bidentate ligand. The gold atom is linearly coordinated, with a P-Au-P angle of 174.45(4)°, and the silver centre has a geometry only slightly distorted from linearity, S-Ag-S 168.24(4)°, in spite of the additional bonds to the $CF_3SO_3^-$ ion (Ag−O2 2.596(4) Å) and the diethyl ether molecule (Ag−O7 2.515(5) Å). In related complexes such as the heterodinuclear compound $[AuAg(PPh_2py)_2](ClO_4)_2$,[13] where the silver centre is also bonded to one of the oxygen atoms of the perchlorate, the angle at silver is far more distorted at 142.3(3)°. The Au ⋯ Ag distance in **2** is 2.9314(5) Å and can be considered as a bonding interaction, similar to those found in other complexes such as $[Ag(\mu\text{-}dppm)_2\{Au(mes)\}_2]ClO_4 \cdot 3\,CH_2Cl_2$ (2.944(2) and 2.946(2) Å; dppm = bis(diphenylphosphino)methane; mes = mesityl)[12k] or $[(AuPPh_3)_2\{\mu\text{-}C(PPh_3)\}(C_5H_4N)\{\mu\text{-}Ag(O_2NO)(OClO_3)\}]$ (2.926(1) and 3.006(1) Å)[12f] or slightly longer than those in $[AuAg(PPh_2py)_2](ClO_4)_2$ (2.820(1) Å)[13]. The Au−P bond lengths are 2.3044(11) and 2.3103(11) Å and differ more than those in $[AuAg(PPh_2py)_2](ClO_4)_2$ (2.296(2) and 2.297(2) Å)[13]; they are longer than those in $[Au_2(PPh_2CH_2SPh)_2](ClO_4)_2$ (2.2721(11) Å)[6]. The Ag−S distances of 2.4738(12) and 2.4860(12) Å are also somewhat unequal, and longer than those found in the complex $[Ag_2(PPh_2CH_2SPh)_2](ClO_4)_2$ (2.4406(12) and 2.4519(13) Å)[6].

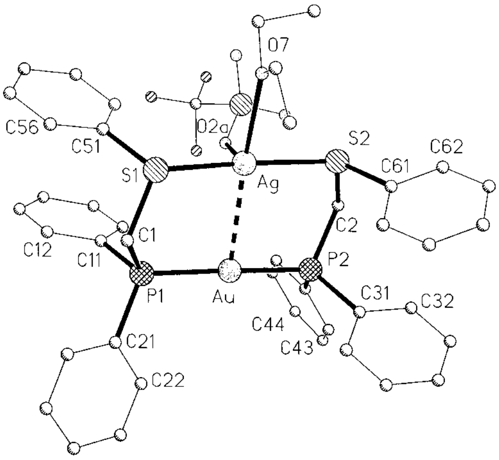


Figure 2. The structure of the cation of complex **2** in the crystal. H atoms are omitted for clarity.

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

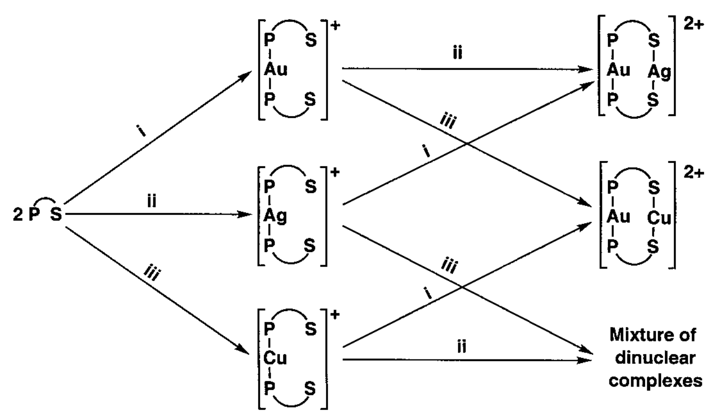
Au−P2	2.3044(11)	Au−P1	2.3103(11)
Au−Ag	2.9314(5)	Ag−S1	2.4738(12)
Ag−S2	2.4860(12)	Ag−O7	2.515(5)
Ag−O2#1	2.596(4)	P1−C1	1.817(5)
P2−C2	1.824(5)	S1−C51	1.789(5)
S1−C1	1.809(5)	S2−C61	1.783(5)
S2−C2	1.810(5)		
P2-Au-P1	174.45(4)	P2-Au-Ag	92.48(3)
P1-Au-Ag	90.85(3)	S1-Ag-S2	168.24(4)
S1-Ag-O7	85.97(14)	S2-Ag-O7	90.06(14)
S1-Ag-O2#1	110.69(10)	S2-Ag-O2#1	81.07(10)
O7-Ag-O2#1	110.9(2)	S1-Ag-Au	90.91(3)
S2-Ag-Au	91.06(3)	O7-Ag-Au	169.66(14)
O2#1-Ag-Au	79.38(13)	C11-P1-Au	111.6(2)
C21-P1-Au	113.8(2)	C1-P1-Au	113.3(2)
C31-P2-Au	114.5(2)	C41-P2-Au	110.9(2)
C2-P2-Au	114.0(2)	C51-S1-Ag	112.1(2)
C1-S1-Ag	112.3(2)	C61-S2-Ag	115.4(2)
C2-S2-Ag	108.0(2)	S1-C1-P1	114.9(2)
S2-C2-P2	116.2(2)	C70-O7-Ag	124.1(5)
C72-O7-Ag	118.7(5)		

[a] Symmetry transformations used to generate equivalent atoms: #1 *x*, *y* − 1,*z*.

