Synthesis of the Ferrocene Derivative FcCHN$(CH_2)_2$SH [Fc = $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$]: Reactivity toward (Phosphine)gold(I) Cations

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The condensation reaction of ferrocenecarbaldehyde with β-mercaptoethylamine gives FcCHN$(CH_2)_2$SH [Fc = $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$], which is easily oxidized to the disulfide derivative FcCHN$(CH_2)_2S_2(CH_2)_2$NCHFc. Treatment of FcCHN$(CH_2)_2$SH with [AuCl(PPh_3)] in the presence of Na_2CO_3 affords the thiolate gold(I) complex [FcCHN$(CH_2)_2$S$(AuPPh_3)$]. Further reaction of the latter with various molar ratios of [Au(TfO)PPh_3] (TfO = trifluoromethanesulfonate) leads to di-, tri-, and tetranuclear gold species in which the metallic centers are bonded to the sulfur and nitrogen ligands. The reaction of FcCHN$(CH_2)_2$SH with [$Au_2(TfO)_2(\mu$-dppf)] in a 1:1 or 1:2 molar ratio has also been carried out to give [FcCHN$(CH_2)_2$S{$Au_2(\mu$-dppf)}]TfO or [FcCHN$(CH_2)_2$S{$Au_2(\mu$-dppf)}$_2$](TfO)$_3$. The crystal structure of [FcCHN$(AuPPh_3)(CH_2)_2$S$(AuPPh_3)_2$](TfO)$_2$ reveals short gold−gold interactions.

Introduction

The design and synthesis of electrochemically responsive ligand systems in which a redox-active center is in close proximity to a host binding site have attracted considerable interest[1,2] because of their importance as electron reservoir systems[3] and in fields such as electrocatalysis.[3,4−6] In recent years a large number of redox-active molecules have been synthesized, mainly with transition metal sandwiches. Among them ferrocene is probably the best known, and a large number of ferrocene derivatives have been obtained by suitable chemical attachment of organic groups to the cyclopentadienyl rings. Furthermore the functionalization of ferrocene with molecules containing coordination sites in order to obtain ligands bearing electroactive groups has received considerable recent attention.[7−14] We are interested in the synthesis of such ligands and their reactivity with metallic centers.

Here we report on the synthesis of the ferrocene derivative FcCHN$(CH_2)_2$SH and the study of some stepwise reactions with gold cations. The coordination of the gold centers can take place through the sulfur or the nitrogen atoms. The crystal structure of the trinuclear species [FcCHN$(AuPPh_3)(CH_2)_2$S$(AuPPh_3)_2$]-(TfO)$_2$ revealed coordination of one gold(phosphine) fragment to the nitrogen and two fragments to the sulfur atom, and formation of short gold−gold contacts.

Results and Discussion

Synthesis. Reaction of ferrocenecarbaldehyde with β-mercaptoethylamine, $NH_2(CH_2)_2SH$, in refluxing tetrahydrofuran resulted in an orange-red solution. Thin layer chromatography showed the presence of two compounds, which were isolated by column chromatography. The first band, separated by elution with CH_2Cl_2/hexane (1:1), corresponded to the starting material, and the second band corresponded to the desired ligand FcCHN-$(CH_2)_2$SH (**1**), obtained in moderate yield (35%).

The IR spectrum shows absorptions arising from the ferrocene moiety at 1412 (s), 1108 (s), and 1001 (m) cm^{-1}, and the vibrations ν(S−H) at 3252 (m) cm^{-1} and ν(N−C) at 1693 (m) cm^{-1}. The ^{1}H NMR spectrum presents the resonances of the substituted cyclopentadienyl ring at 4.18 (m), 4.29 (m), and 4.44 (m) with relative intensity 2:1:1, with the five protons of the unsubstituted Cp ring at 4.21 (s). The methylene protons appear as two overlapped multiplets at 3.06, whereas the signals of the CH and SH protons are found at 3.6 and 5.35 ppm, respectively.

Usually the ^{1}H NMR spectra of monosubstituted ferrocene derivatives show two multiplets for the α and β protons of the substituted Cp ring and a singlet for the unsubstituted Cp. In the solid state these protons are inequivalent because of the different ring conformations; although this inequivalence is

