Substitution Reaction Studies on [Au_2Cl_2(μ-dppf)] (dppf = 1,1′-Bis(diphenylphosphino)ferrocene). Synthesis of the First Gold(I) Complex with a μ_3-2-Pyridinethiolate Ligand

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Substitution of the chlorine ligand in the complex [Au_2Cl_2(μ-dppf)] by other halogens or anionic ligands such as Spy^- (2-pyridinethiolate) or $S_2CNR_2^-$ have been carried out. The complexes [$Au_2(Spy)_2$(μ-dppf)] and [$Au_2(S_2CNR_2)_2$(μ-dppf)] possess a nitrogen or sulfur donor atom that can coordinate to a metallic fragment; thus reactions of these complexes with [Au(OTf)(PR_3)] in various molar ratios have been studied. The crystal structures of [Au_2I_2(μ-dppf)], [Au_2Cl_2(μ-dppf)], and [Au_3(μ_3-Spy)(μ-dppf)(PPh_2Me)]$(OTf)_2$ have been established by X-ray diffraction studies. The last represents the first example where a pyridinethiolate ligand bridges three gold atoms.

Introduction

Ferrocene-containing complexes are currently receiving much attention associated with their increasing role in the rapidly growing area of materials science. Because of its high stability and the well-established methods for its incorporation into more complex structures, ferrocene has become a versatile building block for the synthesis of compounds with tailormade properties.[1] The diphosphine 1,1′-bis(diphenylphosphino)ferrocene (dppf), although synthesized more than two decades ago,[2] has only recently received much attention because of its chemical uniqueness and industrial importance. Its catalytic potential is important because of the increasing use of homogeneous catalysis in organic synthesis and production of materials and fine chemicals.[1,3]

We previously reported on gold and silver complexes with the 1,1′-bis(diphenylphosphine)ferrocene ligand.[4] Here we have studied substitution reactions of the compound [Au_2Cl_2(μ-dppf)], both with other halogen ligands and with homo- or heterodifunctional ligands such as 2-pyridinethiolate or diethyldithiocarbamate. These ligands have been extensively used because of their versatile coordination behavior. In particular, 2-pyridinethiolate can act as a monodentate (as S- or N-donor)[5] or bidentate ligand, in the latter mode either chelating or bridging two, three, or even four metal centers.[6] In contrast, only a few gold(I) derivatives have been obtained, most of them with the ligand acting as an S-donor ligand.[7] Thus we have prepared several gold−dppf derivatives with 2-pyridinethiolate or dithiocarbamate ligands acting as μ_2 and μ_3 ligands. The structure of [Au_3(μ_3-Spy)(μ-dppf)(PPh_2Me)]$(OTf)_2$ has been established by X-ray diffraction and represents the first example of a gold species with a triply bridging pyridinethiolate ligand.

Results and Discussion

The reaction of [Au_2Cl_2(μ-dppf)] **1** (dppf = 1,1′-bis(diphenylphosphino)ferrocene) with KX in acetone leads to the substitution of the chlorine ligand to give [Au_2X_2(μ-dppf)] (X = Br (**2**), I (**3**)). Complexes **2** and **3** are nonconducting in acetone.

The $^{31}P\{^1H\}$ NMR spectra show a singlet for the equivalent phosphorus atoms. In the ^1H NMR spectra, three multiplets with an intensity ratio 1:1:5 appear, corresponding to the α and β cyclopentadienyl protons and the phenyl groups, respectively.

In the positive-ion mass spectra (FAB^+) of complexes **2** and **3**, the molecular peak is not present but the peaks arising from the loss of one bromine or iodine atom appear at m/z = 1026 (**2**, 100%, [$Au_2Br(dppf)$]$^+$) and 1075 (**3**, 100%, [$Au_2I(dppf)$]$^+$).

The structures of complexes **1** (as a bis(dichloromethane) solvate) and **3** have been established by X-ray diffraction methods. The structure of the $^2/_3$ chloroform solvate of **1** was

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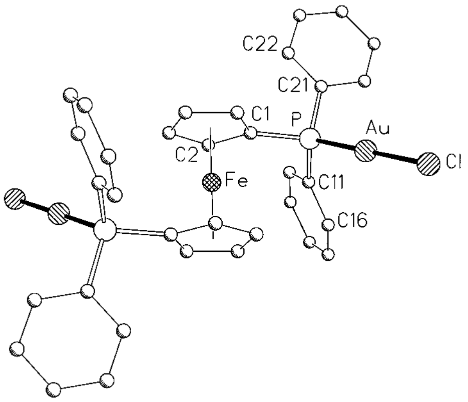

Figure 1. The molecule of complex **1** in the crystal showing the atom-numbering scheme. Radii are arbitrary. H atoms are omitted for clarity.

