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Synthesis of $[Au_2(SC_6F_5)_2(\mu\text{-dppf})]$ and $[Au_2(\mu\text{-}SC_6F_5)(\mu\text{-dppf})]$ (dppf = 1,1′-Bis(diphenylphosphino)ferrocene). Reactivity toward Various Metallic Fragments

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The reaction of $[Au_2Cl_2(\mu\text{-dppf})]$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene) with 2 equiv of pentafluorobenzenethiol in the presence of K_2CO_3 leads to the gold(I) thiolate derivative $[Au_2(SC_6F_5)_2(\mu\text{-dppf})]$ (**1**). Complex **1** reacts with $[Au(OClO_3)(PR_3)]$ in a 1:2 or 1:4 molar ratio to give $[Au_4(\mu_3\text{-}SC_6F_5)_2(\mu\text{-dppf})(PR_3)_2](ClO_4)_2$ ($PR_3 = PPh_3$ (**2**), PPh_2Me (**3**)) or $[Au_6(\mu_4\text{-}SC_6F_5)_2(\mu\text{-dppf})(PR_3)_4](ClO_4)_4$ ($PR_3 = PPh_3$ (**4**), PPh_2Me (**5**)), in which the thiolate ligands bridge two or three gold atoms, respectively. The treatment of **1** with $[Au(C_6F_5)_3OEt_2]$ affords the mixed gold(I)−gold(III) species $[Au_4(\mu_3\text{-}SC_6F_5)_2(C_6F_5)_6(\mu\text{-dppf})]$ (**6**). Heterometallic derivatives have been obtained by reaction of **1** with copper or mercury salts and are of the type $[Au_2Cu(\mu_3\text{-}SC_6F_5)_2Cl(\mu\text{-dppf})(PPh_3)]$ (**7**), $[Au_6Cu_2(\mu_3\text{-}SC_6F_5)_6(\mu\text{-dppf})_3](PF_6)_2$ (**8**), or $[Au_2Hg(\mu_3\text{-}SC_6F_5)_2X_2(\mu\text{-dppf})]$ (X = Cl (**9**), I (**10**)). The reaction of **1** with 1 equiv of $AgClO_4$ gives a precipitate of $[Ag(SC_6F_5)]_n$ and the complex $[Au_2(\mu\text{-}SC_6F_5)(\mu\text{-dppf})]ClO_4$ (**11**) with the thiolate ligand bridging both gold atoms. By reaction of **11** with the gold(III) derivative $[Au(C_6F_5)_2(OEt_2)_2]ClO_4$ the complex $[Au_5(C_6F_5)_2(\mu_3\text{-}SC_6F_5)_2(\mu\text{-dppf})_2](ClO_4)_3$ **12** can be isolated. The complexes **6** and **11** have been characterized by X-ray diffraction studies.

Introduction

Thiolate compounds are the subject of increasing interest because of their versatile chemistry; worthwhile topics for study include the potential of thiolate complexes with respect to S−C bond cleavage reactions and desulfurization,[1] the novel structures of some coordination complexes,[2] and the possibility of stabilization of unusual oxidation states. Applications in the study of biological systems[3] and use in medicine as antiarthritric or cancerostatic drugs[4] also contribute to the growing interest in these compounds and in particular of gold thiolate complexes.[5]

Although numerous transition-metal complexes containing the pentafluorobenzenethiolate ligand have been reported,[6] not many gold derivatives have been described thus far. Anionic derivatives of the type $[Au(SC_6F_5)_2]^-$, $[AuCl(SC_6F_5)]^-$, $[Au(SC_6F_5)_4]^-$, and $[Au_2(SC_6F_5)_6]^{2-}$ were described 20 years ago.[7] Since then only the heterobimetallic derivatives $[(C_5Me_5)M(\mu\text{-}SC_6F_5)_2AuCl_2]Cl$ (M = Rh, Ir)[8] or the salts $[AuL_n][CpM(SC_6F_5)_4]$ (M = Mo, W; L = PR_3, diphosphine),[9] where no coordination of the gold center to the thiolate ligand could take place, have been described.

Here we report on the synthesis of several homo- and heterometallic complexes with the pentafluorobenzenethiolate ligand. Several coordination modes and various structural frameworks are achieved; different metals or

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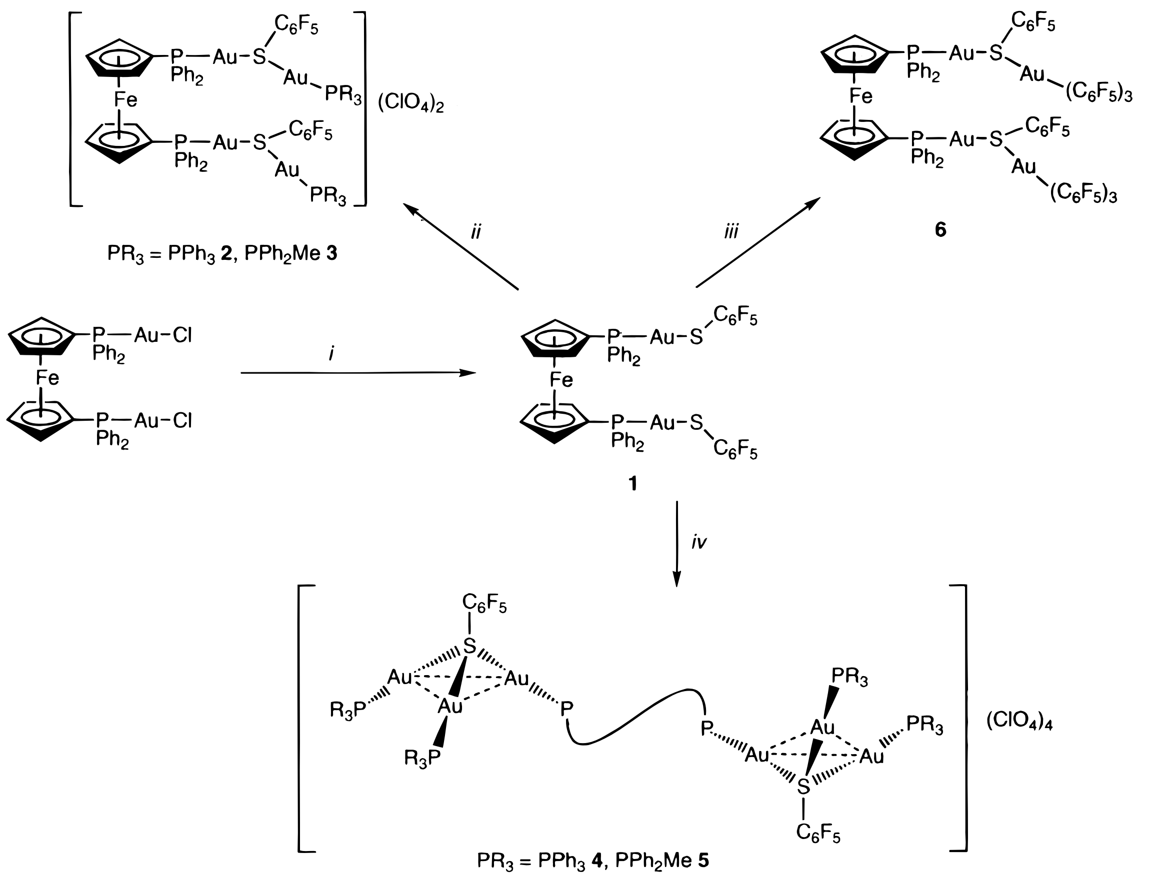
Scheme 1[a]



[a] Legend: (*i*) 2 $HSC_6F_5 + K_2CO_3$: (*ii*) 2 $[Au(OClO_3)PR_3]$: (*iii*) 2 $[Au(C_6F_5)_3(OEt_2)]$; (*iv*) 4 $[Au(OClO_3)PR_3]$.

the same metal in different oxidation states are coordinated to the same thiolate ligand. The crystal structures of the complexes $[Au_4(\mu_3\text{-}SC_6F_5)_2(C_6F_5)_6(\mu\text{-dppf})]$ and $[Au_2(\mu\text{-}SC_6F_5)(\mu\text{-dppf})]ClO_4$ are reported.

