

Aurophilicity at Sulfur Centers. Synthesis and Reactivity of the Complex $[S(Au_2dppf)]$; Formation of Polynuclear Sulfur-Centered Complexes. Crystal Structures of $[S(Au_2dppf)] \cdot 2CHCl_3$, $[(\mu-Au_2dppf)\{S(Au_2dppf)\}_2](OTf)_2 \cdot 8CHCl_3$, and $[S(AuPPh_2Me)_2(Au_2dppf)](ClO_4)_2 \cdot 3CH_2Cl_2$

Fernando Canales,[†] M. Concepción Gimeno,[†] Antonio Laguna,^{*,‡} and Peter G. Jones[‡]

Contribution from the Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-C.S.I.C., 50009 Zaragoza, Spain, and Institut für Anorganische und Analytische Chemie der Technischen Universität, Postfach 3329, D-38023, Braunschweig, Germany

Received May 31, 1995. Revised Manuscript Received September 13, 1995[⊗]

Abstract: Treatment of $[Au_2Cl_2(\mu-dppf)]$ (dppf = 1,1'-bis(diphenylphosphino)ferrocene) with Li_2S (molar ratio 1:1) in ethanol gives a yellow solid $[S(Au_2dppf)]$ (**1**). The sulfur atom in complex **1** can coordinate several neutral or cationic gold(I) fragments giving the trinuclear neutral $[S\{Au(C_6F_5)\}_2(Au_2dppf)]$ (**2**) or cationic derivatives $[S(AuL)(Au_2dppf)]ClO_4$ [L = CH_2PPh_3 (**3**), PPh_3 (**4**), PPh_2Me (**5**)]. A pentanuclear complex $[Au\{S(Au_2dppf)_2\}]ClO_4$ (**6**) is obtained by reaction of 2 equiv of complex **1** with 1 equiv of $[Au(tht)_2]ClO_4$, in which the central gold atom is bonded to two sulfur atoms. Treatment of compound **1** with $[Au_2(OTf)_2(\mu-dppf)]$ (OTf = trifluoromethylsulfonate) in a molar ratio 2:1 affords the hexanuclear complex $[(\mu-Au_2dppf)\{S(Au_2dppf)\}_2](OTf)_2$ (**7**), in which two SAu_3 units are joined through the dppf ligand. The reaction of **1** with 2 equiv of $[Au(OCIO_3)PR_3]$ leads to the quadruply bridging derivatives $[S(AuPR_3)_2(Au_2dppf)](ClO_4)_2$ [$PR_3 = PPh_3$ (**8**), PPh_2Me (**9**)]. Crystal structure determinations were performed for complexes **1**, **7**, and **9**. $[S(Au_2dppf)]$ (**1**) crystallizes in the monoclinic space group $P2_1/n$, with $a = 12.571(4)$ Å, $b = 10.579(4)$ Å, $c = 15.212(4)$ Å, $\beta = 107.84(3)^\circ$, $Z = 2$, $T = -130$ °C. $[(\mu-Au_2dppf)\{S(Au_2dppf)\}_2](OTf)_2$ (**7**) is triclinic, $P\bar{1}$, with $a = 15.177(3)$, $b = 18.408(4)$, $c = 27.894(8)$ Å, $\alpha = 88.83(2)$, $\beta = 84.46(2)$, $\gamma = 67.78(2)$, $Z = 2$, $T = -100$ °C. $[S(AuPPh_2Me)_2(Au_2dppf)](ClO_4)_2$ (**9**) is triclinic, $P\bar{1}$, with $a = 13.727(2)$ Å, $b = 15.952(3)$ Å, $c = 17.763(2)$ Å, $\alpha = 71.738(12)^\circ$, $\beta = 73.264(14)^\circ$, $\gamma = 75.96(2)^\circ$, $Z = 2$, $T = -100$ °C. All three complexes display short gold(I)–gold(I) interactions.

Introduction

In the last few years a great deal of interest has focussed on species where (phosphine)gold fragments coordinate around a central heteroatom.¹ Thus interesting hypercoordinated compounds^{2–6} of the type $[C(AuPPh_3)_5]^+$, $[C(AuPPh_3)_6]^{2+}$, $[N(AuPPh_3)_5]^{2+}$, $[P(AuPPh_3)_5]^{2+}$, and $[P(AuPPh_3)_6]^{3+}$ have been described, apart from other complexes with more conventional stoichiometry. Their structures are fascinating from the theoretical point of view. Usually, the chemistry of the first row elements of the p-block is known to follow classical rules of bonding, and only in cases of extreme electron-deficiency had the traditional electron count to be reconsidered to account for special types of molecular or solid state structures. Many of the heteroatom-centered complexes presented here are electron deficient and the gold–gold interactions provide a significant

contribution to their stability. It is probable that relativistic effects play a role in this type of bonding.^{7–9} The gold–gold interactions of ca. 3.0 Å are associated with bond energies of ca. 33 kJ/mol;^{10–13} their strength is obviously influenced by the electronic effects of the ligand bonded to gold, but it is becoming more and more clear that steric effects are also very important. To illustrate this fact, species of the type $C(AuPR_3)_4$ could only be isolated when sufficient bulky ligands such as tricyclohexylphosphine were used,¹⁴ otherwise penta- and hexanuclear compounds were obtained.

We are interested in such complexes where sulfur is the central heteroatom. The chemistry of this type of gold(I) complexes was originally limited^{15–19} to the triply bridging species $[S(AuPR_3)_3]^+$, but we have since reported the crystal

(7) Pyykkö, P.; Desclaux, J. P. *Acc. Chem. Res.* **1979**, *12*, 276.

(8) Pitzer, K. S. *Acc. Chem. Res.* **1979**, *12*, 271.

(9) Pyykkö, P. *Chem. Rev.* **1988**, *88*, 563.

(10) Dziwok, K.; Lachmann, J.; Wilkinson, D. L.; Müller, G.; Schmidbaur, H. *Chem. Ber.* **1990**, *123*, 423.

(11) Schmidbaur, H.; Dziwok, K.; Grohmann, A.; Müller, G. *Chem. Ber.* **1989**, *122*, 893.

(12) Schmidbaur, H.; Graf, W.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 417.

(13) Narayanaswamy, R.; Young, M. A.; Parkhurst, E.; Ouellette, M.; Kerr, M. E.; Ho, D. M.; Elder, R. C.; Bruce, A. E.; Bruce, M. R. M. *Inorg. Chem.* **1993**, *32*, 2506.

(14) Schmidbaur, H.; Steigelmann, O. *Z. Naturforsch.* **1992**, *47*, 1721.

(15) Kowala, C.; Swan, J. M. *Aust. J. Chem.* **1966**, *19*, 547.

(16) Abel, E. W.; Jenkins, C. R. *J. Organomet. Chem.* **1968**, *14*, 285.

(17) Jones, P. G.; Sheldrick, G. M.; Hädicke, E. *Acta Crystallogr., Sect. B* **1980**, *36*, 2777.

