Synthesis and Reactivity of Trinuclear Gold(III) Dithiolate Complexes. X-ray Structure of [Au(C₆F₅)(S₂C₆H₄)]₃ and [Au(C₆F₅)(S₂C₆H₄)(SC₆H₄SPPh₃)]

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Q₂[Zn(S-S)₂] or [SnMe₂(S-S)] (Q = NBu₄ or PPN, S-S = S₂C₆H₄, S₂C₆H₃CH₃, or C₃S₅ (dmit)) reacts with *trans*-[Au(C₆F₅)Cl₂(tht)] affording trinuclear species [Au(C₆F₅)(S-S)]₃ (**1–3**). When [AuX₃(tht)] (X = Cl or Br) are used instead, [AuBr(S-S)]ₙ (**4–6**) and [AuCl(dmit)]ₙ (**7**) are obtained. Complex **1** further reacts with PPh₃ to give [Au(C₆F₅)(S₂C₆H₄)(SC₆H₄SPPh₃)]. Complexes **1–3** react with neutral (pyridine) or anionic (Cl, Br, or SCN) ligands affording [Au(C₆F₅)(S-S)(py)] (**9a–c**) or Q[Au(C₆F₅)(S-S)X] (**10a–c–12a–c**) complexes. The structures of **1** and **8** have been established by X-ray crystallography. Complex **1** shows a six-membered Au₃S₃ ring which adopts a chair configuration and shows a gold–gold distance of 3.515 Å. Complex **8** is a mononuclear square-planar gold(III) complex with a new SC₆H₄SPPh₃ thiolate ligand, the P–S bond length being 2.058(5) Å.

Introduction

The synthesis of gold complexes containing Au–S bonds has attracted considerable attention in recent years because of their potential applications in various areas such as medicine,[1] mainly as antiarthritic drugs, deposition of gold films in electronic devices, and the glass industry[2] or as gold thiol interfaces.[3] Recent discoveries showing that aurothiolates have some inhibitory effects on HIV-1 (the etiologic agent of AIDS),[4] cytotoxicity, and anticancer activity[5] have encouraged the research activity in these areas.

Au–S complexes are known in oxidation states I, II, or III and in complexes formally containing gold(IV),[6] which probably contain gold(III) with partially oxidized ligands. Most are mononuclear, but there are noteworthy exceptions such as the dinuclear gold(II) complexes,[7] the recently reported [S(AuPR₃)₃] (PR₃ = PPh₃, PPh₂-Me, PMe₃),[8] [S(AuPR₃)₄] (PR₃ = PPh₃),[9] [Au₄(S-S)₂-(PEt₃)₂] (S-S = 1,2-S₂C₆H₄ or 3,4-S₂C₆H₃CH₃),[10,11] [Au₃-

(S-S)(PR₃)₃]⁺,[12] [Au₄(μ-(C₃S₅)₂(μ-dppm)₂],[13] or the benzenehexathiol derivative "golden wheel" [{CSAu(P-Ph₃)}₆].[14] Only a few examples of dinuclear gold(III) complexes have been reported such as [Au₂(CH₂-PPh₂CH₂)₂(S₂C₆H₄)₂][15] and [Au₂Me₂(SR)₂] (R = Ph,[16a] COCH₃,[16b] Et[16c]).

In this paper we report the synthesis of the trinuclear gold(III) derivatives [AuX(S-S)]₃ (S-S = 1,2-benzene-dithiolate (S₂C₆H₄), 3,4-toluenedithiolate (S₂C₆H₃CH₃), and 2-thioxo-1,3-dithiole-4,5-dithiolate (C₃S₅, dmit); X = Br, Cl, or C₆F₅) by dithiolate ligand transfer from Q₂-[Zn(S-S)₂] and [SnMe₂(S-S)]. The reaction of the trinuclear derivatives with various neutral or organic ligands breaks the thiolate bridge, affording [Au(C₆F₅)-(S-S)L] (L = PPh₃ or py) or Q[Au(C₆F₅)(S-S)X] (X = Cl, Br, SCN; Q = NBu₄ or PPN). The reaction of PPh₃ with [Au(C₆F₅)(S₂C₆H₄)]₃ leads to the expected addition product, but a side reaction involves an unprecedented thiolate–phosphine coupling, affording [Au(C₆F₅)-(S₂C₆H₄)(SC₆H₄SPPh₃)] as a byproduct. The molecular structures of [Au(C₆F₅)(S₂C₆H₄)]₃ and [Au(C₆F₅)-(S₂C₆H₄)(SC₆H₄SPPh₃)] have been established by single-