Results and Discussion

The reaction of $[Au_2Cl_2(\mu\text{-dppf})]$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene) with 2 equiv of pentafluorobenzenethiol, HSC_6F_5, in dichloromethane with an excess of K_2CO_3 leads to the dinuclear thiolate gold(I) derivative $[Au_2(SC_6F_5)_2(\mu\text{-dppf})]$ (**1**) (see Scheme 1). Complex **1** is an air- and moisture-stable orange solid that behaves as a nonconductor in acetone solution. The IR spectrum shows the ν(Au−S) vibrations at 335 (w) and 312 (w) cm^{-1} and those arising at the pentafluorophenyl group of the thiolate ligand at 1510 (vs), 1505 (vs), and 970 (vs) cm^{-1}; ν(C−S) appears at 854 (s) cm^{-1}.

The ^1H NMR spectrum displays two multiplets for the α- and β-protons of the cyclopentadienyl rings and a broad multiplet for the phenyl protons. The $^{31}P\{^1H\}$ NMR shows one singlet for the two equivalent phosphorus atoms, and the ^{19}F NMR spectrum presents three resonances for the $SC_6F_5^-$ group, two multiplets for the *ortho* and *meta* fluorines and a triplet for the *para* fluorine. The positive-ion liquid secondary mass spectrum (LSIMS+) of **1** shows the molecular peak at *m/z* 1346, although with very low intensity (1%); a more intense peak (30%) at *m/z* 1147 corresponds to the loss of one thiolate group.

Complex **1** is a suitable starting material since it can react with various metallic fragments. Thus, the reaction with $[Au(OClO_3)(PR_3)]$ in a 1:2 or 1:4 molar ratio affords polynuclear derivatives with a μ_3-SC_6F_5 ligand, $[Au_4(\mu_3\text{-}SC_6F_5)_2(\mu\text{-dppf})(PR_3)_2](ClO_4)_2$ (PR_3 = PPh_3 (**2**), PPh_2Me (**3**)), or with a μ_4-SC_6F_5 ligand, $[Au_6(\mu_4\text{-}SC_6F_5)_2(\mu\text{-dppf})(PR_3)_4](ClO_4)_4$ (PR_3 = PPh_3 (**4**), PPh_2Me (**5**)).

Complexes **2**−**5** are air- and moisture-stable orange solids that behave as 1:2 or 1:3 electrolytes, respectively. In their IR spectra the bands for the pentafluorophenyl group and the ν(C−S) vibration appear in positions close to those cited for complex **1**. Other bands correspond to the anionic perchlorate at 1100 (br, vs) and 620 (m) cm^{-1} and to ν(Au−S) at 334 (w) (**2**), 330 (w) (**3**), 334 (w) (**4**), and 324 (w) cm^{-1} (**5**).

In the $^{31}P\{^1H\}$ NMR of complexes **2** and **3** in $CDCl_3$ at room temperature two signals appear that can be assigned to the two different phosphorus environments (PR_3 and dppf). When the experiment is carried out at −55 °C, four signals can be observed, two of them with lower intensity. If we take into account the unshared lone pair of electrons at the sulfur atom, this center must have a chiral tetrahedral conformation, since the four substituents are different. Consequently, in solution different conformational isomers must exist; depending on the conformation of each sulfur center three diastereoisomers must be present: *R*,*R*, *S*,*S*, and *R*,*S*. The first two must have the same NMR signals, and the other must be different. Then the four signals observed in the ^{31}P NMR spectra can be explained by the presence of two diastereoisomers and the different intensity of the signals is due to the different abundance of the two diastereoisomers. At room temperature we only observed one isomer, which may reasonably be attributed to fast equilibria for pyramidal inversion, as previously studied e.g. for amines, phosphines, arsines, sulfoxides, or sulfonium salts bearing three different substituents.[10] The ^{1}H NMR spectra of **2** and **3** show two broad signals at room temperature that split into four at −55 °C; these signals are still broad and may be the reason both diastereoisomers are not observed. The resonances have the same intensity ratio and are assigned to the different α- and *β*-protons of the cyclopentadienyl ring, which are only equivalent by fluxionality. The ^{19}F spectra at room temperature present the typical pattern of a pentafluorophenyl ring with two multiplets for the *ortho* and *meta* fluorines and a triplet for the *para* fluorine. At low temperature the signals are very broad, and then the two diastereoisomers cannot be distinguished.

The room-temperature ^{31}P{^{1}H} NMR spectra of complexes **4** and **5** show two resonances arising from the two different types of phosphorus atoms. At −55 °C each resonance splits into two as a consequence of the inequivalence of the two "$Au_2(\mu\text{-}SC_6F_5)(PR_3)_2$" units; this is corroborated in the low-temperature ^{19}F NMR spectra, because both thiolate groups are then inequivalent. The ^{1}H NMR spectra at room temperature show two broad resonances for the α- and *β*-protons of the cyclopentadienyl ring; at −55 °C seven signals appear because of the inequivalence of all Cp protons, the resonances for two protons being overlapped. The inequivalence of the thiolate groups and in the phosphorus atoms, we believe, is a consequence of the different gold−gold interactions that can be observed in the low-temperature NMR spectra. We have previously observed this inequivalence in this type of complex.[11]

The reaction of **1** with 2 equiv of $[Au(C_6F_5)_3(OEt_2)]$ gives a mixed gold(I)−gold(III) derivative with a bridging thiolate ligand, $[Au_4(\mu_3\text{-}SC_6F_5)_2(C_6F_5)_6(\mu\text{-dppf})]$ (**6**). Complex **6** is an air- and moisture-stable orange solid that behaves as a nonconductor in acetone solutions. Its IR spectrum presents absorptions from the pentafluorobenzenethiolate unit at 984 (s) and 853 (m) cm^{-1} and from the pentafluorophenyl rings bonded to gold(III) at 1510 (vs) and 971 (vs) cm^{-1}.

The ^{31}P{^{1}H} NMR spectrum shows one singlet for the equivalent dppf phosphorus atoms. In the ^{1}H NMR spectrum the α- and *β*-protons of the cyclopentadienyl rings appears as multiplets. The ^{19}F NMR spectrum presents three different pentafluorophenyl groups; one corresponds to the thiolate ligand and the other two to the cis and trans groups of the "$Au(C_6F_5)_3$" unit. In the LSIMS+ mass spectrum the molecular peak appears at *m/z* 2742 (6%).