[†] Instituto de Ciencia de Materiales de Aragón.

[‡] Institut für Anorganische und Analytische Chemie der Technischen Universität.

[⊗] Abstract published in *Advance ACS Abstracts*, May 1, 1996.

(1) Schmidbaur, H. *Pure Appl. Chem.* **1993**, *65*, 691 and references cited therein.

(2) Scherbaum, F.; Grohmann, A.; Müller, G.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 463.

(3) Scherbaum, F.; Grohmann, A.; Huber, B.; Krüger, C.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1544.

(4) Grohmann, A.; Riede, J.; Schmidbaur, H. *Nature* **1990**, *345*, 140.

(5) Schmidbaur, H.; Weidenhiller, G.; Steigelmann, O. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 433.

(6) Zeller, E.; Schmidbaur, H. *J. Chem. Soc., Chem. Commun.* **1993**, 69.

Scheme 1

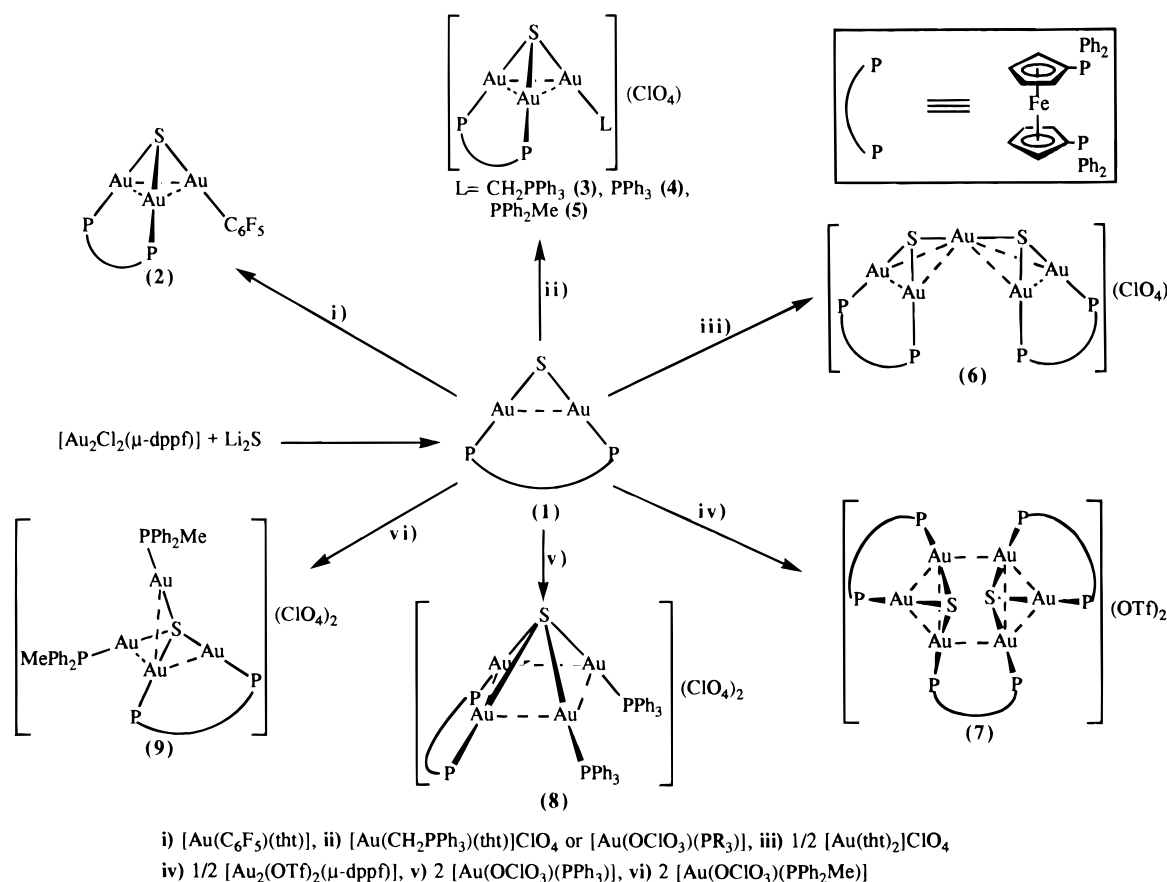


Table 1. Analytical Data and Other Properties for the Complexes 1–9

complex	yield (%)	Anal. (%) ^a			Λ_M^b	$\nu(\text{Au-S})^c$
		C	H	S		
$[\text{S}(\text{Au}_2\text{dppf})]$ (1)	90	41.81 (41.65)	3.05 (2.88)	3.09 (3.27)	<i>d</i>	377 (m) 301 (m)
$[\text{S}\{\text{Au}(\text{C}_6\text{F}_5)\}(\text{Au}_2\text{dppf})]$ (2)	89	36.06 (35.74)	1.97 (2.10)	1.92 (2.38)	12.2	
$[\text{S}\{\text{Au}(\text{CH}_2\text{PPh}_3)\}(\text{Au}_2\text{dppf})](\text{ClO}_4)$ (3)	97	40.52 (40.99)	2.63 (2.92)	1.86 (2.06)	137.6	
$[\text{S}(\text{AuPPh}_3)(\text{Au}_2\text{dppf})](\text{ClO}_4)$ (4)	91	40.15 (40.58)	2.53 (2.82)	1.74 (2.08)	137.7	
$[\text{S}(\text{AuPPh}_2\text{Me})(\text{Au}_2\text{dppf})](\text{ClO}_4)$ (5)	91	37.92 (38.22)	2.49 (2.80)	1.91 (2.17)	142.9	356 (br,w)
$[\text{Au}\{\text{S}(\text{Au}_2\text{dppf})\}_2](\text{ClO}_4)$ (6)	97	35.73 (36.18)	2.33 (2.50)	2.60 (2.84)	<i>d</i>	
$[(\mu\text{-Au}_2\text{dppf})\{\text{S}(\text{Au}_2\text{dppf})\}_2](\text{OTf})_2$ (7)	95	38.84 (38.95)	2.61 (2.64)	3.61 (4.00)	224.5	335 (br,w)
$[\text{S}(\text{AuPPh}_3)_2(\text{Au}_2\text{dppf})](\text{ClO}_4)_2$ (8)	90	40.06 (40.08)	2.61 (2.79)	1.31 (1.53)	254.1	
$[\text{S}(\text{AuPPh}_2\text{Me})_2(\text{Au}_2\text{dppf})](\text{ClO}_4)_2$ (9)	85	36.79 (36.51)	2.71 (2.76)	1.80 (1.62)	255.6	282 (w)

^a Calculated values are given in parentheses ^b In acetone, values in $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. ^c Values in cm^{-1} . ^d Not enough soluble.

structure²⁰ of the electron-deficient derivative $[\text{S}(\text{AuPPh}_3)_4]^{2+}$. Here we report a similar type of complex, with the difference that an $[\text{Au}_2(\mu\text{-PP})]^{2+}$ fragment around the sulfur atom serves as a building block. It can react with several gold(I) derivatives affording tri- and tetranuclear complexes, some of them with unprecedented structural frameworks. Thus we describe the structure of $[\text{S}(\text{AuPPh}_2\text{Me})_2(\text{Au}_2\text{dppf})]^{2+}$ (dppf = 1,1'-bis(diphenylphosphino)ferrocene), which does not correspond to

the square pyramidal form found in $[\text{S}(\text{AuPPh}_3)_4]^{2+}$; it can be regarded as distorted trigonal bipyramidal at sulfur, with one position occupied by the lone pair of electrons.