Using the same synthetic route as employed to obtain complexes **2** and **3**, we have prepared, in a one-step reaction, the corresponding $[Ag(Ph_2PCH_2SPh)_2]CF_3SO_3$ (**4**) and $[Cu(Ph_2PCH_2SPh)_2]CF_3SO_3$ (**5**) (see Scheme 1) in order to test the coordination capabilities of the free thioether functional groups when the metal centre is other than gold.

The new compounds **4** and **5** are obtained as stable white solids with analytical and physical data in accordance with the proposed stoichiometry; they are uni-univalent electrolytes in acetone ($\Lambda_M = 85.5$ (**4**), 78.8 (**5**) $\Omega^{-1}cm^2mol^{-1}$). This fact rules out the formation of species of the type $[M_2(P-S)_2]^{2+}$ for which uni-divalent electrolytes are observed.[6]

Their IR spectra show, among others, the CF_3SO_3 absorptions at 1278 (vs, br), 1238 (s) and 1156 (s) cm^{-1} for **4** and at 1293 (vs, br), 1217 (s) and 1155 (s) cm^{-1} for **5**. The $^{31}P\{^1H\}$ NMR spectrum of complex **4** at 193 K shows two doublets centred at $\delta = 1.92$ arising from the coupling with ^{107}Ag and ^{109}Ag nuclei ($^2J^{109}Ag-P = 567.0$ Hz; $^2J^{107}Ag-P = 497$ Hz). This pattern confirms that the two phosphinothioether ligands are bonded through their phosphorus atoms to the silver centre. In the case of complex **5** a singlet at $\delta = -9.3$ is



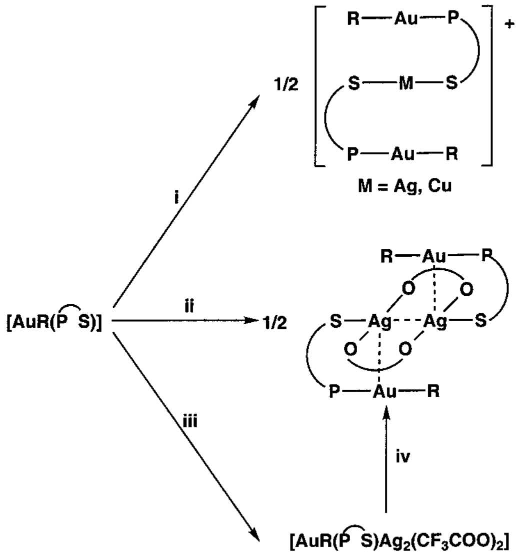
Scheme 1. Reaction scheme for the synthesis of the heterodinuclear complexes. i) $[Au(tht)_2]^+$; ii) $AgCF_3SO_3$; iii) $[Cu(CH_3CN)_4]^+$. $P\frown S = Ph_2PCH_2SPh_2$.

observed. The mass spectra (FAB +) of both complexes show the molecular cation at m/z 725 (100%, **4**) and 679 (98%, **5**).

As mentioned above, complexes **4** and **5** could be used to test the same reactions towards starting materials involving Group 11 metals. In this way two important features can be observed. First, in the reaction of complexes **4** or **5** with $[Au(tht)_2]CF_3SO_3$ in a 1:1 molar ratio, both phosphinothioether ligands change their disposition; phosphorus atoms coordinate at the gold centre, while sulfur atoms of the thioether functions are coordinated at silver or copper atoms. Therefore, the previously described complexes **2** or **3** are isolated, in accordance with ab initio calculations that the corresponding head-to-head phosphorus–gold bonded dinuclear Au–M (M = Ag or Cu) complex has a lower energy than the hypothetical head-to-tail or head-to-head sulfur–silver or sulfur–copper bonded systems. In contrast, reaction of **4** with one equivalent of $[Cu(CH_3CN)_4]CF_3SO_3$ or reaction of **5** with $AgCF_3SO_3$ in a 1:1 molar ratio produces a mixture of homodinuclear derivatives $[M_2(Ph_2PCH_2SPh)_2](CF_3SO_3)_2$ (M = Ag or Cu), as can be observed in solution by $^{31}P\{^1H\}$ NMR spectra at 223 K. Under mass spectral conditions the corresponding $[AgCu(P{-}S)_2{+}CF_3SO_3]^+$ peak at m/z 937 (7%) is observed. This fact, together with the presence of only one broad signal at $\delta = 1.1$ in the $^{31}P\{^1H\}$ NMR spectrum at room temperature, suggests the presence of a rapid ligand exchange equilibrium in solution, thus preventing the synthesis of the expected Ag–Cu complex. These observations are also in agreement with ab initio calculations in which the three possible head-to-head phosphorus–silver bonded, head-to-tail and head-to-head phosphorus–copper bonded isomers are almost isoenergetic (see below).

The complexes thus far described are all coordination compounds in which the phosphinothioether ligand is the only link between the metallic centres. In another perspective we tried to synthesize heteropolynuclear compounds using the organometallic starting material $[Au(C_6F_5)(Ph_2PCH_2SPh)]$ (**6**) prepared by reaction of $[Au(C_6F_5)(tht)]$ and Ph_2PCH_2SPh in a molar ratio 1:1. Spectroscopic and analytical data for **6** are in accordance with this formulation (see Experimental Section).