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(1) Beer, P. D. *Chem. Soc. Rev.* **1989**, *18*, 4; *Adv. Inorg. Chem.* **1992**, *39*, 79.
(2) Jørgensen, T.; Hansen, T. K.; Becher, J. *Chem. Soc. Rev.* **1994**, *23*, 41.
(3) Astruc, D. *New J. Chem.* **1992**, *16*, 305.
(4) Bidau, G.; Ganies, E. M.; Lapkowski, M. *J. Chem. Soc., Chem. Commun.* **1988**, 533.
(5) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J. M.; Halla, F. M.; Savéant, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 3086.
(6) Guerchais, V.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1984**, 881.
(7) Beer, P. D.; Sikanyika, H. *Polyhedron* **1990**, *9*, 1091.
(8) Beer, P. B.; Keefe, A. D. *J. Organomet. Chem.* **1989**, *375*, C40.
(9) Lowe, N. D.; Garner, C. D. *J. Chem. Soc., Dalton Trans.* **1993**, 3333.
(10) Hall, C.; Tucker, J. H. R.; Chu, S. Y. F.; Parkins, A. W.; Nyborg, S. C. *J. Chem. Soc., Chem. Commun.* **1993**, 1505.
(11) Medina, J. C.; Goodnow, T. T.; Rogers, M. T.; Atwood, J. L.; Lynn, B.; Kaifer, A. E.; Gokel, G. W. *J. Am. Chem. Soc.* **1992**, *114*, 10583.
(12) Beer, P. D.; Chen, Z.; Drew, M. G. B.; Kingston, J.; Ogden, M.; Spencer, P. *J. Chem. Soc., Chem. Commun.* **1993**, 1046.
(13) Benito, A.; Cano, J.; Martínez-Máñez, R.; Soto, J.; Payá, J.; Lloret, F.; Julve, M.; Faus, J.; Marcos, M. D. *Inorg. Chem.* **1993**, *32*, 1197.
(14) Constable, E. C.; Martínez-Máñez, R.; Cargill-Thompson, A. M. W.; Walker, J. V. *J. Chem. Soc., Dalton Trans.* **1994**, 1585.

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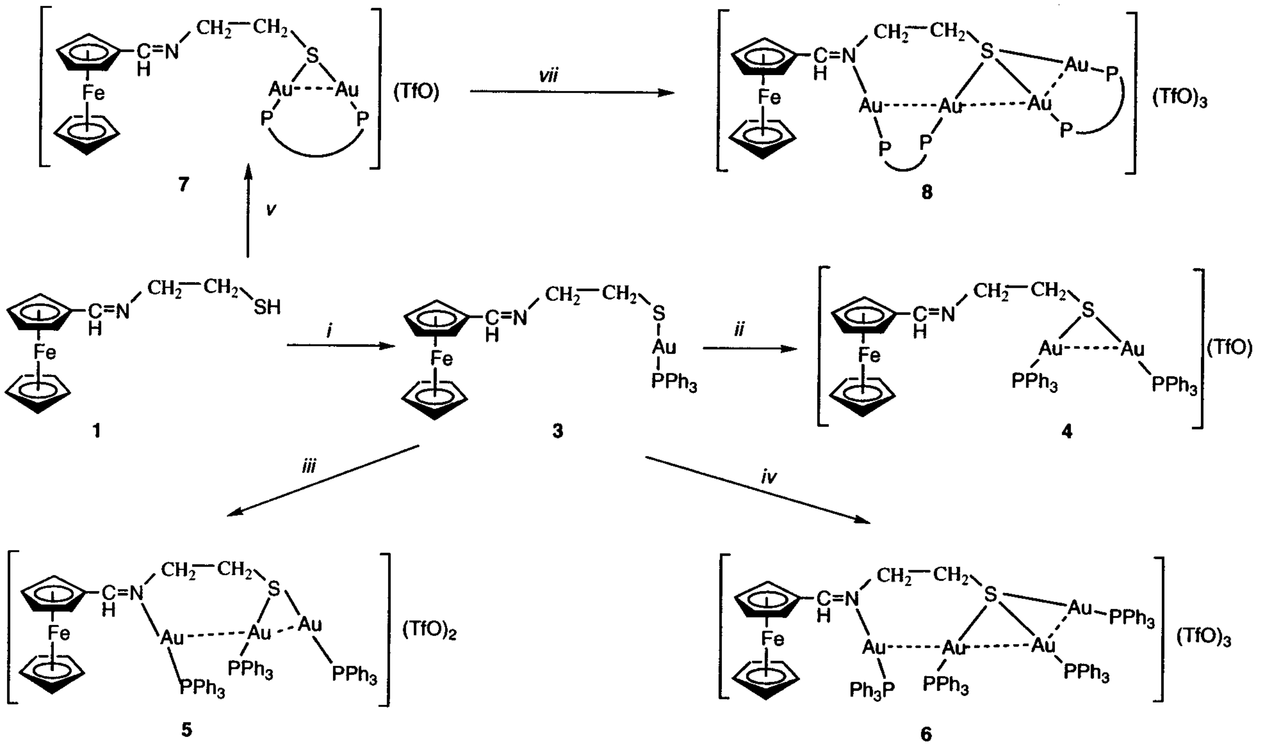
Scheme 1[a]



[a] P-P = dppf; (i) [AuCl(PPh$_3$)] + Na_2CO_3; (ii) [Au(OTf)(PPh$_3$)]; (iii) 2 equiv of [Au(OTf)(PPh$_3$)]; (iv) 3 equiv of [Au(OTf)(PPh$_3$)]; (v) [Au$_2$(OTf)$_2$(μ-dppf)] + Na_2CO_3; (vi) [Au$_2$(OTf)$_2$(μ-dppf)].

rarely observed at room temperature, it can be seen when the experiments are carried out at low temperature. In compound **1** the ferrocenyl protons are inequivalent, although some of them overlap because they have a very similar chemical shift.

In the positive secondary-ion mass spectrum the molecular peak at m/z = 273 is the most intense. Other fragmentation or association peaks are present such as [Fe(C_5H_5)$_2$]$^+$ at m/z = 186 (38%) and FcCHN(CH_2)$_2$$S_2$($CH_2$)$_2$NCHFc at m/z = 545 (12%), respectively.