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

Au−P	2.2262(13)	Au−Cl	2.2815(13)
Fe−C(1)	2.040(5)	Fe−C(5)	2.044(5)
Fe−C(2)	2.046(5)	Fe−C(3)	2.052(5)
Fe−C(4)	2.063(5)	P−C(1)	1.787(5)
P−C(11)	1.809(5)	P−C(21)	1.814(5)
C(1)−C(5)	1.424(7)	C(1)−C(2)	1.437(7)
C(2)−C(3)	1.413(8)	C(3)−C(4)	1.409(9)
C(4)−C(5)	1.415(8)	C(11)−C(12)	1.385(7)
C(11)−C(16)	1.399(7)	C(12)−C(13)	1.372(7)
C(13)−C(14)	1.387(7)	C(14)−C(15)	1.382(7)
C(15)−C(16)	1.377(7)	C(21)−C(22)	1.386(7)
C(21)−C(26)	1.393(7)	C(22)−C(23)	1.400(8)
C(23)−C(24)	1.376(8)	C(24)−C(25)	1.383(9)
C(25)−C(26)	1.379(8)	Cl(1)−C(99)	1.776(8)
Cl(2)−C(99)	1.728(8)		
P−Au−Cl	179.59(5)	C(1)−P−C(11)	107.3(2)
C(1)−P−C(21)	105.7(2)	C(11)−P−C(21)	103.4(2)
C(1)−P−Au	113.4(2)	C(11)−P−Au	114.4(2)
C(21)−P−Au	111.7(2)		

already known;[8] there the compound crystallized with two independent molecules, one of which displayed inversion symmetry. The molecule of **1** in the current structure is shown in Figure 1; selected bond lengths and angles are collected in Table 1. The iron atom lies on a symmetry center. The dppf ligand coordinates the metal centers in an open bridging mode. The P−Au−Cl angle is 179.59(5)°, very close to the ideal linear value. The Au−P and the Au−Cl bond distances are 2.2262(13) and 2.2815(13) Å, respectively, which are similar to those found in the earlier determination [Au−P 2.222−2.239, Au−Cl 2.273−2.300 Å][8] and in the complex $[AuCl(PPh_3)]$.[9] The cyclopentadienyl ring is planar and located 1.655(2) Å from the iron atom; by symmetry, both Cp rings are parallel and staggered. There is no Fe−Au interaction, with the shortest such distance being 4.29(1) Å. In contrast to the other modification,[8] there is no short Au···Au contact (none <5.78Å).

The molecule of complex **3** is shown in Figure 2, and selected bond lenghts and angles are given in Table 2. It too crystallizes with two molecules of dichloromethane, but **1** and **3** are not isostructural. The coordination around the gold atoms is linear with P−Au−I angles of 177.7(2) and 176.3(2)°. The Au−I distances are 2.545(3) and 2.561(2) Å; these fall in the range found for complexes of the type $[AuI(PR_3)]$[10] (2.583(1) Å, PMe_3; 2.553(1) Å, PPh_3). The Au−P distances are slightly longer than those in **1**, 2.248(9) and 2.240(8) Å, although similar to those in $[AuI(PR_3)]$ (2.256(3) Å, PMe_3; 2.249(2) Å, PPh_3). The higher *trans* influence of the iodine compared to the chlorine ligand is presumably the factor responsible for the elongation of the Au−P distances in complex **3**. The cyclopentadienyl rings adopt a staggered conformation.

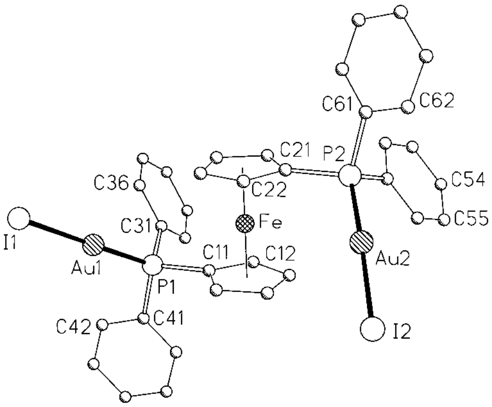

Figure 2. Molecular structure of complex **3** in the crystal. H atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **3**

Au(1)−P(1)	2.248(9)	Au(1)−I(1)	2.545(3)
Au(2)−P(2)	2.240(8)	Au(2)−I(2)	2.561(2)
P(1)−Au(1)−I(1)	177.7(2)	P(2)−Au(2)−I(2)	176.3(2)
C(41)−P(1)−C(31)	104.2(10)	C(41)−P(1)−C(11)	105.3(10)
C(31)−P(1)−C(11)	106.2(10)	C(41)−P(1)−Au(1)	113.4(8)
C(31)−P(1)−Au(1)	114.4(8)	C(11)−P(1)−Au(1)	112.5(8)
C(51)−P(2)−C(21)	108.5(10)	C(51)−P(2)−C(61)	103.2(11)
C(21)−P(2)−C(61)	103.7(10)	C(51)−P(2)−Au(2)	113.9(8)
C(21)−P(2)−Au(2)	111.4(8)	C(61)−P(2)−Au(2)	115.3(7)

We have carried out further substitution reactions on complex **1** with other anionic ligands such as pyridinethiolate (Spy^-) and dithiocarbamate ($S_2CNR_2^-$) with the aim of studying further coordination reactions of the nitrogen or sulfur donor atoms present in these ligands. Thus the treatment of **1** with NaSpy or NaS_2CNEt_2 in dichloromethane affords the species $[Au_2(SR)_2(\mu\text{-dppf})]$ (SR = Spy (**4**), S_2CNEt_2 (**5**)) in good yields. Complexes **4** and **5** behave as nonconductors in acetone. In their IR spectra the vibrations ν(C=N) corresponding to the pyridinethiolate or dithiocarbamate ligands are observed at 1573 (m) and 1550 (s) (Spy^-) and 1482 (m) ($S_2CNEt_2^-$) cm^{-1}.