As in the previous mononuclear compounds **1a** and **1b**, the presence of a free sulfur atom allows the synthesis of higher nuclearity derivatives. Thus, reaction of compound **6** with $AgCF_3SO_3$ or $[Cu(CH_3CN)_4]CF_3SO_3$ in a molar ratio 2:1 produces the "snake"-type complexes $[Au_2M(C_6F_5)_2(Ph_2PCH_2SPh)_2]CF_3SO_3$ (M = Ag (**7**); M = Cu (**8**); see Scheme 2) in which the new metallic fragments are expected to be bonded to the free sulfur atoms of the thioether functions. Complexes **7** and **8** are air- and moisture-stable white solids, and solutions of these compounds in acetone show conductivity values for a 1:1 electrolyte ($\Lambda_M = 87.0$ (**7**), 62.0 (**8**) $\Omega^{-1}cm^2mol^{-1}$).



Scheme 2. $P\frown S = Ph_2PCH_2SPh_2$. i) $1/2\,AgCF_3SO_3$ (M = Ag), $1/2[Cu(CH_3CN)_4]^+$ (M = Cu); ii) $AgCF_3CO_2$; iii) $2\,AgCF_3CO_2$; iv) $[AuR(PPh_2CH_2SPh)]$. $R = C_6F_5$.

The IR spectra of both complexes show absorptions arising from the C_6F_5 group bonded to a gold(I) center at 1500, 957 and 794 cm^{-1} (**7**) and 1505, 955 and 792 cm^{-1} (**8**). The $^{31}P\{^1H\}$ NMR spectra display broadened singlets because of coupling with the fluorine atoms, shifted to low field from the starting material **6** at $\delta = 39.7$ (**7**) and $\delta = 37.4$ (**8**). In the ^{19}F NMR spectrum we observe the pattern for the C_6F_5 groups bonded to gold(I) with different chemical shifts from those of the starting material. Besides, a new singlet for the $CF_3SO_3^-$ ion is observed for the new derivatives with relative intensities as expected for the proposed stoichiometry. Their mass spectra display the peak corresponding to $[M]^+$ at m/z 1453 (12%, **7**) or $[M - CuC_6F_5]^+$ at m/z 1177(15%, **8**).

Changes in the counterion of the silver salt significantly affect the final geometry of the product. Thus, the reaction of $AgCF_3CO_2$, instead of the triflate salt, in a 1:1 or 2:1 molar ratio with complex **6** leads to the synthesis of the tetranuclear complex $[Au_2Ag_2(C_6F_5)_2(CF_3CO_2)_2(Ph_2PCH_2SPh)_2]$ (**9**). Compound **9** is obtained as a stable white solid with analytical and spectroscopic data in accordance with the proposed stoichiometry. The IR spectrum shows a very strong band at 1651 cm^{-1}, corresponding to the $\nu(C{=}O)$ stretching vibration of the CF_3CO_2 ligand. A solution of complex **9** in acetone is non-conducting (10.7 $\Omega^{-1}cm^2mol^{-1}$), showing that the CF_3COO groups are coordinated even in solution.

In the $^{31}P\{^1H\}$ NMR spectrum a broadened singlet at $\delta = 37.6$ is observed and in the ^{19}F NMR spectrum three signals corresponding to the C_6F_5 groups bonded to gold(I) and one signal due to the CF_3CO_2 ligand are observed. The mass spectrum shows the ion peak $[M - CF_3CO_2]^+$ at m/z 1672 (5%, **9**) with an experimental isotopic distribution in agreement with theory.

The crystal structure of complex **9** has been established by an X-ray diffraction study; the molecular structure is shown in Figure 3, with selected bond lengths and angles in Table 3. It is a tetranuclear complex with crystallographic inversion symmetry, and contains two gold and two silver atoms forming a zig-zag chain. The gold and silver atoms are bridged by the ligand PPh_2CH_2SPh. Again the gold centre is coordinated to phosphorus and the silver centre to sulfur; the two silver atoms are bridged by the trifluoroacetate ligands. There are short gold–silver or silver–silver bonding interactions of 3.0335(8) Å (Au–Ag) or 2.8155(9) Å (Ag–Ag; operator $-x+1, -y+1, -z+1$); the former is slightly longer than in complex **2** but of the same order as other Ag ··· Au interactions, whereas the Ag ··· Ag contact is shorter than that in the dinuclear complex $[Ag_2(PPh_2CH_2SPh)_2](ClO_4)_2$ (2.9732(9) Å)[6] and even shorter than the values found in metallic silver (2.89 Å) or in many silver oxides.[17] In fact the distance is close to those found in complexes where a silver–silver bond has been postulated; [12h] the bridging by the trifluoroacetate ligand (O ··· O distance only 2.247 Å) may play a role here. The geometry at the gold centre is distorted from linearity (C11-Au-P 170.16(9)°) perhaps as a consequence of the Au ··· Ag interaction. The silver centre has a more irregular geometry; it can be regarded as square pyramidal if we take into account the contacts with the gold and the other silver centres. The Ag–O2 distance (2.230(3) Å) is very short but Ag–S1 is long (2.5715(10) Å) compared with that in complex **2**.

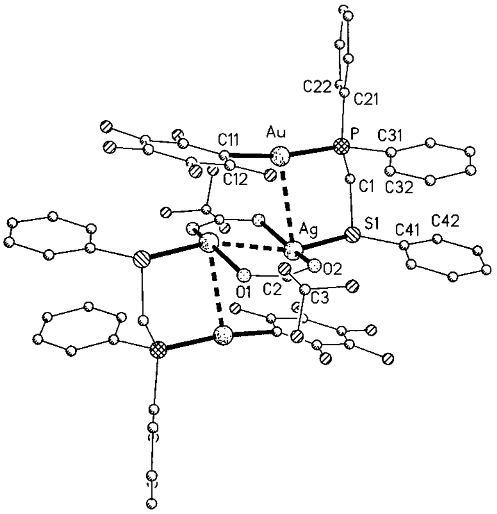


Figure 3. The structure of complex **9** in the crystal. H atoms are omitted for clarity.