If the same reaction is carried out in damp tetrahydrofuran and in air, the product is the disulfide FcCHN(CH_2)$_2$$S_2$($CH_2$)$_2$NCHFc (**2**). Compound **2** is an orange air- and moisture-stable solid that behaves as a nonconductor in acetone solutions. The IR spectrum is similar to that of compound **1**, except that the ν(S−H) band is absent. The ^{1}H NMR spectrum shows three multiplets in a ratio 2:2:5 for the substituted and unsubstituted cyclopentadienyl ring, respectively, two triplets for the methylene protons, and a singlet for the CH proton. In the positive liquid secondary-ion mass spectrum the most intense peak corresponds to the molecular peak at m/z = 545, although the peak assigned to compound **1** at m/z = 273 (52%) is also present.

We have studied the reaction of **1** with [AuCl(PPh$_3$)] in the presence of Na_2CO_3, leading to the thiolate gold derivative [FcCHN(CH_2)$_2$SAuPPh$_3$] (**3**). Complex **3** is an orange air- and moisture-stable solid. Its IR spectrum shows (apart from the bands of the ferrocene moiety) the vibration ν(Au−S) at 352(m) cm^{-1}; ν(S−H) is absent. The ^{1}H NMR spectrum shows three multiplets for the cyclopentadienyl protons with relative intensity 2:2:5 and corresponding to the α and β protons of the substituted Cp ring and to the unsubstituted Cp ring, respectively; the methylene protons appear as triplets, the phenyl protons as multiplets and the CH proton as a singlet. In the ^{31}P{^{1}H} NMR spectrum a singlet for the phosphorus nucleus appears at 39.3 ppm.

The FAB+ mass spectrum of **3** presents the molecular peak at m/z = 732 (17%). The most intense peak corresponds to the fragment [AuPPh$_3$]$^+$ at m/z = 459, and association peaks appear at m/z = 928 ([M + Au]$^+$, 7%) and 1190 ([M + AuPPh$_3$]$^+$, 20%).

Complex **3** reacts further with [Au(TfO)(PPh$_3$)] in various stoichiometries to furnish di-, tri-, or tetranuclear gold species, [FcCHN(CH_2)$_2$S(AuPPh$_3$)$_2$](TfO) (**4**), [FcCHN(AuPPh$_3$)(CH_2)$_2$S(AuPPh$_3$)$_2$](TfO)$_2$ (**5**), or [FcCHN(AuPPh$_3$)(CH_2)$_2$S(AuPPh$_3$)$_3$](TfO)$_3$ (**6**). Complexes **4**−**6** are orange air- and moisture-stable solids that behave as 1:1, 1:2, and 1:3 electrolytes, respectively. The ^{1}H NMR spectra present the same resonances as complex **3**, although with slight differences in the chemical shifts. However, the ^{31}P{^{1}H} NMR spectrum is more diagnostic. Thus for complex **4** only a singlet appears for the two phosphorus atoms at 35.1 ppm, which indicates a coordination of the gold(phosphine) fragment to the sulfur atom. Compound **5** shows two singlets at 34.6 and 29.6 ppm, with approximate relative intensities 2:1. Therefore there must be two different phosphorus environments with the third gold(phosphine) fragment coordinated to the nitrogen atom. With this structure (see Scheme 1) the three phosphorus atoms should be inequivalent; however, only two signals appear, probably because the chemical shifts of the AuPPh$_3$$^+$ fragments bonded to the sulfur ligand are very close. Complex **6** presents three broad resonances in the ^{31}P{^{1}H} NMR spectrum at 34.9, 29.8, and 24.6 with relative intensities 2:1:1 measured at room temperature, which could indicate that the fourth gold atom has coordinated to the sulfur atom (Scheme 1). The ^{31}P{^{1}H} NMR spectra of these complexes at low temperature show the same resonances, but sharpened. The presence of three phosphorus signals in the spectrum of complex **6** instead of the four expected may be for a reason similar to that in complex **5**; the difference in chemical shift of the AuPPh$_3$$^+$ fragments bonded to the sulfur atom could arise as a consequence of the presence of gold−gold contacts. We

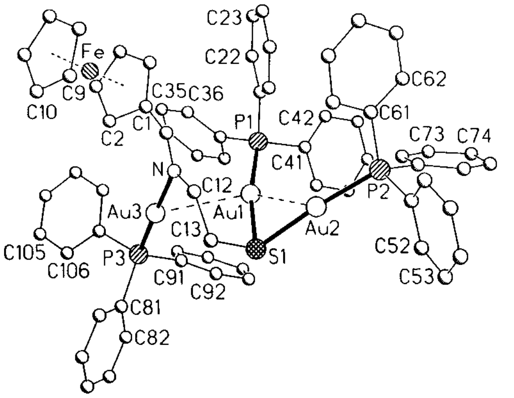


Figure 1. Structure of the cation of complex **5** in the crystal showing the atom-numbering scheme. Radii are arbitrary. The H atoms are omitted for clarity.

have previously observed this type of behavior in the $^{31}P\{^{1}H\}$ spectra of sulfur-centered species, and it proves that gold−gold interactions can be observed in solution.