Results and Discussion

The reaction of $[\text{Au}_2\text{Cl}_2(\mu\text{-dppf})]$ (dppf = 1,1'-bis(diphenylphosphino)ferrocene) with 1 equiv of Li_2S in ethanol affords the dinuclear complex $[\text{S}(\text{Au}_2\text{dppf})]$ (1), in which the two gold atoms are bridged by the 1,1'-bis(diphenylphosphino)ferrocene ligand and the sulfur atom (see Scheme 1). Complex 1 is an orange air- and moisture-stable solid.

(18) Schmidbaur, H.; Kolb, A.; Zeller, E.; Schier, A.; Beruda, H. Z. *Anorg. Allg. Chem.* **1993**, 619, 1575.

(19) Angermaier, K.; Schmidbaur, H. *Chem. Ber.* **1994**, 127, 2387.

(20) Canales, F.; Gimeno, M. C.; Jones, P. G.; Laguna, A. *Angew. Chem., Int. Ed. Engl.* **1994**, 33, 769.

Table 2. NMR Data for Complexes 1–9

complex	NMR ^a						² J _{HP}	
	³¹ P		¹ H					
	dppf	L	H _α Cp	H _β Cp	CH ₃	CH ₂		
[S(Au ₂ dppf)] (1)	30.0 (s)		3.9 (s, br)	4.6 (s, br)				
[S{Au(C ₆ F ₅) ₂ (Au ₂ dppf)}] (2)	25.3 (s)		3.9 (s, br)	4.6 (s, br)				
[S{Au(CH ₂ PPh ₃) ₂ (Au ₂ dppf)}](ClO ₄) (3)	26.1 (s)	30.8 (s)	4.0 (s, br)	4.5 (s, br)		2.14 (d)	12.69	
[S(AuPPh ₃) ₂ (Au ₂ dppf)](ClO ₄) (4)	27.4 (s)	34.1 (s)	4.10 (s, br)	4.46 (s, br)				
[S(AuPPh ₂ Me)(Au ₂ dppf)](ClO ₄) (5)	27.0 (s)	18.9 (s)	4.10 (s, br)	4.50 (s, br)	2.12 (d)		9.76	
[Au{S(Au ₂ dppf)} ₂](ClO ₄) (6)	25.5 (br)		(4.5–3.8) (m, br)					
[(μ-Au ₂ dppf){S(Au ₂ dppf)} ₂](OTf) ₂ (7)	28.5 (s)		(4.7, 4.5, 4.4, 4.1, 4.0, 3.2, 3.0) (m)					
	25.1 (s)							
	23.0 (s)							
[S(AuPPh ₃) ₂ (Au ₂ dppf)](ClO ₄) ₂ (8)	26.4 (s)	32.9 (s)	4.18 (s)	4.59 (s)				
[S(AuPPh ₂ Me) ₂ (Au ₂ dppf)](ClO ₄) ₂ (9)	25.9 (s)	18.6 (s, br)	4.14 (s, br)	4.59 (s, br)	2.07 (d)		10.74	

^a Recorded in CDCl₃, coupling constants in hertz; s = singlet, d = doublet, m = multiplet, br = broad.

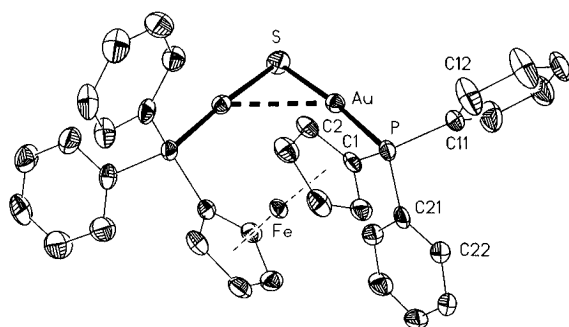


Figure 1. The structure of complex **1** in the crystal. Displacement parameter ellipsoids represent 50% probability surfaces. The H atoms are omitted for clarity. The crystallographic 2-fold axis passes through the atoms S and Fe.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **1**^a

Au–P	2.247(2)	Au–S	2.300(2)
Au–Au#1 ^a	2.8820(10)	Fe–C(4)	2.025(7)
Fe–C(5)	2.035(7)	Fe–C(1)	2.039(7)
Fe–C(2)	2.041(7)	Fe–C(3)	2.056(7)
P–Au–S	173.78(6)	P–Au–Au#1 ^a	122.66(5)
S–Au–Au#1 ^a	51.21(4)	C(1)–P–Au	110.4(2)
C(21)–P–Au	113.9(2)	C(11)–P–Au	116.0(2)
Au–S–Au#1 ^a	77.57(9)		

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

In the IR spectrum the absorptions arising from $\nu(\text{Au–Cl})$ in the starting material are replaced by two bands from $\nu(\text{Au–S})$. The NMR data are consistent with the formulation and only one signal is observed in the ³¹P{¹H} NMR spectrum, because of the equivalence of both phosphorus atoms; in the ¹H NMR spectrum, apart from the multiplets for the phenyl protons, two broad singlets appear for the α and β protons of the cyclopentadienyl rings (Table 2).

The FAB⁺ mass spectrum shows the molecular peak plus a proton at $m/z = 981$ (MH⁺, 42%). The most intense peak corresponds to the species Au(dppf)⁺ at $m/z 751$ and higher peaks appear at $m/z 1177$ [(M + Au)⁺, 8%] and 2158 [(2M + Au)⁺, 57%].

The crystal structure of complex **1** has been confirmed by X-ray diffraction and the molecule is shown in Figure 1. Selected bond lengths and angles are collected in Table 3. The molecule has crystallographic 2-fold symmetry. The two gold atoms are bridged by the sulfur atom and there is a short intramolecular Au[⋯]Auⁱ contact of 2.8820(10) Å, much shorter than that found in the complex [S(AuPPh₃)₂] [3.018(1) Å].²¹ The Au–S–Auⁱ ($i = -x + 1/2, y, -z + 3/2$) angle is very narrow [77.57(9)°] compared to [S(AuPPh₃)₂] [88.77(1)°], thus favoring

the gold–gold interaction. The Au–S distance is 2.300(2) Å and is longer than in the latter complex, 2.157(5) and 2.161(5) Å; however, it falls in the same range as found in [S(AuPPh₃)₃]⁺^{17,18} or [Au{S(AuPPh₃)₂}₂]⁺,²² where the sulfur atom is surrounded by three gold atoms. Also, the Au–P bond length of 2.247(2) Å is longer than in [S(AuPPh₃)₂], although similar to the Au–P distances in bis(diphenylphosphino)ferrocene–gold complexes.²³ The coordination at the gold centers is slightly distorted from linear, with a P–Au–S angle of 173.78(6)°. There is a contact of 3.535 Å between a dichloromethane chlorine and the gold atom. This is the first example of a digold–diphosphine unit coordinated to a sulfur center, and shows the great flexibility of the dppf ligand to adapt to different geometries at the metal center.