The ^1H NMR spectra show, apart from the multiplets arising from the phenyl protons, the two multiplets assigned to the α and β protons of the cyclopentadienyl rings; furthermore, **4** presents the four resonances for the protons of the equivalent pyridine groups and **5** a quartet and a triplet for the ethyl protons of the dithiocarbamate. In the $^{31}P\{^1H\}$ NMR, only one resonance appears for the two equivalent phosphorus atoms.

In the positive-ion fast-atom bombardment (FAB^+) mass spectra, the molecular peaks do not appear but the fragments arising from the loss of one ionic ligand, similar to those observed for complexes **1**−**3**, are the most abundant; this peak appears for **4** at m/z = 1096 and for **5** at m/z = 1057.

As mentioned above, complexes **4** and **5** offer the possibility of studying further coordination reactions of metallic fragments. Thus the treatment of these complexes with 2 equiv of $[Au(OTf)(PPh_2Me)]$ (OTf = trifluoromethanesulfonate) or $[Au(OClO_3)(PPh_2Me)]$ in dichloromethane affords the species $[Au_4(\mu\text{-SR})_2(\mu\text{-dppf})(PPh_2Me)_2]X_2$ (SR = Spy (**6**), X = OTf; SR = S_2CNEt_2 (**7**), X = ClO_4). Their NMR spectra present the same resonances as the starting materials and additionally those arising from the tertiary phospine, which are

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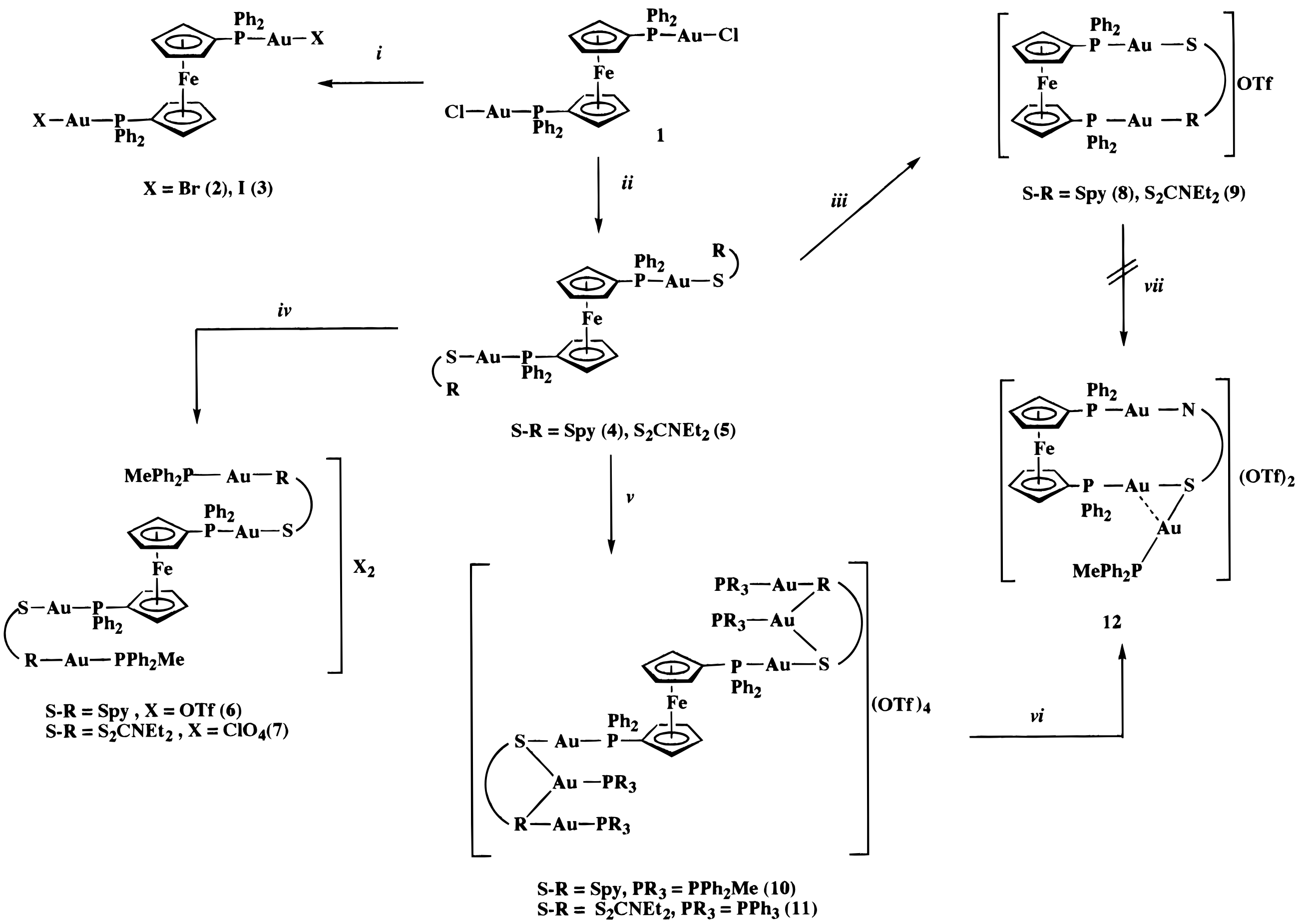
Scheme 1[a]