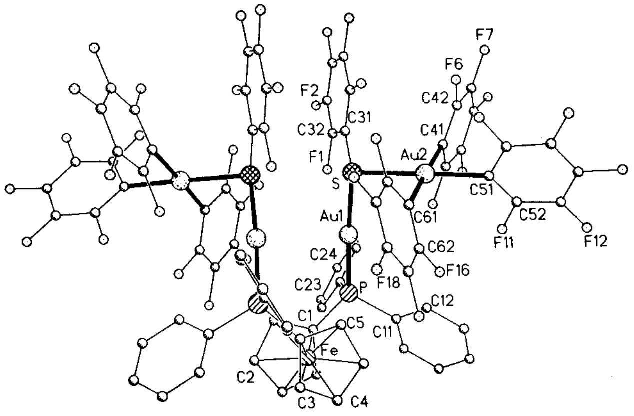


Figure 1. Structure of the molecule of complex **6** in the crystal, showing the atom-numbering scheme of the asymmetric unit. H atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 6

Au(1)−P	2.267(2)	Au(1)−S	2.339(2)
Au(2)-C(51)	2.048(7)	Au(2)−C(41)	2.049(7)
Au(2)−C(61)	2.056(7)	Au(2)−S	2.380(2)
S−C(31)	1.752(7)		
P−Au(1)−S	176.62(7)	C(51)−Au(2)−C(41)	87.9(3)
C(51)−Au(2)−C(61)	89.6(3)	C(41)−Au(2)−C(61)	177.5(3)
C(51)−Au(2)−S	176.3(2)	C(41)−Au(2)−S	95.7(2)
C(61)−Au(2)−S	86.8(2)	C(1)−P−Au(1)	114.6(2)
C(11)−P−Au(1)	112.2.(3)	C(21)−P−Au(1)	111.9(3)
C(31)−S−Au(1)	109.8.(2)	C(31)−S−Au(2)	107.1(2)
Au(1)−S−Au(2)	99.77(7)	C(42)−C(41)−Au(2)	124.9(6)
C(46)−C(41)−Au(2)	120.9(6)	C(52)−C(51)−Au(2)	122.3(6)
C(56)−C(51)−Au(2)	120.3(6)	C(62)−C(61)−Au(2)	124.0(5)
C(66)−C(61)−Au(2)	120.7(6)		

The structure of **6** has been confirmed by X-ray diffraction studies; the molecule is shown in Figure 1. A selection of bond lengths and angles is collected in Table 1. The iron atom lies on a twofold axis, and thus only half of the molecule corresponds to the asymmetric unit. Short gold−gold contacts are usually observed for gold(I) centers, but the gold(I)−gold(I) distance in **6** is, at 3.834(2) Å, probably too long to be considered a significant interaction. The gold atoms bonded to the same thiolate group are gold(I) and gold(III), but nevertheless this Au···Au distance is quite short, 3.608(2) Å, and the angle Au(I)−S−Au(III) is 99.77(7)°, narrower than the others around the sulfur atom (Au−S−C = 109.8(2), 107.1(2)°). This may indicate the presence of a weak interaction between the gold(I) and the gold(III) centers. We have previously pointed out this possibility, as indicated by short gold(I)−gold(III) distances in some of our complexes and corroborated by theoretical studies.[12,13] The geometry of the gold(I) and gold(III) centers is, as expected, linear and square planar, respectively, with only slight distortions. The Au(I)−S distance is 2.339(2) Å and compares well with values found in other gold(I) thiolate complexes such as $[Au_2(\mu\text{-}SCH_2Ph)(PPh_3)_2]$ (2.331−2.345 Å).[14] The Au(III)−S bond length is 2.380(2) Å, but there are not many examples of gold(III) thiolate derivatives for comparison; in the complex $[Au_2Cl_4(\mu\text{-}SPh)_2]$[14] the distances are shorter, 2.332(5) and 2.339(5) Å, but the difference may arise from the trans influence of the phosphine being higher than that of the chloro ligand.

The reaction of complex **1** with other metal complexes affords heterometallic derivatives. Thus, the treatment of **1** with $[CuCl(PPh_3)]_4$ gives the four-coordinate copper compound $[Au_2Cu(\mu_3\text{-}SC_6F_5)_2Cl(\mu\text{-dppf})(PPh_3)]$ **(7)** (see Scheme 2). Complex **7** is slightly conducting in acetone

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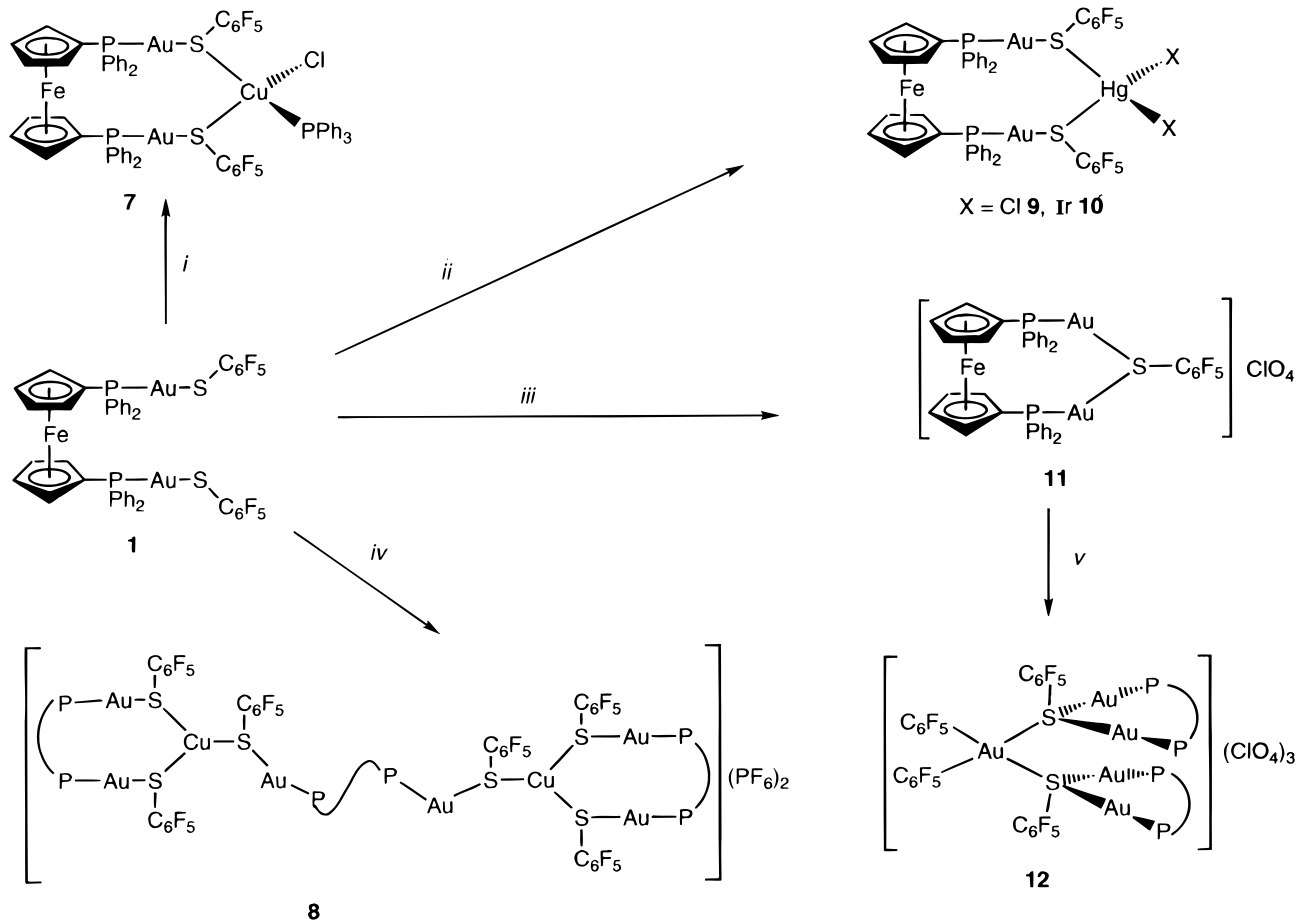
Scheme 2[a]



[a] Legend: (*i*) $[CuCl(PPh_3)]_4$; (*ii*) $HgCl_2$ or HgI_2; (*iii*) $AgClO_4$; (*iv*) $[Cu(NCMe)_4]PF_6$; (*v*) $[Au(C_6F_5)_2(OEt_2)_2]ClO_4$.