Complex **1** can serve as a building block for preparing polynuclear sulfur-centered complexes. We have studied the reactions of **1** with several gold(I) derivatives. Thus the treatment of **1** with 1 equiv of [Au(C₆F₅)tht] affords the neutral derivative [S(Au(C₆F₅)(Au₂dppf)] (**2**), and with [Au(CH₂PPh₃)tht]ClO₄ or [Au(OCIO₃)PR₃] the cationic complexes [S(AuL)(Au₂dppf)]ClO₄ [L = CH₂PPh₃ (**3**), PPh₃ (**4**), PPh₂Me (**5**)] are obtained. They behave as nonconducting (**2**) or as 1:1 electrolytes (**3–5**) in an acetone solution. In the IR spectra the most significant absorptions are weak bands arising from the $\nu(\text{Au–S})$ vibrations, in complex **2** bands of the pentafluorophenyl group bonded to gold(I) at 1499 s and 953 m cm⁻¹, and in compound **3** the $\nu(\text{Au–C})$ band of the ylide ligand at 575 m cm⁻¹.

The ¹H NMR spectra show in all the cases two broad singlets for the cyclopentadienyl protons; the resonances of the methylene and methyl groups of the ylide and the methyl of the phosphine ligand appear as doublets. The ³¹P{¹H} NMR spectra show two signals because of the two different phosphorus environments, with the exception of complex **2** where only one resonance appears. An upfield displacement ($\Delta \approx 3$ ppm) is observed compared to the starting material for the signal of the diphosphine phosphorus. This upfield shift has also been reported in the conversion of (phosphine)gold(I) compounds to homoleptic hypercoordinated species such as [C(AuL)₅]⁺ and [C(AuL)₆]²⁺.

The FAB⁺ mass spectra of complexes **3–5** show the molecular cation peak as the most intense at $m/z 1453$ (**3**), 1439 (**4**), and 1377 (**5**). Other fragments are [AuL]⁺, and [AuL₂]⁺,

(21) Lensch, C.; Jones, P. G.; Sheldrick, G. M. *Z. Naturforsch.* **1982**, *37b*, 944.

(22) Jones, P. G.; Lensch, C.; Sheldrick, G. M. *Z. Naturforsch.* **1982**, *37b*, 141.

(23) Hill, D. T.; Girard, G. R.; McCabe, F. L.; Johnson, R. K.; Stupik, P. D.; Zhang, J. H.; Reifj, W. M.; Eggleston, D. S. *Inorg. Chem.* **1989**, *28*, 3529.

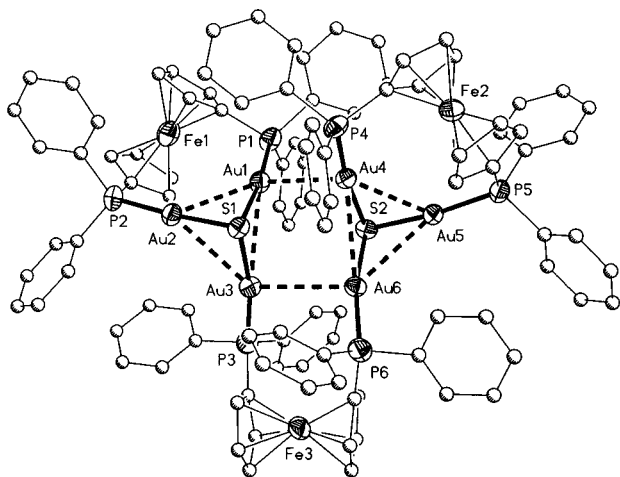


Figure 2. The cation of complex **7** in the crystal. Displacement parameter ellipsoids represent 50% probability surfaces. Carbon atoms are spheres of arbitrary radius. H atoms are omitted for clarity.

and at m/z 2157 the peak assigned to the cation $[\text{Au}\{\text{S}(\text{Au}_2\text{-dppf})\}_2]^+$ appears.

Although these complexes have not been characterized by X-ray diffraction, we assume they have a similar structural framework to that found in the complexes $[\text{S}(\text{AuPR}_3)_3]^+$, with short contacts among the gold(I) centers.

As we have remarked before, all the positive-ion FAB experiments for these complexes reveal with high intensity a peak that corresponds to the species $[\text{Au}\{\text{S}(\text{Au}_2\text{dppf})\}_2]^+$. This indicates the stability of this derivative, and for this reason we have synthesized it by treatment of **1** with $[\text{Au}(\text{tht})_2]\text{ClO}_4$ in a 2:1 molar ratio. The reaction affords the complex $[\text{Au}\{\text{S}(\text{Au}_2\text{-dppf})\}_2]\text{ClO}_4$ (**6**) as an orange solid, scarcely soluble in common solvents. The ^1H NMR spectrum shows broad bands for the cyclopentadienyl protons, and also a broad singlet is observed for the phosphorus atoms of the diphosphine in the $^{31}\text{P}\{^1\text{H}\}$ spectrum. We believe that the solid state structure corresponds to that found in $[\text{Au}\{\text{S}(\text{AuPPh}_3)_2\}[\text{SnMe}_3\text{Cl}_2]]$,²² with a gold(I) atom bonded to two $[\text{S}(\text{AuPPh}_3)_2]$ units in such a manner that the gold and sulfur atoms adopt a boat configuration.

We have also synthesized a hexanuclear derivative which contains two SAu_3 cores connected through a bridging dppf ligand. The reaction of complex **1** with a freshly prepared solution of $[\text{Au}_2(\text{OTf})_2(\mu\text{-dppf})]$ in dichloromethane (molar ratio 2:1) leads to $[(\mu\text{-Au}_2\text{dppf})\{\text{S}(\text{Au}_2\text{dppf})\}_2](\text{OTf})_2$ (**7**). Compound **7** is an orange solid stable to moisture and air and behaves as a 2:1 electrolyte in an acetone solution.

The room temperature NMR spectra show broad bands that sharpen when the experiments are carried out at -55°C . The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum presents three singlets assigned to the three different phosphorus environments (in each SAu_3P_3 unit). The ^1H NMR spectrum is rather complex in the cyclopentadienyl proton region, and shows five multiplets with a 1:6:3:1:1 ratio that makes difficult the assignment to particular protons.