We have also carried out the reaction of the dinuclear gold complex $[Au_2(TfO)_2(\mu\text{-dppf})]$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene) with $FcCHN(CH_2)_2SH$ in the presence of Na_2CO_3 that leads to $[FcCHN(CH_2)_2S\{Au_2(\mu\text{-dppf})\}]TfO$ (**7**). Compound **7** is a yellow air- and moisture-stable solid. It behaves as 1:1 electrolyte in acetone solution.

The NMR data are in agreement with the proposed formulation: the ^{1}H spectrum shows three multiplets in the ratio 2:2:5 for the monosubstituted ferrocene and a multiplet for the disubstituted ferrocene. The methylene protons appear as triplets, and the CH appears as a singlet. The $^{31}P\{^{1}H\}$ spectrum presents only one signal for both phosphorus nuclei. In the low-temperature ^{1}H spectrum the resonances for the disubstituted ferrocene sharpen into two multiplets, and in the $^{31}P\{^{1}H\}$ spectrum two resonances of similar chemical shift appear for the phosphorus atoms.

In the FAB+ mass spectrum the molecular peak appears at $m/z = 1370$ (47%), although the most abundant fragment comes from the loss of the triflate anion ($m/z = 1220$).

According to these data, we proposed a structure where the two gold centers bridged by the diphosphine are bonded to the sulfur atom, as we have observed that, with up to two gold atoms, coordination via sulfur is always preferred.

We have also carried out the same reaction in the molar ratio 1:2 to give the tetranuclear gold derivative $[FcCHN(CH_2)_2S\{Au_2(\mu\text{-dppf})\}_2](TfO)_3$ (**8**). Complex **8** is an air- and moisture-stable red solid that has a conductivity value in accordance with a 1:3 electrolyte. The room temperature NMR spectra show broad signals. At −55 °C the $^{31}P\{^{1}H\}$ NMR spectrum presents four resonances as a consequence of the inequivalence of all phosphorus atoms. The proposed structure is similar to that of complex **6**, where the gold−gold interactions may play an important role in the stability of the molecule.

Crystal Structure of Complex 5. We have confirmed the molecular structure of complex **5** by means of an X-ray crystallographic study. The cation of **5** is shown is Figure 1, with selected bond lengths and angles in Table 1. As we anticipated, two of the gold(phosphine) fragments are bonded to the sulfur atom and one is bonded to the nitrogen atom. They are located in such a manner that there are short gold−gold interactions of 3.0610(10) and 3.0869(10) Å; these values are of the same order as those in other polynuclear complexes. Au(2) and Au(3) exhibit a linear coordination (P(2)−Au(2)−S(1) = 175.5(2)° and P(3)−Au(3)−N = 177.7(3)°, respectively) while the coordination around Au(1) deviates more appreciably from linearity (P(1)−Au(1)−S(1) = 168.9(2)°). This distortion may be a consequence of the gold−gold interactions, and Au(1) can also be regarded as having a strongly distorted tetrahedral geometry. The Au−S bond lengths, 2.322(4) and 2.339(4) Å, are longer than those found in other thiolate complexes such as $[Au(SR)(PPh_3)]$ (R = Ph, 2,4,6-$C_6H_2Et_3$, 2,4,6-$C_6H_2(^{i}Pr)_3$) (2.284(2)−2.302(2) Å),[15] where S atoms are two-coordinate, and are similar to those in the related complex $\{[(Ph_3P)Au]_2S(CH_2)_5S[Au(PPh_3)]_2\}(BF_4)_2$ (2.314(5)−2.331(3) Å),[16] where S atoms are three-coordinate. Au−P bond length distances (2.251(4)−2.271(4) Å) are of the same order as those in other Au−P derivatives.[15−20] The fact that the Au(3)−P(3) distance is shorter than the others may be explained by the higher trans influence of the S atom compared with the N atom.

The Au(3)−N distance, 2.100(12) Å, is longer than those found in other gold(I) complexes containing nitrogen ligands such as $[Au(phthalimide)(PEt_3)]$ (2.030(7) Å)[20] or $[Au(C_6F_5)(Ph_2C{=}N{=}N{=}CPh_2)]$ (2.069(5) Å)[21] and is similar to that found in the linear gold(I) derivative $[Au(NHBu^{t})(PPh_2Me)]$ (2.105(8) Å).[19] The N−C bond distances in the ferrocene ligand are very different; N−C(11), 1.17(2) Å, corresponds to a double bond while N−C(12), 1.47(2) Å, corresponds to a single bond. The cyclopentadienyl rings are staggered by 9.4° around the

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex **5**

Au(1)−P(1)	2.271(4)	Au(1)−S(1)	2.339(4)
Au(1)−Au(2)	3.0610(10)	Au(1)−Au(3)	3.0869(10)
Au(2)−P(2)	2.257(4)	Au(2)−S(1)	2.322(4)
Au(3)−N	2.100(12)	Au(3)−P(3)	2.251(4)
S(1)−C(13)	1.832(14)	P(1)−C(21)	1.814(15)
P(1)−C(31)	1.82(2)	P(1)−C(41)	1.83(2)
P(2)−C(51)	1.79(2)	P(2)−C(61)	1.81(2)
P(2)−C(71)	1.82(2)	P(3)−C(81)	1.78(2)
P(3)−C(101)	1.797(15)	P(3)−C(91)	1.82(2)
N−C(11)	1.17(2)	N−C(12)	1.48(2)
C(12)−C(13)	1.52(2)		