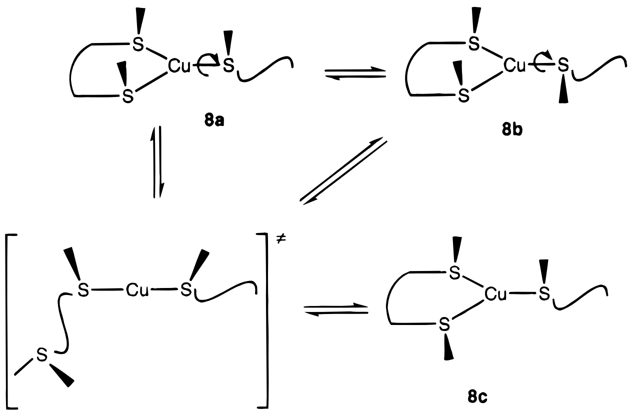
solutions, 22 Ω^{-1} cm^2 mol^{-1}, which could be due to chloride dissociation.

In the $^{31}P\{^1H\}$ NMR spectrum at room temperature two broad signals appear that sharpen into two singlets at 32.3 and −14.3 ppm at low temperature. The ^1H NMR spectrum shows four broad multiplets for the cyclopentadienyl protons; at −55 °C the signals split into poorly resolved multiplets for the eight different Cp protons. Usually, complexes with disubstituted ferrocene ligands show two multiplets in the ^1H NMR spectra for the α- and β-protons of the cyclopentadienyl rings, even though in the solid state (because of the different ring conformations) the eight protons are inequivalent. This inequivalence is sometimes observed, as in this case, at low temperature. The ^{19}F NMR spectrum shows only one type of pentafluorophenyl group.

The reaction of **1** with $[Cu(NCMe)_4]PF_6$ in any molar ratio gives the polynuclear complex $[Au_6Cu_2(\mu^3\text{-}SC_6F_5)_6(\mu\text{-dppf})_3](PF_6)_2$ (**8**), which has two copper atoms surrounded by three thiolate ligands. Its IR spectrum presents the absorption due to the PF_6 anion at 853 (s) cm^{-1}; the bands for the thiolate ligand appear at 1510 (vs), 977 (vs), and ca. 855 cm^{-1} (overlapped with PF_6) and the ν(Au−S) vibrations at 340 (w) and 314 (w) cm^{-1}.

The $^{31}P\{^1H\}$ NMR at room temperature consists of a singlet, but when the experiment is carried out at −55 °C the signal splits into two singlets with a different ratio, approximately 2:1, which can be assigned to the phosphorus of the dppf in the chelating and bridging metallacycles, respectively. The ^1H NMR spectrum shows two broad multiplets for the α- and β-protons of the Cp rings, which split into four multiplets at low temperature. The ^{19}F NMR spectrum at room temperature is also simple and contains the three typical resonances of a pentafluorophenyl group and a doublet for the PF_6 anion. At −55 °C the spectrum is complicated, probably because of the presence of several isomers that are in rapid equilibrium at room temperature (Scheme 3). The three isomers (**8a**−**c**) are detected with different intensities.

Scheme 3



Complex **1** also reacts with HgX_2 to give the heterometallic species $[Au_2Hg(\mu_3\text{-}SC_6F_5)_2X_2(\mu\text{-dppf})]$ (X = Cl

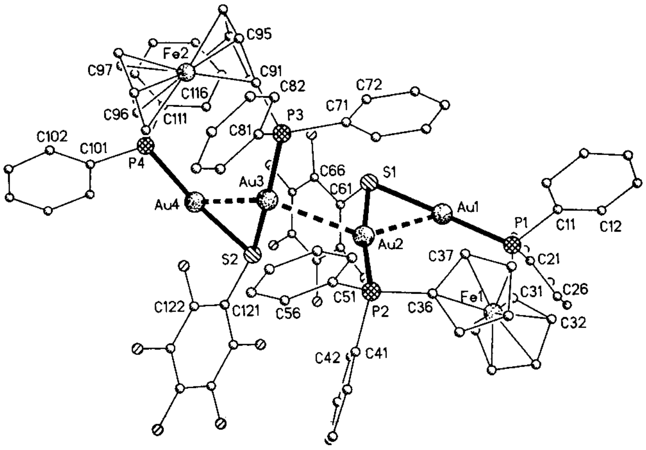


Figure 2. Perspective view of the two linked cations of complex **11**, with the atom-labeling scheme. H atoms are omitted for clarity.

(**9**), I (**10**)). These compounds are air- and moisture-stable orange solids that are nonconductors in acetone solution, although complex **10** has a conductivity of 32 Ω^{-1} cm^2 mol^{-1}, probably due to dissociation of the halogen in acetone. In the IR spectra the bands for the thiolate appear at 1510 (vs), 976 (vs) and 857 (s) cm^{-1} (**9**) and at 1511 (vs), 977 (vs), and 852 (s) cm^{-1} (**10**).

The ^{31}P{^{1}H} NMR spectra show only one resonance because of the equivalence of the phosphorus atoms; in the ^{1}H NMR spectra two multiplets for the α- and β-protons of the cyclopentadienyl protons appear and the ^{19}F NMR spectra show that both pentafluorophenyl groups are also equivalent.

The reaction of **1** with silver salts involves elimination of one thiolate group as $[Ag(SC_6F_5)]_n$ and formation of a cyclic complex with a bridging thiolate ligand, $[Au_2(\mu\text{-}SC_6F_5)(\mu\text{-dppf})]ClO_4$ (**11**). Its IR spectrum shows the presence of the ClO_4 anion with bands at 1100 (vs, br) and 622 (m) cm^{-1}; the thiolate absorptions appear at 1115 (s), 978 (m), and 850 (m) cm^{-1}. The conductivity of **11** corresponds to a 1:1 electrolyte.

The NMR spectra are similar to those of the other complexes, showing equivalent phosphorus atoms for ^{31}P, two multiplets for the cyclopentadienyl protons for ^{1}H, and only one type of pentafluorophenyl group for ^{19}F. In the LSIMS+ spectrum the molecular cation peak at *m/z* 1147 is the most intense.