The structure of complex **7** has been confirmed by an X-ray diffraction study and the cation is shown in Figure 2. Selected bond lengths and angles are given in Table 4. The complex crystallizes with an idealized composition that includes eight molecules of chloroform. The structure consists of an S_2Au_6 core that shows short intramolecular Au–Au interactions. These distances vary from 2.905(2) to 3.272(2) Å. The shortest contacts, $\text{Au}(1)\text{—Au}(4) = 2.905(2)$ Å, $\text{Au}(1)\text{—Au}(2) = 2.922(2)$, and $\text{Au}(4)\text{—Au}(5) = 2.920(2)$ Å, involve gold atoms of the $\text{Au}_2\text{-dppf}^{2+}$ fragment that are bonded to the same sulfur atom. The shortest contact between gold and iron is 4.284 Å. The

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **7**

Au(1)—P(1)	2.250(10)	Au(1)—S(1)	2.337(9)
Au(1)—Au(4)	2.905(2)	Au(1)—Au(2)	2.922(2)
Au(1)—Au(3)	3.247(2)	Au(2)—P(2)	2.266(9)
Au(2)—S(1)	2.328(8)	Au(2)—Au(3)	3.246(2)
Au(3)—P(3)	2.262(10)	Au(3)—S(1)	2.338(9)
Au(3)—Au(6)	3.283(2)	Au(4)—P(4)	2.282(10)
Au(4)—S(2)	2.368(9)	Au(4)—Au(5)	2.920(2)
Au(4)—Au(6)	3.272(2)	Au(5)—P(5)	2.269(9)
Au(5)—S(2)	2.324(9)	Au(5)—Au(6)	3.247(2)
Au(6)—P(6)	2.270(10)	Au(6)—S(2)	2.328(9)
P(1)—Au(1)—S(1)	173.1(3)	P(1)—Au(1)—Au(4)	101.6(3)
S(1)—Au(1)—Au(4)	84.5(2)	P(1)—Au(1)—Au(2)	122.3(2)
S(1)—Au(1)—Au(2)	51.1(2)	Au(4)—Au(1)—Au(2)	134.83(6)
P(1)—Au(1)—Au(3)	135.4(3)	S(1)—Au(1)—Au(3)	46.0(2)
Au(4)—Au(1)—Au(3)	93.59(5)	Au(2)—Au(1)—Au(3)	63.23(5)
P(2)—Au(2)—S(1)	174.2(3)	P(2)—Au(2)—Au(1)	122.8(3)
S(1)—Au(2)—Au(1)	51.4(2)	P(2)—Au(2)—Au(3)	133.8(3)
S(1)—Au(2)—Au(3)	46.0(2)	Au(1)—Au(2)—Au(3)	63.27(5)
P(3)—Au(3)—S(1)	169.6(3)	P(3)—Au(3)—Au(2)	125.4(2)
S(1)—Au(3)—Au(2)	45.8(2)	P(3)—Au(3)—Au(1)	137.1(3)
S(1)—Au(3)—Au(1)	46.0(2)	Au(2)—Au(3)—Au(1)	53.49(4)
P(3)—Au(3)—Au(6)	101.0(2)	S(1)—Au(3)—Au(6)	87.8(2)
Au(2)—Au(3)—Au(6)	131.38(6)	Au(1)—Au(3)—Au(6)	85.69(5)
P(4)—Au(4)—S(2)	171.6(3)	P(4)—Au(4)—Au(1)	102.5(2)
S(2)—Au(4)—Au(1)	85.8(2)	P(4)—Au(4)—Au(5)	120.8(2)
S(2)—Au(4)—Au(5)	50.8(2)	Au(1)—Au(4)—Au(5)	136.38(7)
P(4)—Au(4)—Au(6)	133.3(3)	S(2)—Au(4)—Au(6)	45.3(2)
Au(1)—Au(4)—Au(6)	91.74(6)	Au(5)—Au(4)—Au(6)	62.96(5)
P(5)—Au(5)—S(2)	173.7(3)	P(5)—Au(5)—Au(4)	122.8(2)
S(2)—Au(5)—Au(4)	52.2(2)	P(5)—Au(5)—Au(6)	137.8(3)
S(2)—Au(5)—Au(6)	45.8(2)	Au(4)—Au(5)—Au(6)	63.82(5)
P(6)—Au(6)—S(2)	167.6(3)	P(6)—Au(6)—Au(5)	125.5(2)
S(2)—Au(6)—Au(5)	45.7(2)	P(6)—Au(6)—Au(4)	139.9(3)
S(2)—Au(6)—Au(4)	46.3(2)	Au(5)—Au(6)—Au(4)	53.22(4)
P(6)—Au(6)—Au(3)	99.8(2)	S(2)—Au(6)—Au(3)	90.9(2)
Au(5)—Au(6)—Au(3)	133.50(6)	Au(4)—Au(6)—Au(3)	86.49(5)
Au(2)—S(1)—Au(3)	88.2(3)	Au(2)—S(1)—Au(1)	77.6(2)
Au(3)—S(1)—Au(1)	88.0(3)	Au(5)—S(2)—Au(6)	88.5(3)
Au(5)—S(2)—Au(4)	77.0(3)	Au(6)—S(2)—Au(4)	88.3(3)
C(11)—P(1)—Au(1)	116.1(11)	C(131)—P(1)—Au(1)	107.9(9)
C(21)—P(1)—Au(1)	116.5(9)	C(136)—P(2)—Au(2)	110.9(9)
C(31)—P(2)—Au(2)	114.2(9)	C(41)—P(2)—Au(2)	113.7(9)
C(61)—P(3)—Au(3)	116.5(11)	C(151)—P(3)—Au(3)	113.1(10)
C(51)—P(3)—Au(3)	107.3(9)	C(71)—P(4)—Au(4)	112.5(10)
C(81)—P(4)—Au(4)	115.4(9)	C(141)—P(4)—Au(4)	110.1(9)
C(146)—P(5)—Au(5)	112.1(9)	C(91)—P(5)—Au(5)	111.8(9)
C(101)—P(5)—Au(5)	116.7(9)	C(156)—P(6)—Au(6)	112.2(11)
C(111)—P(6)—Au(6)	118.1(9)	C(121)—P(6)—Au(6)	107.3(9)

sulfur atoms lie 1.465 and 1.466 Å out of the planes formed by their three gold neighbors.

The Au–S–Au angles are very different. There are two very narrow angles, $\text{Au}(2)\text{—S}(1)\text{—Au}(1) = 77.6(2)^\circ$ and $\text{Au}(5)\text{—S}(2)\text{—Au}(4) = 77.0(3)^\circ$, involving the gold atoms linked to the same sulfur atom, and these angles are very similar to those in complex **1**; the other Au–S–Au angles have values of ca. 88° and are similar to those found in $[\text{S}(\text{AuP}_3)]^+$ complexes with bulky tertiary phosphines. The geometry around the gold atoms is slightly distorted from linear, with the major deviations for Au(3) and Au(6) being 169.6(3) and 167.6(3)°, respectively.