Table 3. Selected bond lengths [Å] and angles [°] for complex **9**.[a]

Au–C11	2.056(3)	Au–P	2.2886(10)
Au–Ag	3.0335(8)	Ag–O2	2.230(3)
Ag–O1#1	2.340(3)	Ag–S1	2.5715(10)
Ag–Ag#1	2.8155(9)	P–C31	1.804(4)
P–C21	1.813(3)	P–C1	1.840(3)
S1–C(41)	1.780(3)	S1–C1	1.812(3)
C2–O1	1.233(4)	C2–O2	1.244(4)
C2–C3	1.524(5)	C11-Au-Ag	104.19(9)
C11-Au-P	170.16(9)		
P-Au-Ag	84.46(3)	O2-Ag-O1#1	160.77(9)
O1#1-Ag-S1	77.03(6)	O2-Ag-S1	116.01(7)
O2-Ag-Ag#1	85.04(6)	O1#1-Ag-Ag#1	79.57(6)
S1-Ag-Ag#1	155.39(3)	O2-Ag-Au	88.28(7)
O1#1-Ag-Au	76.02(6)	S1-Ag-Au	95.17(3)
Ag#1-Ag-Au	71.69(2)	C31-P-C21	105.1(2)
C31-P-C1	104.6(2)	C21-P-C1	104.3(2)
C31-P-Au	111.67(12)	C21-P-Au	111.04(11)
C1-P-Au	118.95(11)	C41-S1-C1	105.8(2)
C41-S1-Ag	113.47(11)	C1-S1-Ag	104.0611)
S1-C1-P	115.3(2)	O1-C2-O2	130.2(4)
O1-C2-C3	114.4(3)	O2-C2-C3	115.3(3)

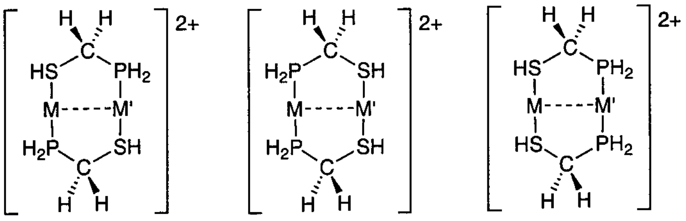
[a] Symmetry transformation used to generate equivalent atoms: #1 $-x+1, -y+1, -z+1$.

Contrastingly, reaction between $[Au(C_6F_5)(Ph_2PCH_2SPh)]$ and $AgCF_3CO_2$ in a 1:2 molar ratio gives the corresponding trinuclear complex $[AuAg_2(C_6F_5)(CF_3CO_2)_2(Ph_2PCH_2SPh)]$ (**10**) in which the thioether group is expected to be coordinated to two silver trifluoroacetate moieties through the silver atoms (see Scheme 2). Complex **10** is an air- and moisture-stable white solid with analytical and spectroscopic data in accordance with the proposed stoichiometry. The IR spectrum shows absorptions arising from CF_3CO_2 at 1633 cm^{-1} and C_6F_5 group at 1503, 851 and 791 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum displays a broadened singlet at $\delta = 38.5$ which could indicate a similar disposition of the phosphinothioether ligand as in the previous compound with a close chemical shift. In the ^{19}F NMR spectrum the same pattern of C_6F_5 and CF_3CO_2 is observed as in complex **9** but in this case the relative intensities are in accordance with two trifluoroacetate ligands for one pentafluorophenyl group. The mass spectrum shows the peak $[M - CF_3CO_2]^+$ at m/z 1001 (10%) for complex **10**. Finally, reaction of complex **10** with one equivalent of $[Au(C_6F_5)(tht)]$ leads to the isolation of complex **9**, showing that complex **10** is the expected trinuclear complex.

Ab Initio Calculations

In order to estimate if the presence of only one gold atom is enough to "promote" metallophillic interactions with the group congeners, we carried out ab initio calculations. The size of the molecule under study necessitates the use of $[MM'(H_2PCH_2SH)_2]^{2+}$ as a model for the ab initio calculations. All calculations were carried out using the Gaussian94 program package.[18] The molecular geometries were initially optimised, without any molecular symmetry constraints, at the Hartree–Fock (HF) self-consistent field level of theory; electron correlation, keeping the core orbitals frozen, was included in further optimisations by using Möller-Plesset perturbation theory[19] with second-order corrections (MP2) employing Schlegel's analytical gradient procedure.[20]

The following basis set combination was employed. For C, S, P and H, the standard split-valence 6-31G(d) basis set,[21, 22] and for Cu, Ag and Au, the pseudorelativistic Hay–Wadt small-core effective core potential,[23] where the minimal basis set has been split to [341/2111/41], [341/3111/31] and [341/3111/21], respectively.[24] This basis set combination will be hereafter referred to as II. The MP2/II level of theory has proved its ability to calculate optimised geometries of transition metal complexes with good accuracy.[6, 24]