P(1)−Au(1)−S(1)	168.9(2)	P(1)−Au(1)−Au(2)	120.56(11)
S(1)−Au(1)−Au(2)	48.72(10)	P(1)−Au(1)−Au(3)	109.88(11)
S(1)−Au(1)−Au(3)	80.66(10)	Au(2)−Au(1)−Au(3)	120.61(3)
P(2)−Au(2)−S(1)	175.5(2)	P(2)−Au(2)−Au(1)	134.20(11)
S(1)−Au(2)−Au(1)	49.20(9)	N−Au(3)−P(3)	177.7(3)
N−Au(3)−Au(1)	69.5(3)	P(3)−Au(3)−Au(1)	108.68(11)
C(13)−S(1)−Au(2)	107.1(5)	C(13)−S(1)−Au(1)	107.8(5)
Au(2)−S(1)−Au(1)	82.09(13)	C(21)−P(1)−C(31)	106.5(7)
C(21)−P(1)−C(41)	106.9(7)	C(31)−P(1)−C(41)	104.2(6)
C(21)−P(1)−Au(1)	109.5(5)	C(31)−P(1)−Au(1)	117.5(5)
C(41)−P(1)−Au(1)	111.5(5)	C(51)−P(2)−C(61)	105.8(7)
C(51)−P(2)−C(71)	105.9(7)	C(61)−P(2)−C(71)	105.9(7)
C(51)−P(2)−Au(2)	109.8(5)	C(61)−P(2)−Au(2)	114.3(6)
C(71)−P(2)−Au(2)	114.5(5)	C(81)−P(3)−C(101)	105.5(7)
C(81)−P(3)−C(91)	106.2(7)	C(101)−P(3)−C(91)	107.1(7)
C(81)−P(3)−Au(3)	115.2(5)	C(101)−P(3)−Au(3)	111.6(5)
C(91)−P(3)−Au(3)	110.7(5)	C(11)−N−C(12)	117.4(14)
C(11)−N−Au(3)	125.0(12)	C(12)−N−Au(3)	117.1(9)
N−C(12)−C(13)	115.4(13)	C(12)−C(13)−S(1)	117.7(11)

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(15) Nakamoto, M.; Hiller, W.; Schmidbaur, H. *Chem. Ber.* **1993**, *126*, 605.

(16) Sladek, A.; Schmidbaur, H. *Inorg. Chem.* **1996**, *35*, 3268.

(17) Forward, J. M.; Bohmann, D.; Fackler, J. P., Jr.; Staples, R. J. *Inorg. Chem.* **1995**, *34*, 6330.

(18) Canales, F.; Gimeno, M. C.; Laguna, A.; Villacampa, M. D. *Inorg. Chim. Acta* **1996**, *244*, 95.

(19) Angermaier, K.; Schmidbaur, H. *J. Chem. Soc., Dalton Trans.* **1995**, 559.

(20) Price, S. J. B.; DiMartino, M. J.; Hill, D. T.; Kuroda, R.; Mazid, M. A.; Sadler, P. J. *Inorg. Chem.* **1985**, *24*, 3425.

(21) Bordoni, S.; Busetto, L.; Cassani, M. C.; Albano, V. G.; Sabatino, P. *Inorg. Chim. Acta* **1994**, *222*, 267.

Table 2. Electrochemical Data for Complexes **1**−**8**

compound	E_1 (V)	E_2 (V)
1, FcCHN$(CH_2)_2$SH	0.49	0.88
2, FcCHN$(CH_2)_2S_2(CH_2)_2$NCHFc	0.54	0.79
3, [FcCHN$(CH_2)_2$S($AuPPh_3$)]	0.57	0.87
4, [FcCHN$(CH_2)_2$S$(AuPPh_3)_2$]TfO	0.59	0.74
5, [FeCHN($AuPPh_3$)$(CH_2)_2$S$(AuPPh_3)_2$](TfO)$_2$	0.76	
6, [FcCHN($AuPPh_3$)$(CH_2)_2$S$(AuPPh_3)_3$](TfO)$_3$	0.78	
7, [FcCHN$(CH_2)_2$S{Au_2(μ-dppf)}]TfO	0.73	1.03
8, [FcCHN$(CH_2)_2$S{Au_2(μ-dppf)}$_2$](TfO)$_3$	1.09	

Cp···Cp axis (Cp = center of cyclopentadienyl ring) defined by the torsion angle C(1)−Cp−Cp−C(9).

Electrochemistry. The electrochemical behavior of these compounds has been studied by cyclic voltammetry at a platinum electrode in CH_2Cl_2. The cyclic voltammograms of compounds **1** and **2**, at a scan rate of 100 mV s^{-1}, show a quasi-reversible redox couple assigned to ferrocene/ferrocenium species at potential values similar to those found in ferrocene itself. A small irreversible wave appears at higher potentials (around 0.8 V) probably due to interference by amine oxidation processes.