Finally, we have studied reactions where further auration of the sulfur atom takes place. Thus, the treatment of **1** with 2 equiv of $[\text{Au}(\text{OCIO}_3)\text{PPh}_3]$ or $[\text{Au}(\text{OCIO}_3)\text{PPh}_2\text{Me}]$ leads to the quadruply bridged species $[\text{S}(\text{AuPR}_3)_2(\text{Au}_2\text{dppf})_2](\text{ClO}_4)_2$ [$\text{PR}_3 = \text{PPh}_3$ (**8**), PPh_2Me (**9**)]. These complexes have similar IR spectra to compounds **4** and **5**, with the exception of the ν -(Au–S) bands, which are too weak to be observed. We have previously observed this pattern of medium, weak, or unobserved ν (Au–S) bands when changing from doubly to triply and to quadruply bridging sulfido ligands. The conductivity

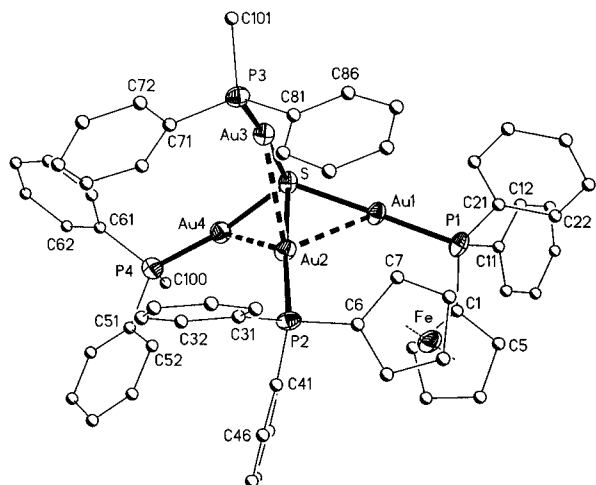


Figure 3. The cation of complex **9** in the crystal. Displacement parameter ellipsoids represent 50% probability surfaces. Carbon atoms are spheres of arbitrary radius. H atoms are omitted for clarity.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Complex **9**

Au(1)–P(1)	2.265(6)	Au(1)–S	2.404(6)
Au(1)–Au(2)	2.9047(13)	Au(1)–Au(3)#1 ^a	2.9520(12)
Au(2)–P(2)	2.263(5)	Au(2)–S	2.416(5)
Au(3)–Au(3)	2.9210(12)	Au(2)–Au(4)	2.9775(14)
Au(3)–P(3)	2.270(5)	Au(3)–S	2.367(5)
Au(4)–P(4)	2.256(6)	Au(4)–S	2.309(5)
P(1)–Au(1)–S	172.9(2)	P(1)–Au(1)–Au(2)	120.9(2)
S–Au(1)–Au(2)	53.14(12)	P(1)–Au(1)–Au(3)#1 ^a	106.0(2)
S–Au(1)–Au(3)#1 ^a	78.46(13)	Au(2)–Au(1)–Au(3)#1 ^a	129.49(4)
P(2)–Au(2)–S	175.7(2)	P(2)–Au(2)–Au(1)	123.0(2)
S–Au(2)–Au(1)	52.74(13)	P(2)–Au(2)–Au(3)	130.69(14)
S–Au(2)–Au(3)	51.60(12)	Au(1)–Au(2)–Au(3)	83.06(3)
P(2)–Au(2)–Au(4)	132.8(2)	S–Au(2)–Au(4)	49.35(12)
Au(1)–Au(2)–Au(4)	90.27(4)	Au(3)–Au(2)–Au(4)	80.88(3)
P(3)–Au(3)–S	170.8(2)	P(3)–Au(3)–Au(2)	117.72(14)
S–Au(3)–Au(2)	53.13(13)	P(3)–Au(3)–Au(1)#1 ^a	101.58(13)
S–Au(3)–Au(1)#1 ^a	87.57(13)	Au(2)–Au(3)–Au(1)#1 ^a	139.70(4)
P(4)–Au(4)–S	171.3(2)	P(4)–Au(4)–Au(2)	134.9(2)
S–Au(4)–Au(2)	52.56(13)	Au(4)–S–Au(3)	109.8(2)
Au(4)–S–Au(1)	124.4(2)	Au(1)–S–Au(1)	108.1(2)
Au(4)–S–Au(2)	78.1(2)	Au(3)–S–Au(2)	75.27(14)
Au(1)–S–Au(2)	74.1(2)	C(1)–P(1)–Au(1)	110.1(6)
C(21)–P(1)–Au(1)	112.7(6)	C(11)–P(1)–Au(1)	116.4(7)
C(41)–P(2)–Au(2)	111.9(6)	C(6)–P(2)–Au(2)	109.7(6)
C(31)–P(2)–Au(2)	115.4(7)	C(71)–P(3)–Au(3)	111.8(6)
C(81)–P(3)–Au(3)	107.6(7)	C(101)–P(3)–Au(3)	115.9(8)
C(61)–P(4)–Au(4)	110.8(7)	C(100)–P(4)–Au(4)	111.5(9)
C(51)–P(4)–Au(4)	114.3(6)		

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

of complexes **4** and **5** in acetone solutions corresponds to that of 2:1 electrolytes.

The ¹H NMR spectra show in both cases, apart from the phenyl protons, two multiplets associated with the α and β protons of the cyclopentadienyl groups, and in the spectrum of complex **9** a doublet for the methyl group appears. The ³¹P NMR spectra show two singlets of similar intensity for the two types of phosphorus environments. An upfield displacement of ca. 1 ppm is observed for the two resonances compared to those in complexes **4** and **5**.

The structure of complex **9** has been confirmed by X-ray diffraction analysis (Figure 3). Selected bond lengths and angles are given in Table 5. The complex crystallizes with three molecules of dichloromethane per asymmetric unit. The structure reveals a new type of structural framework, because it can be regarded as a trigonal bipyramid with one of the apical positions occupied by the lone pair of electrons at the sulfur

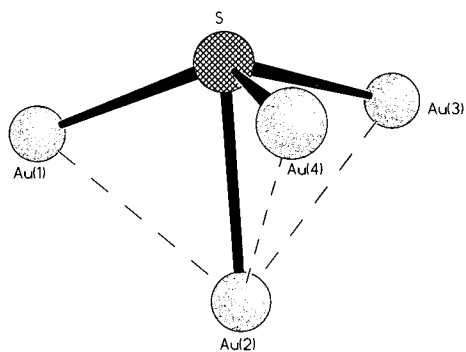


Figure 4. Perspective view of the gold and sulfur atoms in complex **9** showing the coordination geometry of the sulfur atom.