[a] Key: (i) 2 KX; (ii) 2 HSpy + Na_2CO_3 or NaS_2CNEt_2; (iii) $[Ag(OTf)(PPh_3)]$ or Ag(OTf); (iv) 2 $[Au(OTf)(PPh_2Me)]$ or 2 $[Au(OClO_3)(PPh_2Me)]$; (v) 4 $[Au(OTf)(PR_3)]$; (vi) decomposition; (vii) $[Au(OTf)(PPh_2Me)]$.

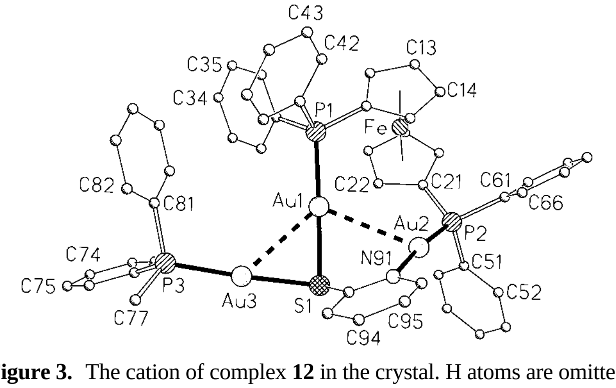


Figure 3. The cation of complex **12** in the crystal. H atoms are omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **12**

Au(1)−P(1)	2.246(4)	Au(1)−S(1)	2.341(4)
Au(1)−Au(3)	3.0985(12)	Au(1)−Au(2)	3.2105(13)
Au(2)−N(91)	2.065(14)	Au(2)−P(2)	2.239(5)
Au(3)−P(3)	2.252(6)	Au(3)−S(1)	2.337(6)
P(1)−Au(1)−S(1)	177.9(2)	P(1)−Au(1)−Au(3)	129.55(14)
S(1)−Au(1)−Au(3)	48.47(14)	P(1)−Au(1)−Au(2)	114.59(14)
S(1)−Au(1)−Au(2)	67.23(14)	Au(3)−Au(1)−Au(2)	115.12(3)
N(91)−Au(2)−P(2)	173.3(5)	N(91)−Au(2)−Au(1)	76.6(5)
P(2)−Au(2)−Au(1)	110.00(14)	P(3)−Au(3)−S(1)	176.8(2)
P(3)−Au(3)−Au(1)	128.27(13)	S(1)−Au(3)−Au(1)	48.56(10)
C(92)−S(1)−Au(3)	108.1(6)	C(92)−S(1)−Au(1)	96.5(5)
Au(3)−S(1)−Au(1)	83.0(2)	C(11)−P(1)−C(41)	103.3(7)
C(11)−P(1)−C(31)	106.1(6)	C(41)−P(1)−C(31)	107.5(7)
C(11)−P(1)−Au(1)	115.3(5)	C(41)−P(1)−Au(1)	114.1(4)
C(31)−P(1)−Au(1)	109.9(5)	C(21)−P(2)−C(51)	107.8(7)
C(21)−P(2)−C(61)	105.8(7)	C(51)−P(2)−C(61)	104.5(7)
C(21)−P(2)−Au(2)	116.5(5)	C(51)−P(2)−Au(2)	109.0(5)
C(61)−P(2)−Au(2)	112.5(5)	C(77)−P(3)−C(81)	109.0(10)
C(77)−P(3)−C(71)	102.4(10)	C(81)−P(3)−C(71)	104.4(7)
C(77)−P(3)−Au(3)	113.8(9)	C(81)−P(3)−Au(3)	111.1(5)
C(71)−P(3)−Au(3)	115.4(6)	C(92)−N(91)−C(96)	118(2)
C(92)−N(91)−Au(2)	121.0(13)	C(96)−N(91)−Au(2)	121.0(14)

a doublet for the methyl protons in the ^1H NMR spectra and a singlet for the equivalent phosphorus atoms in the $^{31}P\{^1H\}$ NMR spectra.

The positive-ion fast-atom bombardment (FAB^+) mass spectra of **6** and **7** do not show the molecular peaks as expected for dicationic species; however, the fragments arising from the loss of one ClO_4^- or OTf^-, respectively, appear at $m/z = 2111$ (**6**, 2%) and 2137 (**7**, 45%).