The coordination of one or two gold(phosphine) fragments to the thiolate unit does not greatly affect the values of the potentials; thus complexes **3** and **4** show a pattern similar to that of the ligand **1**, with only a slight anodic shift in the Fe^{II}/Fe^{III} couple ($\Delta = 0.08$ or 0.1 V, respectively). The coordination of three $AuPPh_3^+$ units to the ferrocene derivative (complex **5**), two of them to the sulfur atom, and one to the nitrogen, has a more marked effect on the potentials. The potential for the ferrocene/ferrocenium wave increases considerably (0.73 V) whereas no amine oxidation wave is observed. The cyclic voltammogram of complex **6** is similar, showing that the coordination of gold to the nitrogen atom produces an anodic shift in the ferrocene-based oxidation wave and a stabilization of the amine toward oxidation. In the complexes **7** and **8** there are two or three ferrocene units, the peak potentials are very close, and thus the waves are not well-defined. The electrochemical data for complexes **1**−**8** are collected in Table 2.

Conclusion

We have succeeded in preparing the ligand FcCHN$(CH_2)_2$SH, which has been allowed to react with gold(phosphine) cations. The proton of the thiol function can be easily removed with a mild base such as Na_2CO_3, and several gold centers can be coordinated to the heterofunctional ligand. The coordination of one or two gold atoms takes place at the sulfur atom, the third gold atom coordinates to the nitrogen atom, and the fourth gold center coordinates again at sulfur. The complex [FcCHN($AuPPh_3$)$(CH_2)_2$S$(AuPPh_3)_2$](TfO)$_2$ has been structurally characterized and has confirmed the coordination of the gold centers to the sulfur and nitrogen atoms; short gold−gold interactions were found. Cyclic voltammetry studies were performed; these showed that the coordination of the gold centers to the sulfur atom did not greatly affect the potential for the ferrocene/ferrocenium couple, and that amine oxidation processes occurred. The coordination of the gold center to the nitrogen produced an anodic shift of the ferrocene/ferrocenium couple, and no amine oxidation was observed in this case.

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 conductimeter. C, H, N, and S analyses were carried out with a Perkin-Elmer 2400 microanalyzer. Mass spectra were recorded on a VG autospec, with the LSIMS 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 $SiMe_4$ (^{1}H, external) and 85% H_3PO_4 (^{31}P, external). Cyclic voltammetric experiments were performed by employing an EG&G PARC model 273 potentiostat. A three-electrode system was used, which consisted of a platinum disk working electrode, a platinum wire auxiliary electrode, and a saturated calomel reference electrode. The measurements were carried out in CH_2Cl_2 solutions with 0.1 M Bu_4NPF_6 as a supporting electrolyte. Under the present experimental conditions, the ferrocenium/ferrocene couple was located at 0.47 V vs SCE.

Materials. Ferrocenecarbaldehyde and β-mercaptoethylamine were purchased from Aldrich. [AuCl(PPh_3)][22] was prepared by published procedures. [Au(TfO)(PPh_3)] and [Au_2(TfO)$_2$(μ-dppf)] were obtained by reaction of [AuCl(PPh_3)] or [Au_2Cl_2(μ-dppf)][23] with AgTfO.

Syntheses. FcCHN$(CH_2)_2$SH (1). To a solution of FcCHO (1.072 g, 5 mmol) in tetrahydrofuran (40 mL) under a nitrogen atmosphere was added $NH_2(CH_2)_2SH$ (0.385 g, 5 mmol). The mixture was refluxed for 1 day, then the solvent was evaporated to dryness, and the product was redissolved in the minimum quantity of a 1:1 mixture of diethyl ether/hexane and chromatographed on alumina. The first band, separated by elution with CH_2Cl_2/hexane (1:1), corresponded to the starting material, and the second band corresponded to the ligand **1**. Yield: 35%. Λ_M 0.1 Ω^{-1} cm^2 mol^{-1} (Found: C, 58.61; H, 5.29; N, 4.18; S, 8.35. Calcd for $C_{17}H_{25}FeNOS$ (**1**·OEt_2): C, 58.79; H, 7.25; N, 4.03; S, 9.23). ^{1}H NMR: δ 3.06 (m, 4H, CH_2), 3.6 (m, 1H, CH), 4.18 (m, 2H, C_5H_4), 4.2 (s, 5H, C_5H_5), 4.29 (m, 1H, C_5H_4), 4.44 (m, 1H, C_5H_4), 5.35 (s, 1H, SH).

FcCHN$(CH_2)_2S_2(CH_2)_2$NCHFc (2). To a solution of FcCHO (1.072 g, 5 mmol) in damp tetrahydrofuran (40 mL) was added $NH_2(CH_2)_2SH$ (0.385 g, 5 mmol). The mixture was refluxed for 1 day, then the solvent was evaporated to dryness, and the product was redissolved in the minimum quantity of a 1:1 mixture of diethyl ether/hexane and chromatographed on alumina. The first band, separated by elution with CH_2Cl_2/hexane (1:1), corresponded to the starting material, and the second band corresponded to compound **2**. Yield: 60%. Λ_M 24 Ω^{-1} cm^2 mol^{-1} (Found: C, 57.31; H, 4.84; N, 5.20; S, 11.49. Calcd for $C_{26}H_{28}Fe_2N_2S_2$: C, 57.36; H, 5.18; N, 5.14; S, 11.78). ^{1}H NMR: δ 2.94 (t, 2H, CH_2, J(HH) 2.67 Hz), 3.72 (t, 2H, CH_2, J(HH) 2.79 Hz), 4.14 (s, 5H, C_5H_5), 4.31 (m, 2H, C_5H_4), 4.57 (m, 2H, C_5H_4), 8.10 (s, 1H, CH).