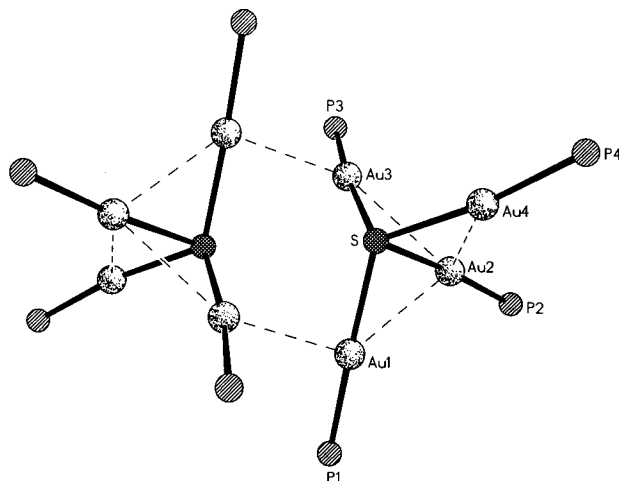


Figure 5. Association of two cations of **9** in the crystal. Phenyl rings and H atoms are omitted for clarity.

atom and the other by the gold atom Au(2) (Figure 4). The complex is then electron-deficient, since only three bonding molecular orbitals are occupied, as has been proposed for the complexes $[\text{As}(\text{AuPPh}_3)_4]^+$ ²⁴ and $[\text{S}(\text{AuPPh}_3)_4]^{2+}$ ²⁰

There are intramolecular gold–gold contacts, the shortest being between the equatorial gold atoms and the gold atom perpendicular to them, with values of 2.9047(12), 2.9210(12), and 2.9775(14) Å. These distances are of the same order as those found in $[\text{S}(\text{AuPPh}_3)_4]^{2+}$ [2.883(2)–2.938(2) Å]. In the crystal the cations of **9** are paired across symmetry centers (Figure 5); the intermolecular interactions, $\text{Au}(1)–\text{Au}(3i) = 2.9520(12)$ Å ($i = 1 - x, 1 - y, 1 - z$), are much shorter than in $[\text{S}(\text{AuPPh}_3)_4]^{2+}$ (3.202 Å).

The Au–S–Au angles for the three gold atoms located in the equatorial plane are 124.4(2), 109.8(2) and 108.1(2)°; these values differ from the ideal 120°, which may be a consequence of the interaction with the other gold atom. These angles are big enough to prevent further contacts between the equatorial gold atoms, $\text{Au}(1)–\text{Au}(3) = 3.863$ Å, $\text{Au}(1)–\text{Au}(4) = 4.170$ Å, and $\text{Au}(3)–\text{Au}(4) = 3.826$ Å. The Au–S–Au angles between the gold atom in the apical position and the gold atoms in the plane are very narrow, 74.1(2)–78.1(2)°, because of the gold–gold contacts. These values are similar to those found in complex **1** and in $[\text{S}(\text{AuPPh}_3)_4]^{2+}$.

The sulfur atom lies 0.57 Å out of the plane formed by Au(1), Au(3), and Au(4), whereas Au(2) lies 1.84 Å below that plane. The Au–S bond lengths are different, the longest corresponds to the gold atom in the apical position, $\text{Au}(2)–\text{S} = 2.416(5)$ Å, and the shortest, $\text{Au}(3)–\text{S} = 2.367(5)$ Å and

(24) Zeller, E.; Beruda, H.; Kolb, A.; Bissinger, P.; Riede, J.; Schmidbauer, H. *Nature* **1991**, 352, 141.

Table 6. Details of Data Collection and Structure Refinement for the Complexes **1**, **7**, and **9**

compound	1.2CHCl ₃	7.8CHCl ₃	9.3CH ₂ Cl ₂
chemical formula	C ₃₆ H ₃₂ Au ₂ Cl ₆ FeP ₂ S	C ₁₁₂ H ₉₂ Au ₆ Cl ₂₄ F ₆ Fe ₃ O ₆ P ₆ S ₄	C ₆₃ H ₆₀ Au ₄ Cl ₈ FeO ₈ P ₄ S
crystal habit	orange prism	yellow plate	orange plate
crystal size/mm	0.65 × 0.35 × 0.25	0.45 × 0.25 × 0.10	0.70 × 0.45 × 0.03
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 1̄	<i>P</i> 1̄
<i>a</i> /Å	12.571(4)	15.177(3)	13.727(2)
<i>b</i> /Å	10.579(4)	18.408(4)	15.952(3)
<i>c</i> /Å	15.212(4)	27.894(8)	17.763(2)
α/deg		88.83(2)	71.738(12)
β/deg	107.84(3)	84.46(2)	73.264(14)
γ/deg		67.78(2)	75.96(2)
<i>U</i> /Å ³	1925.7(11)	7180(3)	3487.5(9)
<i>Z</i>	2	2	2
<i>D_c</i> /Mg m ⁻³	2.106	1.925	2.122
<i>M</i>	1221.10	4162.08	2228.37
<i>F</i> (000)	1160	3960	2112
<i>T</i> /°C	-130	-100	-100
2θ _{max} /deg	50	43	50
μ(Mo Kα)/mm ⁻¹	8.55	7.03	9.07
transmission	0.24–0.55	0.18–0.60	0.19–0.72
no. of reflcns measd	3617	15950	11617
no. of unique reflcns	3415	15877	11512
<i>R</i> _{int}	0.042	0.180	0.106
<i>R</i> ^a (<i>F</i> , <i>F</i> > 4σ(<i>F</i>))	0.040	0.078	0.077
<i>wR</i> ^b (<i>F</i> ² , all reflcns)	0.114	0.218	0.194
no. of parameters	218	556	797
no. of restraints	158	403	1096
<i>S</i> ^c	1.072	0.865	1.086
max Δρ/e Å ⁻³	2.32	1.88	2.93

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

Au(4)–S = 2.309(5) belong to the gold atoms bonded to PPh₂Me; it is well-known that axial bonds tend to be longer than equatorial in trigonal bipyramidal systems. The Au–P distances fall in the range 2.256(6)–2.265(6) Å and are longer than those found in complex **1** or [S(AuPPh₂Me)₃]⁺, but slightly shorter than those in the complex [S(AuPPh₃)₄]²⁺.

Studies carried out with the sulfur-centered cations [S(AuPR₃)₃]⁺ have shown the influence of the size and electronic/inductive effects of the phosphine ligand;¹⁹ thus with PMe₃ the [S(AuPMe₃)₃]⁺ pyramids are grouped in pairs through Au–Au contacts, which are further linked by other Au–Au interactions to give strings. The cations [S(AuPPh₂Me)₃]⁺ are paired across symmetry centers, while [S(AuPⁱPr)₃]⁺ are monomers. We have shown that the ligand attached to gold may also influence the structure of the monomers [S(AuL)₄]²⁺.