The structure of complex **11** has been determined by X-ray diffraction studies and is shown in Figure 2. A selection of bond lengths and angles is collected in Table 2. The asymmetric unit consists of two independent formula units, which show short intra- and intermolecular gold–gold contacts. One discrete cation of complex **11** consist of two gold atoms bridged by the diphosphine and the thiolate ligands. The intramolecular Au–Au distances are 2.9610(16) and 2.9788(14) Å, and the intermolecular Au(2)–Au(3) distance is of the same order, 2.9666(14) Å. The solid-state structure is different from that obtained for the complex $[Au_2(\mu\text{-}SCH_2Ph)(PPh_3)_2]$, in which the thiolate ligand bridges two $AuPPh_3$ units in a similar manner, but the association of two cations through gold–gold interactions leads to a six-membered ring, with a chair conformation.[14] The Au–S–Au angles in **11** are very narrow, 77.59(17) and 78.75(16)°, whereas the Au–S–C angles are close to ideal tetrahedral values. These Au(I)–S–Au(I) angles are much narrower than that of complex **6** (see above), which corresponds to Au(I)–S–Au(III).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex 11

Au(1)–P(1)	2.260(6)	P(1)–C(21)	1.80(2)
Au(1)–S(1)	2.352(6)	P(1)–C(31)	1.81(2)
Au(1)–Au(2)	2.9610(16)	P(1)–C(11)	1.823(19)
Au(2)–P(2)	2.273(6)	P(2)–C(36)	1.78(2)
Au(2)–S(1)	2.374(6)	P(2)–C(51)	1.82(3)
Au(2)–Au(3)	2.9666(14)	P(2)–C(41)	1.84(2)
Au(3)–P(3)	2.280(5)	P(3)–C(81)	1.78(2)
Au(3)–S(2)	2.343(5)	P(3)–C(91)	1.80(2)
Au(3)–Au(4)	2.9788(14)	P(3)–C(71)	1.83(2)
Au(4)–P(4)	2.248(6)	P(4)–C(96)	1.802(19)
Au(4)–S(2)	2.352(5)	P(4)–C(101)	1.82(2)
S(1)–C(61)	1.74(2)	P(4)–C(111)	1.85(2)
S(2)–C(121)	1.81(2)		

P(1)–Au(1)–S(1)	175.4(2)	Au(3)–S(2)–Au(4)	78.75(16)
P(1)–Au(1)–Au(2)	124.42(16)	C(21)–P(1)–C(31)	105.3(8)
S(1)–Au(1)–Au(2)	51.53(15)	C(21)–P(1)–C(11)	107.3(9)
P(2)–Au(2)–S(1)	170.9(2)	C(31)–P(1)–C(11)	105.0(8)
P(2)–Au(2)–Au(1)	120.28(17)	C(21)–P(1)–Au(1)	111.6(6)
S(1)–Au(2)–Au(1)	50.88(14)	C(31)–P(1)–Au(1)	111.2(6)
P(2)–Au(2)–Au(3)	104.88(17)	C(11)–P(1)–Au(11)	115.7(6)
S(1)–Au(2)–Au(3)	83.83(15)	C(36)–P(2)–C(51)	103.9(9)
Au(1)–Au(2)–Au(3)	134.67(4)	C(36)–P(2)–C(41)	108.2(8)
P(3)–Au(3)–S(2)	169.8(2)	C(51)–P(2)–C(41)	104.9(9)
P(3)–Au(3)–Au(2)	97.36(15)	C(36)–P(2)–Au(2)	111.1(6)
S(2)–Au(3)–Au(2)	85.02(14)	C(51)–P(2)–Au(2)	115.5(7)
P(3)–Au(3)–Au(4)	122.52(14)	C(41)–P(2)–Au(2)	112.7(6)
S(2)–Au(3)–Au(4)	50.77(13)	C(81)–P(3)–C(91)	106.9(8)
Au(2)–Au(3)–Au(4)	130.49(4)	C(81)–P(3)–C(71)	108.4(8)
P(4)–Au(4)–S(2)	172.02(18)	C(91)–P(3)–C(71)	106.1(8)
P(4)–Au(4)–Au(3)	121.70(14)	C(81)–P(3)–Au(3)	114.3(6)
S(2)–Au(4)–Au(3)	50.49(13)	C(91)–P(3)–Au(3)	110.2(5)
C(61)–S(1)–Au(1)	109.4(5)	C(71)–P(3)–Au(3)	110.7(6)
C(61)–S(1)–Au(2)	107.9(5)	C(96)–P(4)–C(101)	105.4(9)
Au(1)–S(1)–Au(2)	77.59(17)	C(96)–P(4)–C(111)	104.6(8)
C(121)–S(2)–Au(3)	110.3(5)	C(101)–P(4)–C(111)	106.3(9)
C(121)–S(2)–Au(4)	106.0(5)	C(96)–P(4)–Au(4)	109.9(5)
C(101)–P(4)–Au(4)	114.5(6)	C(111)–P(4)–Au(4)	115.2(6)

The four gold atoms have a slightly distorted linear geometry; the largest deviations are 10.2 and 9.1° for Au(3) and Au(2) respectively, the gold atoms with both intra- and intermolecular gold–gold interactions. The Au–S distances range from 2.343(5) to 2.374(6) Å; they are somewhat dissimilar, although the difference may not be significant. They are of the same order as those found in complex **6**.

Complex **11** can further react with other metallic centers; thus, the treatment with $[Au(C_6F_5)_2(OEt_2)_2]ClO_4$ in the molar ratio 2:1 leads to the polynuclear compound $[Au_5(C_6F_5)_2(\mu_3\text{-}SC_6F_5)_2(\mu\text{-dppf})_2](ClO_4)_3$ (**12**). Complex **12** is an air- and moisture-stable orange solid that behaves as a 1:3 electrolyte in acetone solution. The IR spectrum shows the absorptions arising from pentafluorophenyl groups at 1514 (s), 975 (s), and 851 (s) cm^{-1}. The vibration ν(Au–S) appears at 314 (w) cm^{-1}.

The ^{31}P{^{1}H} NMR spectrum of **12** at room temperature shows one broad resonance that splits into two at −55 °C; this indicates that both phosphorus atoms of the diphosphine are inequivalent, conceivably because of the presence of different gold(I)–gold(I) or gold(I)–gold(III) interactions. In the ^{1}H NMR spectrum at room temperature the resonances due to the Cp protons are very broad, whereas at −55 °C six multiplets appear because the signals of some of the protons are overlapped. The ^{19}F NMR spectrum at room temperature shows the resonances arising from two types of pentafluorophenyl groups; however, at low temperature the signals become broader.

In the LSIMS+ spectrum the molecular peak does not appear, perhaps because of the high charge of the complex. The peak arising from the loss of one $Au_2(dppf)_2^{2+}$ fragment from the molecular cation, $[Au_3(dppf)(C_6F_5)_2(SC_6F_5)_2]^+$, is observed at m/z 1877 (5%).

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, 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 $SiMe_4$ (^1H, external), $CFCl_3$ (^{19}F, external), and 85% H_3PO_4 (^{31}P, external).

Materials. The starting materials $[Au_2Cl_2(\mu\text{-dppf})]$,[15] $[Au(C_6F_5)_3OEt_2]$,[16] $[Cu(NCMe)_4]PF_6$,[17] and $[Au(C_6F_5)_2(OEt_2)_2]ClO_4$[18] were prepared by published procedures. $[Au(OClO_3)PPh_3]$ was prepared from $[AuCl(PPh_3)]$[19] and $AgClO_4$ in dichloromethane in the molar ratio 1:1; the mixture was stirred for 1 h, and then the AgCl was filtered off and the solution containing $[Au(OClO_3)PPh_3]$ was used inmediately. Similarly $[Au_2(OClO_3)_2(\mu\text{-dppf})]$ was obtained from $[Au_2Cl_2(\mu\text{-dppf})]$ and 2 equiv of $AgClO_4$ in dichloromethane and also used inmediately. All other reagents were commercially available.