[FcCHN$(CH_2)_2$S($AuPPh_3$)] (3). To a solution of **1** (0.082 g, 0.3 mmol) in dichloromethane (30 mL) were added [AuCl(PPh_3)] (0.385 g, 0.3 mmol) and excess Na_2CO_3 (0.53 g, 5 mmol). The mixture was stirred for 1 h and then filtered to remove solid sodium carbonate. The solution was evaporated to ca. 5 mL, and addition of diethyl ether gave complex **3** as an orange solid. Yield: 84%. Λ_M 30 Ω^{-1} cm^2 mol^{-1} (Found: C, 51.17; H, 4.20; N, 1.90; S, 4.56. Calcd for $C_{31}H_{30}AuFeNPS$: C, 50.90; H, 3.99; N, 1.91; S, 4.38). ^{1}H NMR: δ 3.26 (t, 2H, CH_2, J(HH) 3.16 Hz), 3.79 (t, 2H, CH_2, J(HH) 2.97 Hz), 4.17 (s, 5H, C_5H_5), 4.28 (m, 2H, C_5H_4), 4.57 (m, 2H, C_5H_4), 7.4−7.8 (m, 15H, Ph), 8.20 (s, 1H, CH).

[FcCHN$(CH_2)_2$S$(AuPPh_3)_2$](TfO) (4). To a solution of **3** (0.073 g, 0.1 mmol) in dichloromethane (30 mL) was added [Au(TfO)(PPh_3)] (0.061 g, 0.1 mmol), and the mixture was stirred for 30 min. The solution was concentrared to ca. 5 mL, and addition of diethyl ether gave complex **4** as a red solid. Yield: 84%. Λ_M 116.3 Ω^{-1} cm^2 mol^{-1} (Found: C, 44.58; H, 2.91; N, 0.92; S, 4.97. Calcd for $C_{50}H_{44}Au_2F_3FeNO_3P_2S_2$: C, 44.83; H, 3.1; N, 1.04; S, 4.78). ^{1}H NMR: δ 3.60 (t, 2H, CH_2, J(HH) 2.18 Hz), 3.82 (t, 2H, CH_2, J(HH) 2.27 Hz), 4.09 (s, 5H, C_5H_5), 4.06 (m, 2H, C_5H_4), 4.39 (m, 2H, C_5H_4), 7.25−7.54 (m, 30H, Ph), 8.31 (s, 1H, CH).

[FcCHN($AuPPh_3$)$(CH_2)_2$S$(AuPPh_3)_2$](TfO)$_2$ (5). To a solution of **3** (0.073 g, 0.1 mmol) in dichloromethane (30 mL) was added [Au(TfO)(PPh_3)] (0.122 g, 0.2 mmol), and the mixture was stirred for 30

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[22] Usón, R.; Laguna, A. *Inorg. Synth.* **1989**, *21*, 71.

[23] Gimeno, M. C.; Laguna, A.; Sarroca, C.; Jones, P. G. *Inorg. Chem.* **1993**, *32*, 5926.

min. The solution was concentrated to ca. 5 mL, and addition of diethyl ether gave complex **5** as a red solid. Yield: 98%. Λ_M 187.5 Ω^{-1} cm^2 mol^{-1} (Found: C, 41.87; H, 2.67; N, 0.71; S, 4.34. Calcd for $C_{69}H_{59}Au_3F_6FeNO_6P_3S_3$: C, 42.55; H, 3.05; N, 0.72; S, 4.92). ^{1}H NMR: δ 3.99 (m, 2H, CH_2), 4.43 (m, 2H, CH_2), 4.14 (s, 5H, C_5H_5), 4.58 (m, 2H, C_5H_4), 5.0 (m, 2H, C_5H_4), 7−8 (m, 45H, Ph), 9.26 (m, 1H, CH).

[FcCHN(AuPPh$_3$)(CH$_2$)$_2$S(AuPPh$_3$)$_3$](TfO)$_3$ (6). To a solution of **3** (0.073 g, 0.1 mmol) in dichloromethane (30 mL) was added [Au(TfO)(PPh$_3$)] (0.183 g, 0.2 mmol), and the mixture was stirred for 30 min. The solution was concentrared to ca. 5 mL, and addition of diethyl ether gave complex **6** as a red solid. Yield: 73%. Λ_M 293 Ω^{-1} cm^2 mol^{-1} (Found: C, 41.70; H, 3.19; N, 0.70; S, 1.09. Calcd for $C_{80}H_{74}Au_4F_9FeNO_9P_4S_4$: C, 41.35; H, 2.92; N, 0.55; S, 1.25). ^{1}H NMR: δ 4.0 (m, 2H, CH_2), 4.42 (m, 2H, CH_2), 4.30 (s, 5H, C_5H_5), 4.59 (m, 2H, C_5H_4), 5.01 (m, 2H, C_5H_4), 7−7.8 (m, 60H, Ph), 9.25 (m, 1H, CH).