Similar reactions have been carried out with silver complexes, but in this case the result is different because we obtain the same complexes irrespective of the silver precursor used. Thus the treatment of **4** or **5** with $[Ag(OTf)PR_3]$ or AgOTf affords the dinuclear gold complexes bridged by two different ligands, $[Au_2(\mu\text{-SR})(\mu\text{-dppf})]OTf$ (SR = Spy (**8**), S_2CNEt_2 (**9**)), and the formation of $[Ag(Spy)]_n$ or $[Ag(S_2CNEt_2)]_n$. The ease of formation of $[Ag(Spy)]_n$ and $[Ag(S_2CNEt_2)]_n$ may be due to their insolubility in the reaction media.

Complexes **8** and **9** behave as 1:1 electrolytes in acetone solutions. Their IR spectra show bands arising from the diphosphine and the triflate anion and $\nu(C{=}N)$ vibrations at 1513 (w) and 1590 (m) cm^{-1}.

The ^1H NMR spectra present signals similar to those observed for the previous compounds, but now the dppf:ligand ratio is 1:1. The $^{31}P\{^1H\}$ spectra show only a singlet for the two

Table 4. NMR Data for Complexes **2**−**11**

		^1H			^{31}P	
complex	no.	δ(dppf)	δ(SR)	δ(L)	δ(dppf)	δ(L)
$[Au_2Br_2(\mu\text{-dppf})]$	**2**	4.29 (m) 4.73 (m)			27.5 (s)	
$[Au_2I_2(\mu\text{-dppf})]$	**3**	4.33 (m) 4.69 (m)			34.42 (s)	
$[Au_2(Spy)_2(\mu\text{-dppf})]$	**4**	4.34 (m) 4.80 (m)	6.84 (d) 7.29 (t) 8.23 (d)		32.3 (s)	
$[Au_2(S_2CNEt_2)_2(\mu\text{-dppf})]$	**5**	4.30 (m) 4.82 (m)	1.35 (t) 3.94 (q)		27.7 (s)	
$[Au_4(\mu\text{-Spy})_2(\mu\text{-dppf})(PPh_2Me)_2\}](OTf)_2$	**6**	4.27 (m) 4.57 (m)	7.43 (d) 7.69 ("t") 8.45 ("t")	2.02 (s)	28.0 (s)	17.9 (s)
$[Au_4(\mu\text{-}S_2CNEt_2)(\mu\text{-dppf})(PPh_2Me)_2](ClO_4)_2$	**7**	4.40 (m) 4.47 (m)	1.57 (t) 4.07 (q)	1.45 (d)	32.1 (s)	21.2 (s)
$[Au_2(\mu\text{-Spy})(\mu\text{-dppf})]OTf$	**8**	4.28 (m) 4.56 (m)	7.39 (d) 7.74 (t)		32.9 (s) 27.4 (br)[a]	
$[Au_2(\mu\text{-}S_2CNEt_2)(\mu\text{-dppf})]OTf$	**9**	4.36 (m) 4.45 (m)	1.44 (t) 4.05 (q)		32.9 (s)	
$[Au_6(\mu\text{-Spy})_2(\mu\text{-dppf})(PPh_2Me)_4](OTf)_4$	**10**	4.18 (m) 4.67 (m)	7−9 (m)	1.96 (s)	27.1 (s) 22.8 (s)[a]	17.2 (s) 18.9 (s), 12.6 (s)[a]
$[Au_6(\mu\text{-}S_2CNEt_2)_2(\mu\text{-dppf})(PPh_3)_4](OTf)_4$	**11**	4.28 (m) 4.52 (m)	1.63 (t) 4.07 (q)		34.6 (s) 36.8 (s)[b]	31.0 (m) 32.8 (s), 31.1 (s)[b]

[a] Measured at −85 °C in CD_2Cl_2. [b] Measured at −80 °C in $(CD_3)_2CO$.

phosphorus atoms. The $^{31}P\{^1H\}$ spectrum of **8** has been recorded at low temperature (at −55 °C in $CDCl_3$ and at −85 °C in CD_2Cl_2) and a broadening of the signal is observed (at −85 °C, $\Delta = 726$ Hz) but the signal does not split into two singlets as expected. Fluxional processes involving the 2-pyridinethiolate ligand (through intermediates in which the ligand acts as an S-donor bridge) have already been proposed for rhodium and gold complexes.[7e,11]

The positive-ion fast-atom bombardment mass spectra show the cation molecular peaks at $m/z = 1058$ (**8**, 100%) and 1096 (**9**, 100%). There also appears with high abundance the fragment $[Au(dppf)]^+$ at $m/z = 751$.