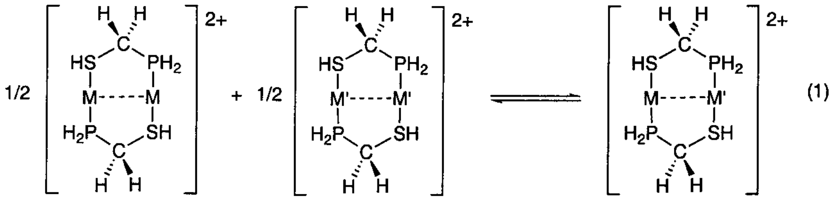
M	M'		A	B	C
Au	Ag	Energy	-1837.943811	-1837.952589	-1837.930605
			(5.5)	(0.0)	(13.8)
		M-M'	3.100	3.060	3.133
		M-P	2.319	2.362, 2.362	- - -
		M-S	2.422	- - -	2.383, 2.383
		M'-P	2.518	- - -	2.518, 2.518
		M'-S	2.575	2.579, 2.579	- - -
Au	Cu	Energy	-1888.248192	-1888.255578	-1888.236189
			(4.6)	(0.0)	(12.2)
		M-M'	2.901	2.873	2.923
		M-P	2.318	2.360, 2.360	- - -
		M-S	2.424	- - -	2.384, 2.384
		M'-P	2.264	- - -	2.275, 2.275
		M'-S	2.291	2.282, 2.282	- - -
Cu	Ag	Energy	-1898.598770	-1898.598935	-1898.596958
			(0.1)	(0.0)	(1.2)
		M-M'	3.084	3.055	3.105
		M-P	2.506	2.278, 2.278	- - -
		M-S	2.555	- - -	2.269, 2.269
		M'-P	2.263	- - -	2.512, 2.512
		M'-S	2.281	2.554, 2.554	- - -

Figure 4. MP2/II//MP2/II absolute [Hartrees] and relative [kcal mol^{-1}, in parentheses] energies and selected optimised structural parameters [Å] calculated for $[MM'(H_2PCH_2SH)_2]^{2+}$.

The absolute and relative energies and the most relevant geometrical parameters of the head-to-tail and the two possible head-to-head $[MM'(H_2PCH_2SH)_2]^{2+}$-optimised structures with the MP2/II wave function are given in Figure 4. Several features are noteworthy. As may be observed, the calculated metal–metal interatomic distances for Au–M′ (M′ = Ag or Cu) complexes are larger for the head-to-head sulfur–gold bonded structures (**C**, 3.133 and 2.923 Å for Cu and Ag, respectively) than for the head-to-tail geometries (**A**, 3.100 and 2.901 Å for Cu and Ag, respectively). Furthermore, in both cases the shortest distances are calculated for the phosphorus–gold bonded systems (**B**, 3.060 and 2.873 Å for Cu and Ag, respectively). Likewise, the calculated Cu–Ag distance for the head-to-tail structure (**A**, 3.084 Å) is intermediate between that of head-to-head phosphorus (**B**, 3.055 Å) and head-to-head sulfur (**C**, 3.105 Å) copper complexes. Despite the differences in the M–M′ distances, the calculated P-C-S bond angles are almost identical in all cases (between 115.0 and 116.0°, not shown in Figure 4). Taking into account the radii for two-coordinate M^I compounds (Cu: 1.13, Ag: 1.33 and Au: 1.25 Å)[25] and the covalent radii for S (1.03 Å) and P (1.10 Å),[26] the shortening in the Cu–Ag or Au–Ag distances when going from **C** to **A** or from **A** to **B** could be explained; since the coordination of the larger P with the shorter Cu or Au is the most suitable grouping in the cyclic system. However, this argument does not explain the shortening in the Au–Cu distances; since Au is larger than Cu.

Looking at the calculated energies (Figure 1), the obtained increase in the M–M′ interatomic distances is accompanied by a large energy stabilization for the Au–Ag (5.5 and 8.3 kcal mol^{-1}, for **B** ⇒ **A** and **A** ⇒ **C**, respectively) and Au–Cu (4.6 and 7.6 kcal mol^{-1}, for **B** ⇒ **A** and **A** ⇒ **C**, respectively) complexes but not for the Cu–Ag complex (0.1 and 1.1 kcal mol^{-1}, for **B** ⇒ **A** and **A** ⇒ **C**, respectively). Moreover, since the interaction energy increases when going from a harder ligand (SH) to a softer one (PH_2) at the gold atom, these results could be explained considering that *the presence of only one gold atom is enough to induce metallophilic attractions in the group congeners and this effect could be modulated depending on the gold ligand*; in a similar way to that already evidenced for the Au–Au attraction at both theoretical[27] and experimental[28] levels.

We were also interested in comparing the relative energies between the head-to-tail structures **A** and the previously calculated head-to-tail M–M complexes (M = Au, Ag, Cu).[6] For this purpose, we use the isodesmic process depicted in Equation 1. According to our calculations, for M = Au and M′ = Ag or Cu, the formation of the M–M′ **A** structure is favoured by 1.2 or 2.1 kcal mol^{-1}, respectively. For M = Cu and M′ = Ag, the formation of the M-M′ **A** complex is only favoured by 0.2 kcal mol^{-1}. In addition, since the Cu–Ag **B**



A

M = Au, M' = Ag: ΔH = -1.2 kcal mol^{-1}
M = Au, M' = Cu: ΔH = -2.1 kcal mol^{-1}
M = Cu, M' = Ag: ΔH = -0.2 kcal mol^{-1}

structure is only 0.1 kcal mol^{-1} more stable than **A**, **B** is almost isoenergetic with a mixture of head-to-tail Cu–Cu and Ag–Ag complexes.

Conclusion

According to our calculations, we derive that the presence of only one gold atom is enough to induce metallophilic attractions in the group congeners and this effect could be modulated depending on the gold ligand. Since theoretically predicted geometries are in close agreement with the experimental ones, we can assume that our calculations are accurate enough to obtain valid conclusions.