[FcCHN(CH$_2$)$_2$S{Au$_2$(μ-dppf)}]TfO (7). To a solution of **1** (0.027 g, 0.1 mmol) in dichloromethane (30 mL) were added [Au$_2$(OTf)$_2$(μ-dppf)] (0.125 g, 0.1 mmol) and excess Na_2CO_3 (0.53 g, 5 mmol). The mixture was stirred for 1 h and then filtered to remove solid sodium carbonate. The solution was evaporated to ca. 5 mL, and addition of diethyl ether gave complex **7** as an orange solid. Yield: 84%. Λ_M 120 Ω^{-1} cm^2 mol^{-1} (Found: C, 39.19; H, 1.92; N, 0.68; S, 4.13. Calcd for $C_{48}H_{42}Au_2F_3Fe_2NO_3P_2S_2\cdot CH_2Cl_2$: C, 39.52; H, 2.91; N, 0.94; S, 4.68). ^{1}H NMR: δ 3.65 (m, 2H, CH_2), 3.85 (m, 2H, CH_2), 4.13 (s, 5H, C_5H_5), 4.09 (m, 2H, C_5H_4), 4.52 (m, 2H, C_5H_4), 4.43(m, 8H, C_5H_4), 7.48−7.52 (m, 20H, Ph), 8.47 (s, 1H, CH).

[FcCHN(CH$_2$)$_2$S{Au$_2$(μ-dppf)}$_2$](TfO)$_3$ (8). To a solution of **1** (0.027 g, 0.1 mmol) in dichloromethane (30 mL) were added [Au$_2$(OTf)$_2$(μ-dppf)] (0.250 g, 0.2 mmol) and excess Na_2CO_3 (0.53 g, 5 mmol). The mixture was stirred for 1 h and then filtered to remove solid sodium carbonate. The solution was evaporated to ca. 5 mL, and addition of diethyl ether gave complex **8** as an orange solid. Yield: 97%. Λ_M 311 Ω^{-1} cm^2 mol^{-1} (Found: C, 38.28; H, 2.42; N, 0.40; S, 3.73. Calcd for $C_{84}H_{70}Au_4F_9Fe_3NO_9P_4S_4$: C, 38.57; H, 2.67; N, 0.53; S, 4.9).

Crystal Structure Determination. Crystals of **5**·5CH$_2$Cl$_2$ were grown from dichloromethane/petroleum ether. A red lath ca. 0.75 × 0.25 × 0.05 mm was mounted in inert oil on a glass fiber. A total of 11 580 intensities were registered using monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å, $2\Theta_{max} = 50°$) on a Siemens P4 four-circle diffractometer; 10 792 unique reflections ($R_{int} = 0.0618$) were used for all calculations. Cell constants were refined from setting angles of 61 reflections in the range $2\Theta = 10-25°$. An absorption correction based on Ψ scans was applied, with transmission factors 0.393−0.837. The structure was solved by direct methods; Au, Fe, S, P, O, F, and Cl (of ordered dichloromethane) atoms were refined anisotropically on F^2 using the program SHELXL-93.[24] H atoms were included using a riding model. Disorder in two of the five dichloromethane solvent molecules was observed: half occupancies were used for some of its atoms during the final stage of refinement; no hydrogen atoms were located for these molecules. The composition and related parameters are based on the ratio 5:1 dichloromethane:complex, although the exact value cannot be determined. The final $R_w(F^2)$ was 0.105 for all reflections, with a conventional $R(F)$ of 0.052, for 581 parameters. A total of 395 restraints were applied involving local phenyl and cyclopentadienyl ring symmetry (FLAT/SAME commands) in addition to distance restraints to S−O, C−F (triflate groups), and C−Cl (dichloromethane solvent). $S = 0.776$; maximum $\Delta\rho = 1.278$ eÅ^{-3}. Further details are shown in Table 3.

Table 3. Details of Data Collection and Structure Refinement for the Complex **5**

compound	**5**·5CH$_2$Cl$_2$
empirical formula	$C_{74}H_{69}Au_3Cl_{10}F_6FeNO_6P_3S_3$
fw	2372.64
space group	*C*2/*c*
V (Å^3)	17007(4)
Z	8
D_{calc} (Mg m^{-3})	1.853
a (Å)	60.200(6)
b (Å)	14.977(2)
c (Å)	19.066(3)
β (deg)	98.367(14)
T (K)	173
μ(Mo Kα) (mm^{-1})	5.834
R^a (F, $F > 4\sigma(F)$)	0.0520
$R_w{}^b$ (F^2, all reflns)	0.1050

^{a} $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w(F^2) = [\sum\{w(F_o{}^2 - F_c{}^2)^2\}/\sum\{w(F_o{}^2)^2\}]^{0.5}$.

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Supporting Information Available: One X-ray crystallographic file, in CIF format, of [FcCHN(AuPPh$_3$)(CH$_2$)$_2$S(AuPPh$_3$)$_2$](TfO)$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) Sheldrick, G. M. *SHELXL-93, a program for crystal structure refinement*; University of Göttingen: Göttingen, Germany, 1993.