We have also studied further reactions of **4** and **5** with $[Au(OTf)PR_3]$ (molar ratio 1:4) with the aim of incorporating more $AuPR_3^+$ fragments at the thiolate or dithiocarbamate ligands. The complexes $[Au_6(\mu\text{-SR})_2(\mu\text{-dppf})(PR_3)_4](OTf)_4$ (SR = Spy, $PR_3 = PPh_2Me$ (**10**); SR = S_2CNEt_2, $PR_3 = PPh_3$ (**11**)) have been isolated as yellow solids, stable to air and moisture. Their conductivities measured in acetone are in agreement with the proposed formulas, 315 (**10**) and 356 (**11**) Ω^{-1} cm^2 mol^{-1}. Although there are not many data for conductivities of highly charged compounds, the values obtained seem appropriate for tetracationic species; we obtained similar values for the $[S(AuPR_3)_6]^{4+}$ species.[12]

The ^1H NMR spectra of **10** and **11** are similar to those of complexes **6** and **7**; the most significant differences are seen in the integral ratio for the protons, which is consistent with the coordination of four $AuPR_3^+$ fragments. The $^{31}P\{^1H\}$ NMR spectra at room temperature show in both cases two singlets in a 1:2 ratio which should correspond to two phosphorus environments, namely the phosphorus of dppf and that of the tertiary phosphines. When the experiments are carried out at low temperature, three singlets of an approximate 1:1:1 ratio appear for complexes **10** and **11**, which indicates that there are three different phosphorus enviroments because the two $AuPR_3^+$ fragments bonded to the same SR^- ligand are not equivalent. The chemical shifts of complexes **6** and **10** can be compared, and a high-field displacement is observed in the resonances of complex **10** as a consequence of the further coordination of a (phosphine)gold unit. This upfield shift was previously observed by us in the complexes $[S(AuPR_3)_n]^{(n-2)+}$ ($n = 2-6$).[12] These data lead us to propose the structure shown in Scheme 1; this type of structure has been found for dithiolate complexes such as $[Au_3(3,4\text{-}S_2C_6H_3Me)(PPh_3)_3]ClO_4$,[13] $[Au_3\{S_2(CH_2)_2\}(PPh_3)_3]BF_4$,[14]or$[(Ph_3PAu)SCH_2CHS(AuPPh_3)CH_2S(AuPPh_3)_2]BF_4$.[15]

In an attempt to structurally characterize complex **10** or **11**, we obtained single crystals by slow diffusion of hexane into a dichloromethane solution of complex **10**. However, the consequent X-ray diffraction studies revealed the compound $[Au_3(\mu_3\text{-Spy})(\mu\text{-dppf})(PPh_2Me)](OTf)_2$, **12** (as a tetrachloroethane solvate) (Figure 3), presumably having arisen by decomposition of complex **10**. We tried to synthesize complex **12** deliberately by reaction of $[Au_2(\mu\text{-Spy})(\mu\text{-dppf})]OTf$ (**8**) with $[Au(OTf)PPh_2Me]$ in dichloromethane, but a mixture of complexes was obtained.

Selected bond lengths and angles are collected in Table 3. The cation of **12** consists of two gold atoms bridged by two different ligands, dppf and 2-pyridinethiolate; the third gold atom is bonded to a tertiary phosphine and to the sulfur atom of the thiolate ligand. In this manner Spy^- acts as a triply bridging ligand.

The gold atoms have geometries slightly distorted from linearity with angles P(1)−Au(1)−S 177.9(2), N(91)−Au(2)−P(2) 173.3(5), and P(3)−Au(3)−S(1) 176.8(2)°; the latter deviations from 180° may be associated with the imposed restrictions of the 2-pyridinethiolate ligand and the weak gold−gold interactions, Au(1)−Au(2) 3.2105(13) and Au(1)−Au(3) 3.0985(12) Å. The gold−gold distance in the ring is considerably longer than was found in the complex $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}(\mu\text{-Spy})]$ (2.8623(7) Å),[7e] which also has two different bridging ligands. The Au−S distances, 2.341(4) and 2.337(6) Å, are as

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Table 5. Details of Data Collection and Structure Refinement for Complexes **1**, **3**, and **12**

	$\mathbf{1}\cdot CH_2Cl_2$	$\mathbf{3}\cdot 2CH_2Cl_2$	$\mathbf{12}\cdot C_2H_4Cl_2$
empirical formula	$C_{36}H_{32}AuCl_6FeP_2$	$C_{36}H_{32}Au_2Cl_4FeI_2P_2$	$C_{56}H_{49}Au_3Cl_2F_6FeNO_6P_3S_3$
crystal habit	colorless prism	yellow needle	colorless prism
crystal size/mm	0.60 × 0.50 × 0.50	0.70 × 0.20 × 0.04	0.40 × 0.40 × 0.20
crystal system	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a/Å	8.671(2)	11.955(3)	13.831(3)
b/Å	9.867(2)	13.472(3)	14.181(3)
c/Å	12.359(3)	14.596(2)	31.059(7)
α/deg	81.82(2)	85.85(2)	
β/deg	74.45(3)	70.16(2)	102.17(2)
γ/deg	70.56(2)	66.04(2)	
V/Å^3	959.0(4)	2015.1(7)	5955(2)
Z	1	2	4
D_c/g cm^{-3}	2.059	2.261	2.067
M	1189.04	1371.94	1852.70
$F(000)$	564	1272	3536
T/°C	−100	−100	−100
$2\theta_{max}$/deg	50	50	50
μ(Mo $K\alpha$)/cm^{-1}	85.31	95.20	79.51
transm	0.553−1.0	0.035−0.839	0.340−0.968
no. of reflns measd	4365	7067	11278
no. of unique reflns	3342	6796	10472
R_{int}	0.021	0.241	0.027
R^a ($F > 4\sigma(F)$)	0.026	0.111	0.067
$R_w{}^b$ (F^2, all reflns)	0.068	0.312	0.188
no. of reflns used	3340	6776	10460
no. of parameters	215	178	281
no. of restraints	154	0	46
S^c	1.022	1.065	0.865
max $\Delta\rho$/e Å^{-3}	1.503	3.048	1.585