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

Syntheses. $[Au_2(SC_6F_5)_2(\mu\text{-dppf})]$ (1). To a solution of $[Au_2Cl_2(\mu\text{-dppf})]$ (0.102 g, 0.1 mmol) in dichloromethane (20 mL) was added HSC_6F_5 (0.029 mL, 0.2 mmol) and K_2CO_3 (0.69 g, 5 mmol). The mixture was stirred for 2 h and then filtered to eliminate the salts. The resulting solution was concentrated to ca. 5 mL, and addition of hexane gave an orange solid of **1**. Yield: 98%. $\Lambda_M = 0.86\ \Omega^{-1}\ cm^2\ mol^{-1}$. Anal. Found: C, 40.57; H, 1.80; S, 4.96. Calcd for $C_{46}H_{28}Au_2F_{10}P_2S_2$: C, 41.03; H, 2.10; S, 4.76. ^1H NMR: δ 4.23 (m, 4H, C_5H_4), 4.67 (m, 4H, C_5H_4), 7.2−7.6 (m, 20H, Ph) ppm. $^{31}P\{^1H\}$ NMR: δ 29.1 (s, 2P, dppf) ppm. ^{19}F NMR: δ −132.8 (m, 4F, *o*-F), −164.4 (m, 4F, *m*-F), −162.7 (t, 2F, *p*-F, $^3J(FF)$ = 21.36 Hz) ppm.

$[Au_4(\mu_3\text{-}SC_6F_5)_2(\mu\text{-dppf})(PR_3)_2](ClO_4)_2$ ($PR_3 = PPh_3$ (2), PPh_2Me (3)). To a dichloromethane solution (20 mL) of $[Au_2(SC_6F_5)_2(\mu\text{-dppf})]$ (0.136 g, 0.1 mmol) was added $[Au(OClO_3)PPh_3]$ (0.111 g, 0.2 mmol) or $[Au(OClO_3)PPh_2Me]$ (0.099 g, 0.2 mmol) and the mixture stirred for 15 min. Concentration of the solution to ca. 5 mL and addition of hexane gave orange solids of complex **2** or **3**. Complex **2**: yield 81%. $\Lambda_M = 197\ \Omega^{-1}\ cm^2\ mol^{-1}$. Anal. Found: C, 40.0; H, 2.11; S, 2.55. Calcd for $C_{82}H_{58}Au_4Cl_2F_{10}O_8P_4S_2$: C, 39.97; H, 2.37; S, 2.60. ^1H NMR (room temperature): δ 4.28 (m, 4H, C_5H_4), 4.66 (m, 4H, C_5H_4), 7.2−7.6 (m, 50H, Ph). ^1H NMR (−55 °C): δ 3.60 (m, 2H, C_5H_4), 4.17 (m, 2H, C_5H_4), 4.78 (m, 2H, C_5H_4), 5.04 (m, 2H, C_5H_4), 7.2−7.6 (m, 50H, Ph) ppm. $^{31}P\{^1H\}$ NMR (room temperature): δ 29.2 (s, 2P, dppf), 33.5 (br, 2P, PPh_3). $^{31}P\{^1H\}$ NMR (−55 °C): δ 23.3 (s), 28.2 (s), 33.0 (s), 34.7 (s) ppm. ^{19}F NMR: δ −129.9 (m, 4F, *o*-F), −160.1 (m, 4F, *m*-F), −154.0 (t, 2F, *p*-F, $^3J(FF)$ = 21.33 Hz) ppm. Complex **3**: yield 92%. $\Lambda_M = 211\ \Omega^{-1}\ cm^2\ mol^{-1}$. Anal. Found: C, 37.4; H, 2.32; S, 2.60. Calcd for $C_{72}H_{54}Au_4Cl_2F_{10}O_8P_4S_2$: C, 36.96; H, 2.33; S, 2.74. ^1H NMR (room temperature): δ 2.18 (d, 6H, $J(PH)$ = 10.69 Hz), 4.24 (m, 4H, C_5H_4), 4.64 (m, 4H, C_5H_4), 7.2−7.6 (m, 40H, Ph). ^1H NMR (−55 °C): δ 2.14 (d, 6H, $J(PH)$ = 9.50 Hz), 3.59 (m, 2H, C_5H_4), 4.18 (m, 2H, C_5H_4), 4.75 (m, 2H, C_5H_4), 5.03 (m, 2H, C_5H_4), 7.2−7.6 (m, 40H, Ph) ppm. $^{31}P\{^1H\}$ NMR (room temperature): δ 19.5 (br, 2P, PPh_2Me), 29.4 (s, 2P, dppf). $^{31}P\{^1H\}$ NMR (−55 °C) δ 17.0 (s), 19.9 (s), 28.3 (s), 31.2 (s) ppm. ^{19}F NMR: δ −129.8 (m, 4F, *o*-F), −160.3 (m, 4F, *m*-F), −154.3 (t, 2F, *p*-F, $^3J(FF)$ = 20.73 Hz) ppm.

$[Au_6(\mu_3\text{-}SC_6F_5)_2(\mu\text{-dppf})(PR_3)_4](ClO_4)_4$ ($PR_3 = PPh_3$ (4), PPh_2Me (5)). To a dichloromethane solution (20 mL) of $[Au_2(SC_6F_5)_2(\mu\text{-dppf})]$ (0.136 g, 0.1 mmol) was added $[Au(OClO_3)PPh_3]$ (0.222 g, 0.4 mmol) or $[Au(OClO_3)PPh_2Me]$ (0.198 g, 0.4 mmol) and the mixture stirred for 15 min. Concentration of the solution to ca. 5 mL and addition of hexane gave orange solids of complex **4** or **5**. Complex **4**: yield 90%. $\Lambda_M = 300.8\ \Omega^{-1}\ cm^2\ mol^{-1}$. Anal. Found: C, 39.95; H, 2.40; S, 1.80. Calcd for $C_{118}H_{88}Au_6Cl_4F_{10}O_{16}P_6S_2$: C, 39.57; H, 2.48; S, 1.79. ^1H NMR (room temperature): δ 4.27 (m, 4H, C_5H_4), 4.64 (m, 4H, C_5H_4), 7.2−7.7 (m, 80H, Ph). ^1H NMR (−55 °C): δ 3.52 (m, 1H, C_5H_4), 3.64 (m, 1H, C_5H_4), 4.15 (m, 1H, C_5H_4), 4.21 (m, 1H, C_5H_4), 4.74 (m, 1H, C_5H_4), 4.77 (m, 1H, C_5H_4), 5.03 (m, 2H, C_5H_4), 7.2−7.7 (m, 80H, Ph) ppm. $^{31}P\{^1H\}$ NMR (room temperature): δ 29.0 (s, 2P, dppf), 33.1 (br, 4P, PPh_3). $^{31}P\{^1H\}$ NMR (−55 °C): δ 28.0 (s, 1P, dppf), 28.4 (s, 1P, dppf), 31.0 (s, 2P, PPh_3), 33.9 (s, 2P, PPh_3) ppm. ^{19}F NMR (room temperature): δ −129.7 (m, 4F, *o*-F), −160.0 (m, 4F, *m*-F), −153.6 (br, 2F, *p*-F). ^{19}F NMR (−55 °C): δ −129.2 (m, 2F, *o*-F), −129.4 (m, 2F, *o*-F), −158.8 (m, 4F, *m*-F), −152.2 (t, 1F, *p*-F, $^3J(FF)$ = 21.31 Hz), −152.7 (t, 1F, *p*-F, $^3J(FF)$ = 22.15 Hz) ppm. Complex **5**: yield 86%. $\Lambda_M = 314\ \Omega^{-1}\ cm^2\ mol^{-1}$. Anal. Found: C, 34.99; H, 2.50; S, 1.88. Calcd for $C_{98}H_{80}Au_6Cl_4F_{10}O_{16}P_6S_2$: C, 35.31; H, 2.42; S, 1.92. ^1H NMR (room temperature): δ 2.19 (d, 12H, $J(PH)$ = 10.85 Hz), 4.30 (m, 4H, C_5H_4), 4.68 (m, 4H, C_5H_4), 7.2−7.8 (m, 60H, Ph). ^1H NMR (−55 °C): δ 2.08 (br, 6H, PMe), 2.17 (br, 6H, PMe), 3.54 (m, 1H, C_5H_4), 3.61 (m, 1H, C_5H_4), 4.15 (m, 1H, C_5H_4), 4.20 (m, 1H, C_5H_4), 4.75 (m, 1H, C_5H_4), 5.03 (m, 1H, C_5H_4), 5.08 (m, 2H, C_5H_4), 7.2−7.8 (m, 60H, Ph) ppm. $^{31}P\{^1H\}$ NMR (room temperature): δ 18.0 (br, 4P, PPh_2Me), 28.8 (s, 2P, dppf). $^{31}P\{^1H\}$ NMR (−55 °C): 16.4 (s, 2P, PPh_2Me), 19.4 (s, 2P, PPh_2Me), 28.1 (s, 1P, dppf), 28.2 (s, 1P, dppf) ppm. ^{19}F NMR (room temperature): δ −129.6 (m, 4F, *o*-F), −160.5 (m, 4F, *m*-F), −153.9 (br, 2F, *p*-F). ^{19}F NMR (−55 °C): δ −129.3 (m, 2F, *o*-F), −129.5 (m, 2F, *o*-F), −159.0 (m, 2F, *m*-F), −159.5 (m, 2F, *m*-F), −152.7 (t, 1F, *p*-F, $^3J(FF)$ = 21.31 Hz), −153.2 (t, 1F, *p*-F, $^3J(FF)$ = 22.01 Hz) ppm.