Experimental Section

General Procedures. Infrared spectra were recorded in the range 4000–200 cm⁻¹ on a Perkin-Elmer 883 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in *ca.* 5 × 10⁻⁴ mol dm⁻³ solutions with a Philips 9509 conductimeter and Λ_m is given in Ω⁻¹ cm² mol⁻¹. C, H, S analyses were carried out with a Perkin-Elmer 240C microanalyzer. NMR spectra were recorded on Varian 300 Unity and Bruker 300 spectrometers in CDCl₃. Chemical shifts are relative to SiMe₄ (¹H, external), 85% H₃PO₄ (³¹P, external), and CFC₃ (¹⁹F, external). Mass spectra were recorded on a VG Autospec using FAB techniques and nitrobenzyl alcohol as the matrix. The yields, analysis, conductivities, and infrared ν(Au–S) band are collected in Table 1. The starting materials [Au₂Cl₂(μ-dppf)],^{23,25} [Au(C₆F₅)tth],²⁶ [Au(CH₂PPh₃)tth]ClO₄,²⁷ and [Au(tth)₂]ClO₄²⁸ were pre-

pared by published procedures. [Au(OCIO₃)PR₃] was prepared from [AuCl(PR₃)₂]²⁹ and AgClO₄.

Synthesis of [S(Au₂dppf)] (1). To a solution of Li₂S (0.046 g, 1 mmol) in ethanol (50 mL) was added [Au₂Cl₂(μ-dppf)] (1.019 g, 1 mmol). The orange suspension was stirred for 2 h, and then the solid was filtered off to yield complex **1**.

Synthesis of [S(Au₂C₆F₅)(Au₂dppf)] (2). To a solution of [S(Au₂dppf)] (0.098 g, 0.1 mmol) in dichloromethane (20 mL) was added [Au(C₆F₅)tth] (0.045 g, 0.1 mmol) and then the mixture was stirred for 30 min. The solution was concentrated to *ca.* 5 mL and addition of hexane (15 mL) gave a yellow solution of complex **2**.

Synthesis of [S(AuL)(Au₂dppf)]ClO₄ (L = CH₂PPh₃ (3), PPh₃ (4), PPh₂Me (5)). To a solution of [S(Au₂dppf)] (0.098 g, 0.1 mmol) in 20 mL of dichloromethane was added [Au(CH₂PPh₃)tth]ClO₄ (0.066 g, 0.1 mmol) or [Au(OCIO₃)PPh₃] (0.1 mmol) or [Au(OCIO₃)PPh₂Me] (0.1 mmol) and then the mixture was stirred for 30 min. Solvent was evaporated to *ca.* 5 mL and addition of diethyl ether (15 mL) gave complexes **3–5**.

Synthesis of [(μ-Au){S(Au₂dppf)}₂]ClO₄ (6). To a dichloromethane solution (20 mL) of [S(Au₂dppf)] (0.196 g, 0.2 mmol) was added [Au(tth)₂]ClO₄ (0.047 g, 0.1 mmol). The solution was stirred for 5 min and the solvent was evaporated to *ca.* 5 mL. Addition of diethyl ether (15 mL) gave complex **6**.

Synthesis of [(μ-Au₂dppf){S(Au₂dppf)}₂](OTf)₂ (7). To a dichloromethane (20 mL) solution of [Au₂Cl₂(μ-dppf)] (0.102 g, 0.1 mmol) was added AgOTf (0.051 g, 0.2 mmol) and then the mixture was stirred for 2 h. The precipitated AgCl was filtered off and to the resulting solution containing [Au₂(OTf)₂(μ-dppf)] was added [S(Au₂dppf)] (0.196 g, 0.2 mmol), and then the mixture was stirred for 5 min. Evaporation of the solvent to *ca.* 5 mL and addition of hexane (10 mL) gave a yellow solid of complex **7**.

Synthesis of [S(AuPR₃)₂(Au₂dppf)](ClO₄)₂ (L = PPh₃ (8), PPh₂Me (9)). To a solution of [S(Au₂dppf)] (0.098 g, 0.1 mmol) in 20 mL of dichloromethane was added [Au(OCIO₃)PR₃] (0.2 mmol) and the mixture was stirred for 5 min. Evaporation of solvent to *ca.* 5 mL and addition of n-hexane (15 mL) gave complexes **8** or **9**.

X-ray Structure Determinations. Crystals were mounted in inert oil on glass fibres. Data were collected using monochromated Mo Kα

(25) Gimeno, M. C.; Laguna, A.; Sarroca, C.; Jones, P. G. *Inorg. Chem.* **1993**, *32*, 5926.

(26) Usón, R.; Laguna, A. *Organomet. Synth.* **1989**, *3*, 322.

(27) Aguirre, C. J.; Gimeno, M. C.; Laguna, A.; Laguna, M.; López de Luzuriaga, J. M.; Puente, F. *Inorg. Chim. Acta* **1993**, *208*, 31.

(28) Usón, R.; Laguna, A.; Laguna, M.; Jiménez, J.; Gómez, M. P.; Sainz, A.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1990**, 3457.

(29) Usón, R.; Laguna, A. *Inorg. Synth.* **1982**, *21*, 71.

radiation ($\lambda = 0.71073$). Diffractometer type: Stoe-STADI-4 (**1**), Siemens P4 (**7**, **9**), both with a Siemens low-temperature attachment. Scan type ω/θ (**1**), ω (**7**, **9**). Cell constants were refined from $\pm\omega$ angles (**1**) or setting angles (**7**, **9**) of *ca.* 60 reflections in the range 2θ 20–22°. Absorption corrections were applied on the basis of Ψ -scans (**9**) or with the program SHELXA (**1**, **7**).³⁰

Structures were solved by direct methods (**1**, **9**) or by the heavy-atom method (**7**) and refined on F^2 using the program SHELXL-93.³¹ All non-hydrogen atoms were refined anisotropically for complexes **1** and **9**, and for compound **7** only Au, Fe, S, and P atoms, with the others refined isotropically. Hydrogen atoms were included using a riding model. Because of the moderate quality of the X-ray data, the refinements were stabilized by an extensive system of restraints to light atom temperature factors and ring symmetry. Special refinement details were the following: Complex **7** contains eight identifiable chloroform sites, but the high displacement parameters indicate partial occupation. All calculations, however, assume the idealized composition. Complex **9** contains three CH₂Cl₂ sites; for two of these molecules, the two chlorine atoms are disordered over three positions. However, the true

(30) Sheldrick, G. M. SHELXA. A Program for Absorption Corrections (unpublished).

(31) Sheldrick, G. M. SHELXL-93. A Program for Crystal Structure Refinement; University of Göttingen, 1993.

disorder is probably more complicated. The precision of the structures of **7** and **9** necessarily suffers from the presence of solvent of crystallization with high displacement parameters. Other data are collected in Table 6.

Acknowledgment. We thank the Dirección General de Investigación Científica y Técnica (No. PB94-0079) and the Fonds der Chemischen Industrie for financial support. M.C.G. thanks the C.O.N.A.I. for financial support for a stay in Braunschweig.

Supporting Information Available: Tables of crystal data, data collection, and solution and refinement parameters, hydrogen atomic coordinates and thermal parameters, bond distances and angles, and anisotropic thermal parameters for **1**, **7**, and **9** (27 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA9517678