Experimental Section

Instrumentation: Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer 883 spectrophotometer and on a Perkin-Elmer FT-IR Spectrum 1000 spectrophotometer using Nujol mulls between polyethylene sheets. C, H analysis was carried out with a Perkin-Elmer 240C microanalyser. Mass spectra were recorded on a VG Autospec using the LSIMS techniques and nitrobenzyl alcohol as matrix. ^{1}H, ^{19}F and ^{31}P NMR spectra were recorded on a Bruker ARX 300 in $CDCl_3$ and $(CD_3)_2CO$ solutions. Chemical shifts are quoted relative to $SiMe_4$ (^{1}H, external), $CFCl_3$ (^{19}F, external) and H_3PO_4 (85 %) (^{31}P, external).

Solvent and reagent pretreatment: Dichloromethane and hexane were distilled from CaH_2 and diethyl ether from sodium, under nitrogen atmosphere. $[Cu(CH_3CN)_4]CF_3SO_3$ was prepared as described[29] using triflic acid instead of tetrafluoroboric acid or perchloric acid; $[Au(C_6F_5)(tht)]$[30], $[Au(tht)_2]X$[31] and Ph_2PCH_2SPh[32] were prepared by reported literature methods.

Caution!: perchlorate salts with organic cations may be explosive.

Synthesis of $[Au(Ph_2PCH_2SPh)_2]X$ (X = ClO_4 (1a), CF_3SO_3 (1b)): To a solution of $[Au(tht)_2]ClO_4$ (0.2 mmol, 0.095 g) or $[Au(tht)_2]CF_3SO_3$ (0.2 mmol, 0.104 g) in dichloromethane (20 mL) under N_2 was added Ph_2PCH_2SPh (0.4 mmol; 0.123 g) and a colourless solution was obtained. The reaction mixture was stirred for 1/2 h, the filtrate was evaporated to about 5 mL and addition of diethyl ether (20 mL) led to precipitation of complexes **1a** or **1b** as white solids. Yield: 91 (**1a**), 86 % (**1b**). FAB/MS: *m/z* (%): 813 (100, **1a** and **1b**) $[M]^+$; elemental analysis calcd (%) for $C_{38}H_{34}AuClO_4P_2S_2$ (**1a**): C 49.98, H 3.75; found: C 49.78, H 3.36. $C_{39}H_{34}AuF_3O_3P_2S_3$ (**1b**): C 48.65, H 3.56; found: C 48.84, H 3.52; $^{31}P\{^1H\}$ NMR ($CDCl_3$): (**1a**): $\delta = 39.7$ (s); (**1b**): $\delta = 39.9$ (s); ^{19}F NMR ($CDCl_3$): (**1b**): $\delta = -78.24$ (s, 3F; CF_3SO_3); ^{1}H NMR ($CDCl_3$): (**1a**): $\delta = 7.76-7.03$ (m, 30H; Ph), 4.09 (m, 4H; CH_2); (**1b**): $\delta = 7.76-7.03$ (m, 30H; Ph), 4.11 (m, 4H; CH_2).

Synthesis of $[AuAg(Ph_2PCH_2SPh)_2](CF_3SO_3)_2$ (2): To a solution of **1b** (0.2 mmol, 0.192 g) in dichloromethane (20 mL) under N_2, $AgCF_3SO_3$ (0.2 mmol, 0.051 g) was added. After 4 h of stirring a colourless solution was obtained which was evaporated to about 5 mL. Addition of diethyl ether (20 mL) gave complex **2** as a white solid. Yield: 57 %. FAB/MS: *m/z* (%): 1070 (10) $[M+CF_3SO_3]^+$; elemental analysis calcd (%) for $C_{40}H_{34}AgAuF_6O_6P_2S_4$: C 39.39, H 2.81; found: C 39.20, H 2.83; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 43.1$ (s); ^{19}F NMR ($CDCl_3$): $\delta = -77.90$ (s, 6F; CF_3SO_3); ^{1}H NMR ($CDCl_3$): $\delta = 7.74-7.18$ (m, 30H; Ph), 4.63 (m, 4H, CH_2).

Synthesis of $[AuCu(Ph_2PCH_2SPh)_2](CF_3SO_3)_2$ (3): To a solution of $[Cu(CH_3CN)_4]CF_3SO_3$ (0.2 mmol, 0.075 g) in acetonitrile (3 mL) under N_2, **1b** (0.2 mmol, 0.192 g) dissolved in dichloromethane was added, and the mixture was stirred for 4 h. Evaporation to about 5 mL and addition of diethyl ether (20 mL) led to the precipitation of **3** as a white solid. Yield: 53 %. FAB/MS: *m/z* (%): 1025 (3) $[M+CF_3SO_3]^+$; elemental analysis calcd (%) for $C_{40}H_{34}AuCuF_6O_6P_2S_4$: C 40.87, H 2.92; found: C 40.63, H 2.73; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 42.3$ (s); ^{19}F NMR ($CDCl_3$): $\delta = -77.94$ (s, 6F; CF_3SO_3); ^{1}H NMR ($CDCl_3$): $\delta = 7.71-7.16$ (m, 30H; Ph), 4.50 (m, 4H; CH_2).

Synthesis of $[Ag(Ph_2PCH_2SPh)_2](CF_3SO_3)$ (4): To a solution of $AgCF_3SO_3$ (0.2 mmol, 0.051 g) in diethyl ether (3 mL) under N_2, Ph_2PCH_2SPh (0.4 mmol, 0.123 g) was added and a white precipitate whose appearance is different to that of the starting material was inmediately produced. The mixture was stirred for 2 h and subsequent filtration of the solvent led to the formation of complex **4** as a white solid. Yield: 53 %. FAB/MS: *m/z* (%): 725 (100) $[M]^+$; elemental analysis calcd (%) for $C_{39}H_{34}AgF_3O_3P_2S_3$: C 53.61, H 3.92; found: C 53.82, H 3.94; $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$, 298 K): $\delta = 5.1$ (m); (193 K): $\delta = 1.92$ (m) ($^2J(^{109}Ag,P) = 567.0$ Hz; $^2J(^{107}Ag,P) = 497.0$ Hz); ^{19}F NMR ($(CD_3)_2CO$): $\delta = -77.81$ (s, 3F; CF_3SO_3); ^{1}H NMR ($(CD_3)_2CO$): $\delta = 7.69-6.86$ (m, 30H; Ph), 3.80 (m, 4H; CH_2).