$[Au_4(\mu_3\text{-}SC_6F_5)_2(C_6F_5)_6(\mu\text{-dppf})]$ (6). To a solution of $[Au_2(SC_6F_5)_2(\mu\text{-dppf})]$ (0.136 g, 0.1 mmol) in dichloromethane (20 mL) was added $[Au(C_6F_5)_3OEt_2]$ (0.144 g, 0.2 mmol) and the mixture stirred for 15 min. Evaporation of the solvent to ca. 5 mL and addition of hexane afforded complex **6** as an orange solid. Yield: 80%. $\Lambda_M = 10.4\ \Omega^{-1}\ cm^2\ mol^{-1}$. Anal. Found: C, 35.47; H, 0.96; S, 2.34. Calcd for $C_{82}H_{28}Au_4F_{40}FeP_2S_2$: C, 35.91; H, 1.02; S, 2.34. ^1H NMR: δ 4.28 (m, 4H, C_5H_4), 4.74 (m, 4H, C_5H_4), 7.4−7.6 (m, 20H, Ph) ppm. $^{31}P\{^1H\}$ NMR: δ 31.0 (s, 2P, dppf) ppm. ^{19}F NMR: δ −120.0 (m, 8F, *o*-F), −122.2 (m, 4F, *o*-F), −129.1 (m, 4F, *o*-F), −160.6 (m, 4F, *m*-F), −160.7 (m, 8F, *m*-F), −161.4 (m, 4F, *m*-F), −151.3 (t, 2F, *p*-F, $^3J(FF)$ = 21.36 Hz), −156.3 (t, 4F, *p*-F, $^3J(FF)$ = 19.98 Hz), −156.8 (t, 2F, *p*-F, $^3J(FF)$ = 19.98 Hz) ppm.

$[Au_2Cu(\mu_3\text{-}SC_6F_5)_2Cl(\mu\text{-dppf})(PPh_3)]$ (7). To a solution of $[Au_2(SC_6F_5)_2(\mu\text{-dppf})]$ (0.136 g, 0.1 mmol) in dichloromethane (20 mL) was added $[CuCl(PPh_3)]_4$ (0.036 g, 0.25 mmol), and the mixture was stirred for 1 h. Evaporation of the solvent to ca. 5 mL and addition of hexane gave complex **7** as an orange solid. Yield: 40%. $\Lambda_M = 22\ \Omega^{-1}\ cm^2\ mol^{-1}$. Anal. Found: C,

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45.47; H, 2.55; S, 3.01. Calcd for $C_{64}H_{43}Au_2CuF_{10}FeClP_3S_2$: C, 45.01; H, 2.54; S, 3.75. ^{1}H NMR: δ 3,8 (m, br, 2H, C_5H_4), 4.2 (m, br, 2H, C_5H_4), 4.3 (m, br, 2H, C_5H_4), 4,5 (m, br, 2H, C_5H_4), 7.2−7.6 (m, 35H, Ph) ppm. ^{31}P{^{1}H} NMR: δ 32.0 (br, 2P, dppf), −12.1 (br, 1P, PPh_3) ppm. ^{19}F NMR: δ −132.4 (m, br, 4F, *o*-F), −163.2 (m, br, 4F, *m*-F), −161.0 (m, br, 2F, *p*-F).

[$Au_6Cu_2(\mu_3$-$SC_6F_5)_6(\mu$-dppf$)_3](PF_6)_2$ (8). To a solution of [$Au_2(SC_6F_5)_2(\mu$-dppf)] (0.136 g, 0.1 mmol) in dichloromethane (20 mL) was added [$Cu(NCMe)_4]PF_6$ (0.037 g, 0.05 mmol), and the mixture was stirred for 1 h. Evaporation of the solvent to ca. 5 mL and addition of hexane gave complex **8** as an orange solid. Yield: 56%. $\Lambda_M = 200\ \Omega^{-1}\ cm^2\ mol^{-1}$. Anal. Found: C, 37.69; H, 1.43; S, 5.02. Calcd for $C_{114}H_{84}Au_6Cu_2F_{32}Fe_3P_8S_4$: C, 37.19; H, 1.90; S, 4.31. ^{1}H NMR (room temperature): δ 4.38 (m, 12H, C_5H_4), 4.45 (m, 12H, C_5H_4), 7.2−7.8 (m, 60H, Ph). ^{1}H NMR (−55 °C): δ 4.0 (m, br, 4H, C_5H_4), 4.3 (m, br, 12H, C_5H_4), 4.5 (m, br, 4H, C_5H_4), 4.9 (m, 4H, C_5H_4), 7.2−7.8 (m, 60H, Ph) ppm. ^{31}P{^{1}H} NMR (room temperature): δ 27.8 (br, 6P, dppf); −55 °C, 30.7 (s, 2P, dppf), 29.1 (s, 4P, dppf). ^{19}F NMR (room temperature): δ −74.0 (d, 12F, PF_6, *J*(PF) = 713.69 Hz), −131.6 (br, 12F, *o*-F), −162.4 (br, 12F, *m*-F), −158.3 (br, 6F, *p*-F). ^{19}F NMR (−55 °C): isomer A, δ −132.1 (m, 8F, *o*-F, SR_1), −162.9 (m, 8F, *m*-F, SR_1), −158.0 (br, 4F, *p*-F, SR_1), −132.1 (m, 8F, *o*-F, SR_2), −163.0 (m, 8F, *m*-F, SR_2), −158.1 (br, 4F, *p*-F, SR_2) ppm; isomer B, δ −132.3 (m, 8F, *o*-F, SR_1), −161.4 (m, 8F, *m*-F, SR_1), −156.2 (br, 4F, *p*-F, SR_1), −132.8 (m, 8F, *o*-F, SR_2), −163.3 (m, 8F, *m*-F, SR_2), −156.8 (br, 4F, *p*-F, SR_2) ppm.