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F^2) = [\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]]^{0.5}$; $w^{-1} = \sigma^2(F_o{}^2) + (aP)^2 + bP$, 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.

expected longer than those in the latter compound since in **10** the sulfur atom is bonded to two metals. The Au−N bond length of 2.065(14) Å is similar to that found in $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}(\mu\text{-Spy})]$ (2.060(10) Å).

The cyclopentadienyl rings adopt a conformation approximately midway between staggered and eclipsed.

Experimental Section

Instrumentation. 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 conductometer. C and H analyses were carried out with a Perkin-Elmer 2400 microanalyzer. Mass spectra were recorded on a VG Autospec, with the FAB technique, using nitrobenzyl alcohol as matrix. NMR spectra were recorded on a Varian Unity 300 spectrometer and a Bruker ARX 300 spectrometer in $CDCl_3$. Chemical shifts are cited relative to $SiMe_4$ (^1H, external) and 85% H_3PO_4 (^{31}P, external) (Table 4).

Materials. The starting materials $[Au_2Cl_2(\mu\text{-dppf})]$[4a] and $[AuCl(PR_3)]$[16] were prepared by published procedures. $[Au(OTf)(PR_3)]$ or $[Au(OClO_3)PR_3]$ was obtained from $[AuCl(PR_3)]$ by reaction with AgOTf or $AgClO_4$, respectively.

Safety Note! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of materials should be prepared, and these should be handled with great caution.

Syntheses. $[Au_2X_2(\mu\text{-dppf})]$ (X = Br (2), I (3)). To a solution of $[Au_2Cl_2(\mu\text{-dppf})]$ (0.102 g, 0.1 mmol) in acetone (20 mL) was added KX (0.024 g, X = Br; 0.034 g, X = I; 0.2 mmol). The mixture was stirred for 1 day; then the solvent was evaporated to dryness and the product redissolved in dichloromethane (20 mL) in order to eliminate the insoluble KX. The solution was concentrated to ca. 5 mL, and addition of diethyl ether (15 mL) gave complex **2** or **3** as an orange solid. Complex **2**: yield 84%; Λ_M 1 Ω^{-1} cm^2 mol^{-1}. Anal. Calc for $C_{34}H_{28}Au_2Br_2FeP_2$: C, 36.85; H, 2.55. Found: C, 37.15; H, 2.33. Complex **3**: yield 60%; Λ_M 7 Ω^{-1} cm^2 mol^{-1}. Anal. Calc for $C_{34}H_{28}Au_2FeI_2P_2$: C, 33.97; H, 2.35. Found: C, 34.24; H, 2.35.

$[Au_2(Spy)_2(\mu\text{-dppf})]$, 4. To a solution of $[Au_2Cl_2(\mu\text{-dppf})]$ (0.102 g, 0.1 mmol) in dichloromethane (25 mL) were added HSpy (0.022 g, 0.2 mmol) and Na_2CO_3 (0.4 g). The mixture was stirred for 3 h and then filtered to remove sodium carbonate. The solution was concentrated to ca. 5 mL, and addition of diethyl ether (15 mL) gave complex **4** as a yellow solid: yield 86%; Λ_M 0.6 Ω^{-1} cm^2 mol^{-1}. Anal. Calc for $C_{44}H_{36}Au_2FeN_2P_2S_2$: C, 45.22; H, 3.10; N, 2.39; S, 5.48. Found: C, 44.52; H, 2.83; N, 2.18; S, 4.84.

$[Au_2(S_2CNEt_2)_2(\mu\text{-dppf})]$, 5. To a solution of $[Au_2Cl_2(\mu\text{-dppf})]$ (0.102 g, 0.1 mmol) in a dichloromethane−water mixture (20:5 mL) was added $NaS_2CNEt_2\cdot 3H_2O$ (0.045 g, 0.2 mmol). The mixture was stirred for 2 h, and then the organic phase was separated from the mixture. The solution was concentrated to ca. 5 mL, and addition of diethyl ether (15 mL) gave complex **5** as a yellow solid: yield 99%; Λ_M 0.8 Ω^{-1} cm^2 mol^{-1}. Anal. Calc for $C_{44}H_{38}Au_2FeN_2P_2S_4$: C, 42.45; H, 3.89; N, 2.26; S, 10.3. Found: C, 42.58; H, 3.40; N, 2.26; S, 9.90.