Synthesis of $[Cu(Ph_2PCH_2SPh)_2](CF_3SO_3)$ (5): To a solution of $[Cu(CH_3CN)_4]CF_3SO_3$ (0.2 mmol, 0.075 g) in acetonitrile (3 mL) under N_2, Ph_2PCH_2SPh (0.4 mmol, 0.123 g) dissolved in dichloromethane was added and the mixture was stirred for 2 h. The mixture of solvents were evaporated to about 5 mL. Addition of diethyl ether (20 mL) gave **5** as a white solid. Yield: 88 %. FAB/MS: *m/z* (%): 679 (98) $[M]^+$; elemental analysis calcd (%) for $C_{39}H_{34}CuF_3O_3P_2S_3$: C 56.48, H 4.13; found: C 56.43, H 4.11; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -9.3$ (s); ^{19}F NMR ($CDCl_3$): $\delta = -77.80$ (s, 3F; CF_3SO_3); ^{1}H NMR ($CDCl_3$): $\delta = 7.65-7.04$ (m, 30H; Ph), 3.72 (m, 4H; CH_2).

Synthesis of $[Au(C_6F_5)(Ph_2PCH_2SPh)]$ (6): To a solution of $[Au(C_6F_5)(tht)]$ (0.2 mmol, 0.090 g) in dichloromethane (20 mL) under N_2, Ph_2PCH_2SPh (0.2 mmol, 0.062 g) was added and the reaction mixture was stirred for 1 h. Partial evaporation of the solvent and addition of hexane gave complex **6** as a white solid. Yield: 67 %. FAB/MS: *m/z* (%): 612 (12) $[M]^+$; elemental analysis calcd (%) for $C_{25}H_{17}AuF_5PS$: C 44.66, H 2.55; found: C 44.83, H 2.48; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 36.1$ (m); ^{19}F NMR ($CDCl_3$): $\delta = -116.09$ (m, 2F; F_o), -158.64 (t, 1F, $J(F_p,F_m) = 20.01$ Hz; F_p), -162.64 (m, 2F; F_m); ^{1}H NMR ($CDCl_3$): $\delta = 7.83-7.12$ (m, 15H; Ph), 3.90 (d, 2H, $J(H,P) = 5.5$ Hz; CH_2).

Synthesis of $[Au_2Ag(C_6F_5)_2(Ph_2PCH_2SPh)_2](CF_3SO_3)$ (7): To a solution of $AgCF_3SO_3$ (0.2 mmol, 0.051 g) in diethyl ether (5 mL) under N_2, complex **6** (0.4 mmol, 0.269 g) in dichloromethane (15 mL) was added and the solution was stirred for 2 h. Evaporation of the mixture of solvents to about 2 mL and addition of hexane (20 mL) led to complex **7** as a white solid. Yield: 75 %. FAB/MS: *m/z* (%): 1453 (12) $[M]^+$; elemental analysis calcd (%) for $C_{51}H_{34}Au_2AgF_{13}O_3P_2S_3$: C 38.34, H 2.14; found: C 38.61, H 2.21; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 39.7$ (m); ^{19}F NMR ($CDCl_3$): $\delta = -77.74$ (s, 3F; CF_3SO_3), -115.09 (m, 4F; F_o), -156.87 (t, 2F, $J(F_p,F_m) = 20.0$ Hz; F_p), -161.50 (m, 4F; F_m); ^{1}H NMR ($CDCl_3$): $\delta = 7.64-7.10$ (m, 30H; Ph), 4.25 (d, 4H, $J(H,P) = 6.5$ Hz; CH_2).

Synthesis of $[Au_2Cu(C_6F_5)_2(Ph_2PCH_2SPh)_2](CF_3SO_3)$ (8): To a solution of $[Cu(CH_3CN)_4]CF_3SO_3$ (0.2 mmol, 0.075 g) in CH_3CN (5 mL) under N_2, complex **6** (0.4 mmol, 0.269 g) in dichloromethane (15 mL) was added and the solution was stirred for 4 h. Evaporation of the mixture of solvents to about 5 mL and addition of diethyl ether (20 mL) led to complex **7** as a crystalline white solid. Yield: 52 %. FAB/MS: *m/z* (%): 735 (42) [*M* –

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Table 4. Details of data collection and structure refinement for the complexes **1a**, **2** and **9**.