[$Au_2Hg(\mu_3$-$SC_6F_5)_2X_2(\mu$-dppf)] (X = Cl (9), I (10)). To a solution of [$Au_2(SC_6F_5)_2(\mu$-dppf)] (0.136 g, 0.1 mmol) in dichloromethane (20 mL) was added $HgCl_2$ (0.027 g, 0.1 mmol) or HgI_2 (0.046 g, 0.1 mmol), and the mixture was stirred for 1 h. The solution was evaporated to ca. 5 mL, and addition of hexane gave complex **9** or **10** as orange solids. Complex **9**: yield 88%. $\Lambda_M = 4\ \Omega^{-1}\ cm^2\ mol^{-1}$. ^{1}H NMR: δ 4.30 (m, 4H, C_5H_4), 4.67 (m, 4H, C_5H_4), 7.3−7.6 (m, 20H, Ph) ppm. ^{31}P{^{1}H} NMR: δ 25.2 (s, 2P, dppf) ppm. ^{19}F NMR: δ −132.2 (m, 4F, *o*-F), −161.7 (m, 4F, *m*-F), −156.6 (t, 2F, *p*-F, ^3J(FF) = 21.36 Hz) ppm. Complex **10**: yield 70%. $\Lambda_M = 32\ \Omega^{-1}\ cm^2\ mol^{-1}$. ^{1}H NMR: δ 4.41 (m, 4H, C_5H_4), 4.57 (m, 4H, C_5H_4), 7.3−7.7 (m, 20H, Ph) ppm. ^{31}P{^{1}H} NMR: δ 32.4 (s, 2P, dppf) ppm. ^{19}F NMR: δ −131.1 (m, 4F, *o*-F), −162.6 (m, 4F, *m*-F), −158.8 (t, 2F, *p*-F, ^3J(FF) = 21.16 Hz) ppm.

[$Au_2(\mu$-$SC_6F_5)(\mu$-dppf$)]ClO_4$ (11). To a solution of [$Au_2(SC_6F_5)_2(\mu$-dppf)] (0.136 g, 0.1 mmol) in dichloromethane (20 mL) was added $AgClO_4$ (0.021 g, 0.1 mmol), and the mixture was stirred for 1 h protected from light. Then the white precipitate of $[Ag(SC_6F_5)]_n$ was filtered off and the solution concentrated to ca. 5 mL. Addition of diethyl ether gave an orange solid of complex **11**. Yield: 86%. $\Lambda_M = 128\ \Omega^{-1}\ cm^2\ mol^{-1}$. Anal. Found: C, 38.16; H, 1.86; S, 3.03. Calcd for $C_{40}H_{28}Au_2ClF_5FeO_4P_2S$: C, 38.53; H, 2.26; S, 2.57. ^{1}H NMR: δ 4.26 (m, 4H, C_5H_4), 4.63 (m, 4H, C_5H_4), 7.3−7.6 (m, 20H, Ph) ppm. ^{31}P{^{1}H} NMR: δ 29.6 (s, 2P, dppf) ppm. ^{19}F NMR: δ −129.8 (m, 2F, *o*-F), −159.9 (m, 2F, *m*-F), −153.8 (t, F, *p*-F, ^3J(FF) = 21.36 Hz) ppm.

[$Au_5(C_6F_5)_2(\mu_3$-$SC_6F_5)_2(\mu$-dppf$)_2](ClO_4)_3$ (12). To a solution of [$Au_2(\mu$-$SC_6F_5)(\mu$-dppf$)]ClO_4$ (0.249 g, 0.2 mmol) in dichloromethane (20 mL) was added a diethyl ether solution (20 mL) of [$Au(C_6F_5)_2(OEt_2)_2]ClO_4$ (0.078 g, 0.1 mmol) and the mixture stirred for 15 min. Then evaporation of the solvent to ca. 5 mL and addition of hexane afforded complex **12** as an orange solid. Yield: 90%. $\Lambda_M = 256\ \Omega^{-1}\ cm^2\ mol^{-1}$. Anal. Found: C, 35.09; H, 1.94; S, 2.09. Calcd for $C_{92}H_{56}Au_5Cl_3F_{20}Fe_2O_{12}P_4S_2$: C, 35.37; H, 1.81; S, 2.05. ^{1}H NMR (room temperature): δ 4.3 (m, br, 16H, C_5H_4), 7.2−7,6 (m, 40H, Ph). ^{1}H NMR (−55 °C): δ 3.65 (m, 2H, C_5H_4), 3.67 (m, 2H, C_5H_4), 4.21 (m, 2H, C_5H_4), 4.23 (m, 2H, C_5H_4), 4.76 (m, 4H, C_5H_4), 5.03 (m, 4H, C_5H_4), 7.2−7.6 (m, 40H, Ph) ppm. ^{31}P{^{1}H} NMR (room temperature): δ 25.0 (br, 4P, dppf). ^{31}P{^{1}H} NMR (−55 °C): δ 29.1 (br, 2P, dppf), 28.7 (br, 2P, dppf) ppm. ^{19}F NMR (room temperature): δ −123.8 (m, 4F, *o*-F, C_6F_5), −130.0 (m, br, 4F, *o*-F, SC_6F_5), −160.0 (m, 10F, *m*-F, C_6F_5 + SC_6F_5 + *p*-F, C_6F_5), −153.6 (t, 2F, *p*-F, SC_6F_5, *J*(FF) = 21.15 Hz).

Table 3. Details of Data Collection and Structure Refinement for Complexes 6 and 11

	6	11·2.5CH_2Cl_2
chem formula	$C_{82}H_{28}Au_4F_{40}FeP_2S_2$	$C_{42.5}H_{32}Au_2Cl_6F_5FeO_4P_2S$
cryst habit	orange prism	orange plate
cryst size/mm	0.40 × 0.30 × 0.25	0.50 × 0.20 × 0.05
cryst syst	monoclinic	monoclinic
space group	*C*2/*c*	*P*2$_1$/*c*
a/Å	13.5150(10)	14.953(5)
b/Å	21.974(2)	30.587(8)
c/Å	27.244(3)	21.606(5)
β/deg	94.716(9)	107.01(2)
U/Å^3	8063.5(13)	9450(5)
Z	4	8
D_{calcd}/Mg m^{-3}	2.259	2.050
M_r	2742.82	1458.16
F(000)	5136	5568
T/°C	−100	−100
$2\theta_{max}$/deg	50	45
μ(Mo Kα)/mm^{-1}	7.649	7.010
transmissn	0.520−0.687	0.265−0.797
no. of rflns measd	10 642	15 834
no. of unique rflns	7073	12 113
R_{int}	0.051	0.067
$R(F)^a$ ($F > 4\sigma(F)$)	0.033	0.070
$R_w(F^2)^b$ (all rflns)	0.063	0.171
no. of rflns used	7068	12113
no. of params	591	665
no. of restraints	475	237
S^c	0.872	0.911
max $\Delta\rho$/e Å^{-3}	0.904	2.469

[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* is the number of parameters.

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 Oxford (**6**) or Siemens LT-2 (**11**) low-temperature attachment. Data were collected using monochromated Mo Kα radiation (λ = 0.710 73 Å). The scan type was $\theta - 2\theta$ (**6**) or ω (**11**). 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 direct methods and refined on F^2 using the programs SHELXL-93 and SHELXL-97.[20] All non-hydrogen atoms except C and O atoms of **11** were refined anisotropically. Hydrogen atoms were included using a riding model. A systems of restraints to light-atom displacement-factor components and local ring symmetry was used. The structure of complex **11** contains 2.5 independent dichloromethane molecules, one of which is badly resolved (C atom not located). One perchlorate is also badly resolved. Further details are given in Table 3.

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Supporting Information Available: Two X-ray crystallographic files, in CIF format, for **6** and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Sheldrick, G. M. SHELXL-93 and SHELXL-97, Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1993 and 1997.