$[Au_4(\mu\text{-SR})_2(\mu\text{-dppf})(PPh_2Me)_2]X_2$ (SR = Spy (6), X = OTf; SR = S_2CNEt_2 (7), X = ClO_4). To a dichloromethane solution (15 mL) of complex **4** (0.117 g, 0.1 mmol) or **5** (0.124 g, 0.1 mmol) was added a freshly prepared solution of $[Au(OTf)PPh_2Me]$ or $[Au(OClO_3)PPh_2Me]$ (0.2 mmol, 20 mL). The mixture was stirred for 30 min, and then the solvent was evaporated under vacuum to ca. 5 mL; addition of diethyl ether (15 mL) afforded complex **6** or **7** as a yellow solid. Complex **6**: yield 96%; Λ_M 186 Ω^{-1} cm^2 mol^{-1}. Anal. Calc for $C_{72}H_{62}Au_4F_6FeN_2O_6P_4S_4$: C, 38.3; H, 2.76; N, 1.23; S, 5.66. Found: C, 38.6; H, 2.86; N, 1.36; S, 4.80. Complex **7**: yield 75%; Λ_M 204 Ω^{-1} cm^2 mol^{-1}. Anal. Calc for $C_{70}H_{64}Au_4Cl_2FeN_2O_8P_4S_4$: C, 37.6; H, 3.33; N, 1.25; S, 5.73. Found: C, 38.4; H, 2.81; N, 1.20; S, 5.29.

$[Au_2(\mu\text{-SR})(\mu\text{-dppf})]OTf$ (SR = Spy (8), S_2CNEt_2 (9)). To a dichloromethane solution (20 mL) of complex **4** (0.117 g, 0.1 mmol) or **5** (0.124 g, 0.1 mmol) was added AgOTf (0.026 g, 0.1 mmol). The mixture was stirred for 30 min, and then the $[Ag(SR)]_n$ formed was filtered off. The solution was concentrated under vacuum to ca. 5 mL; addition of diethyl ether (15 mL) afforded complex **8** or **9** as a yellow solid. Complex **8**: yield 88%; Λ_M 121.5 Ω^{-1} cm^2 mol^{-1}. Anal. Calc for $C_{40}H_{32}Au_2F_3FeNO_3P_2S_2$: C, 39.8; H, 2.65; N, 1.16; S, 5.31.

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Found: C, 39.7; H, 2.70; N, 1.27; S, 3.01. Complex **9**: yield 96%; Λ_M 100.3 Ω^{-1} cm^2 mol^{-1}. Anal. Calc for $C_{39}H_{38}Au_2F_3FeN_2O_3P_2S_4$: C, 37.6; H, 3.07; N, 1.12; S, 12.8. Found: C, 37.5; H, 2.64; N, 1.82; S, 10.1.

[Au_6(μ-SR)$_2$(μ-dppf)(PR_3)$_4$](OTf)$_4$ (SR = Spy (10), PR_3 = PPh_2Me; SR = S_2CNEt_2 (11), PR_3 = PPh_3). To a dichloromethane solution (15 mL) of complex **4** (0.117 g, 0.1 mmol) or **5** (0.124 g, 0.1 mmol) was added a freshly prepared solution of [Au(OTf)PPh_2Me] or [Au(OTf)PPh_3] (0.4 mmol, 20 mL). The mixture was stirred for 30 min, and then the solvent was evaporated in vacuum to ca. 5 mL; addition of diethyl ether (15 mL) afforded complex **10** or **11** as a yellow solid. Complex **10**: yield 76%; Λ_M 315 Ω^{-1} cm^2 mol^{-1}. Anal. Calc for $C_{100}H_{88}Au_6F_{12}FeN_2O_{12}P_6S_6$: C, 35.8; H, 2.64; N, 0.83; S, 5.73. Found: C, 36.14; H, 2.65; N, 0.86; S, 5.65. Complex **11**: yield 96%; Λ_M 356 Ω^{-1} cm^2 mol^{-1}. Anal. Calc for $C_{120}H_{98}Au_6F_{12}FeN_2O_{12}P_6S_8$: C, 39.2; H, 2.94; N, 0.76; S, 6.97. Found: C, 39.6; H, 3.20; N, 0.92; S, 7.54.

Crystal Structure Determinations

The crystals were mounted in inert oil on glass fibers and transferred to the cold gas stream of a Siemens P4 diffractometer equipped with an LT-2 low-temperature device. Data were collected using monochromated Mo Kα radiation (λ = 0.710 73 Å). Scan type: ω. Cell constants were refined from setting angles of *ca.* 60 reflections in the 2θ range 10−25°. Absorption corrections were applied on the basis of Ψ scans. Structures were solved by the heavy-atom method and refined on F^2 using the program SHELXL-93.[17] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included using a riding model. Further details are given in Table 5. Special problems for **12**: The triflate ions are badly resolved although recognizable; the dichloroethane is severely disordered and was refined solely as three chlorine sites, two of which are half-occupied. For complex **1** a system of restraints on light-atom displacement-factor components and local ring symmetry was used.

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Supporting Information Available: Three X-ray crystallographic files, in CIF format, are available on the Internet only. Access information is given on any current masthead page.

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