Compound	**1a**	**2**	**9**
chemical formula	$C_{38}H_{34}AuClO_4P_2S_2$	$C_{44}H_{44}AgAuF_6O_7P_2S_4$	$C_{54}H_{34}Ag_2Au_2F_{16}O_4P_2S_2$
crystal habit	colourless prism	colourless prism	colourless tablet
crystal size [mm]	0.35 × 0.30 × 0.30	0.40 × 0.30 × 0.30	0.45 × 0.40 × 0.20
crystal system	orthorhombic	triclinic	monoclinic
space group	$Pca2_1$	$P\bar{1}$	$C2/c$
a [Å]	17.030(2)	12.632(1)	30.659(6)
b [Å]	11.063(2)	13.826(1)	11.720(2)
c [Å]	19.076(2)	15.425(1)	21.377(4)
α [°]	90	81.371(6)	90
β [°]	90	69.559(5)	133.721(12)
γ [°]	90	87.875(6)	90
U [Å^3]	3594.0(9)	2495.4(3)	5551(2)
Z	4	2	4
ρ_{calcd} [g cm^{-3}]	1.688	1.722	2.138
M_r	913.13	1293.81	1786.54
$F(000)$	1808	1276	3392
T [°C]	−100	−100	− 100
$2\theta_{max}$ [°]	50	50	50
$\mu(Mo_{K\alpha})$ [cm^{-1}]	4.413	3.629	6.197
transmission	0.690–0.893	0.538–0.822	0.657–0.986
no. of reflections measured	6930	9166	9055
no. of unique reflections	4653	8726	4823
R_{int}	0.031	0.030	0.022
R ($F > 4\sigma(F)$)[a]	0.027	0.032	0.019
wR (F^2, all refl.)[b]	0.052	0.083	0.041
no. of reflections used	4653	8720	4823
no. of parameters	409	588	371
no. of restraints	341	0	308
S[c]	0.906	0.966	0.949
max. $\Delta\rho$ [eÅ^{-3}]	0.905	1.364	0.976

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR(F^2) = [\Sigma\{w(F_o^2 - F_c^2)2\}/\Sigma\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and a and b are constants adjusted by the program. [c] S

$Au(C_6F_5)(Ph_2PCH_2SPh)]^+$; elemental analysis calcd (%) for $C_{51}H_{34}Au_2CuF_{13}O_3P_2S_3$: C 39.43, H 2.21; found: C 39.69, H 2.25; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 37.4$ (m); ^{19}F NMR ($CDCl_3$): $\delta = -77.69$ (s, 3F; CF_3SO_3), −115.90 (m, 4F; F_o), −158.29 (t, 2F $J(F_p,F_m) = 20.0$ Hz; F_p), −162.48 (m, 4F; F_m); ^1H NMR ($CDCl_3$): $\delta = 7.72-7.16$ (m, 30H; Ph), 4.03 (m, 4H; CH_2).

Synthesis of $[Au_2Ag_2(C_6F_5)_2(CF_3CO_2)_2(Ph_2PCH_2SPh)_2]$ (9): To a solution of complex **6** (0.2 mmol, 0.134 g) in dichloromethane (20 mL) under N_2, $AgCF_3CO_2$ (0.2 mmol, 0.044 g) was added. After 4 h of stirring, evaporation of the solvent to about 3 mL and addition of hexane (20 mL) led to the precipitation of complex **9** as a white solid. Yield: 72%. FAB/MS: m/z (%): 1672 (16) $[M - CF_3CO_2]^+$; elemental analysis calcd (%) for $C_{54}H_{34}Au_2Ag_2F_{16}O_4P_2S_2$: C 36.30, H 1.92; found: C 36.29, H 1.87; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 37.6$ (m); ^{19}F NMR ($CDCl_3$): $\delta = -73.51$ (s, 6F; CF_3CO_2), −113.44 (m, 4F; F_o), −153.99 (m, 2F; F_p), −160.98 (m, 4F; F_m); ^1H NMR ($CDCl_3$): $\delta = 7.70-7.48$ (m, 30H; Ph), 4.10 (d, 4H, $J(H,P) = 7.0$ Hz; CH_2).

Synthesis of $[AuAg_2(C_6F_5)(CF_3CO_2)_2(Ph_2PCH_2SPh)]$ (10): To a solution of complex **6** (0.2 mmol, 0.134 g) in dichloromethane (20 mL) under N_2, $AgCF_3CO_2$ (0.4 mmol, 0.088 g) was added. After 4 h of stirring, evaporation of the solvent to about 3 mL and addition of hexane (20 mL) led to the precipitation of complex **10** as a white solid. Yield: 77%. FAB/MS: m/z (%): 1001 (10) $[M - CF_3CO_2]^+$; elemental analysis calcd for $C_{29}H_{17}AuAg_2F_{11}O_4PS$: C 31.26, H 1.54; found: C 31.28, H 1.44; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 38.5$ (m); ^{19}F NMR ($CDCl_3$): $\delta = -73.37$ (s, 6F; CF_3CO_2), −110.83 (m, 2F; F_o), −149.41 (t, 1F, $J(F_p,F_m) = 19.8$ Hz; F_p), −159.38 (m, 2F; F_m); ^1H NMR ($CDCl_3$): $\delta = 7.71-7.28$ (m, 15H; Ph), 4.24 (d, 2H, $J(H,P) = 8.6$ Hz; CH_2).

Crystallography: Single crystals suitable for X ray diffraction studies were grown from solutions of the compounds **1a**, **2** and **9** in dichloromethane layered with diethyl ether at room temperature. The crystals were mounted in inert oil on a glass fibre and transferred to the cold gas stream of a Siemens P4 diffractometer equipped with an LT-2 or Oxford low temperature attachment. Data were collected using monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Scan type ω or θ-2θ (**2**). Cell constants were refined from setting angles of about 60 reflections in the range 2θ 6–25°. Psi-scans were applied for all the complexes. The structures were solved by direct methods (**2**), otherwise by the heavy-atom method, and refined on F^2 using the programs SHELXL-93 or SHELXL-97.[33] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included using a riding model. Special refinement details: A system of restraints to light-atom displacement-factor components and local ring symmetry was used. The structure of complex **1a** was refined as a racemic twin. The origin was fixed by the method of Flack and Schwarzenbach.[34] Further details of the data collection are given in Table 4. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-123600 (**1a**), -125027 (**2**) and -123601 (**9**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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