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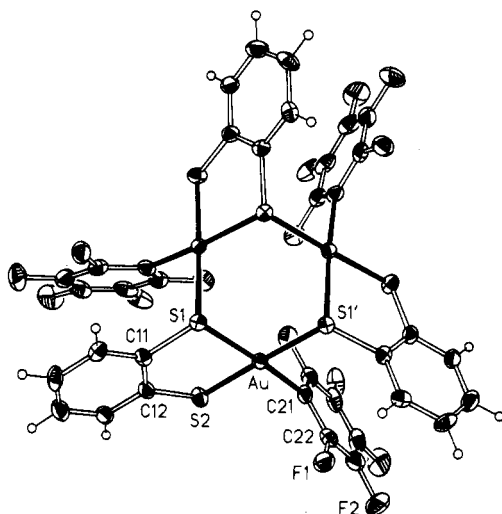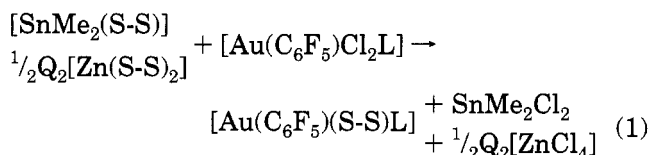
Figure 1. Molecule of compound **1** in the crystal with view direction (approximately) along the crystallographic 3-fold axis. Ellipsoids correspond to 50% probability levels. Hydrogen radii are arbitrary. The asymmetric unit and the equivalent atom S1′ are labeled.

crystal analysis, showing a six-membered Au_3S_3 ring in the former and the above-mentioned combination of dithiolate and triphenylphosphine in the latter.

Results and Discussion

Recently[17] we have shown that dithiolate complexes [SnMe₂(S-S)] or Q₂[Zn(S-S)₂] [S-S = 1,2-benzenedithiolate ($S_2C_6H_4$), 3,4-toluenedithiolate ($S_2C_6H_3CH_3$), and 2-thioxo-1,3-dithiole-4,5-dithiolate (dmit); Q = NEt₄ or PPh₃=N=PPh₃ (PPN)] transfer dithiolate groups to gold centers, on reaction with gold(III) complexes *cis*-[Au-(C_6F_5)Cl₂L] (L = phosphine or arsine ligand) (eq 1).

$$\begin{array}{c} \text{[SnMe}_2\text{(S-S)]} \\ ^1/_2\text{Q}_2\text{[Zn(S-S)}_2\text{]} \end{array} + \text{[Au(C}_6\text{F}_5\text{)Cl}_2\text{L]} \rightarrow$$

$$\text{[Au(C}_6\text{F}_5\text{)(S-S)L]} \begin{array}{c} + \text{ SnMe}_2\text{Cl}_2 \\ + ^1/_2\text{Q}_2\text{[ZnCl}_4\text{]} \end{array} \quad (1)$$

The analogous reaction starting from *cis*- or *trans*-[Au(C_6F_5)Cl₂(tht)] (tht = tetrahydrothiophene), in acetone or dichloromethane, and S-S = 1,2-$S_2C_6H_4$ affords a brown complex **1**, and from the mother liquors SnMe₂-Cl₂ or (PPN)₂[ZnCl₄] can be recovered. The reaction thus proceeds in a similar way to the previous one[17] (eq 1), but the spectroscopic properties of complex **1** indicate that there are important differences (eq 2). Thus ¹H NMR shows only signals assignable to the dithiolate ligand and no tetrahydrothiophene resonances, in accordance with the stoichiometry [Au(C_6F_5)($S_2C_6H_4$)] deduced by elemental analysis. ¹⁹F NMR of complex **1** shows five signals of equal intensity, which can be assigned to one type of C_6F_5 with hindered rotation around the *ipso*-carbon atom.

A polymeric formulation for complex **1** is further evidenced by mass spectrometry (FAB+); it shows peaks at *m/z* 1512 (80%), which can be assigned to [Au(C₆F₅)-(S₂C₆H₄)]₃⁺, and species lacking 1, 2, or 3 C₆F₅ groups of the parent ion (75%, 40%, 35%, respectively).

Final proof of the structure of complex **1** was furnished by X-ray diffraction (Figures 1 and 2). Atomic coordinates are given in Table 2 and selected bond lengths and angles in Table 3.
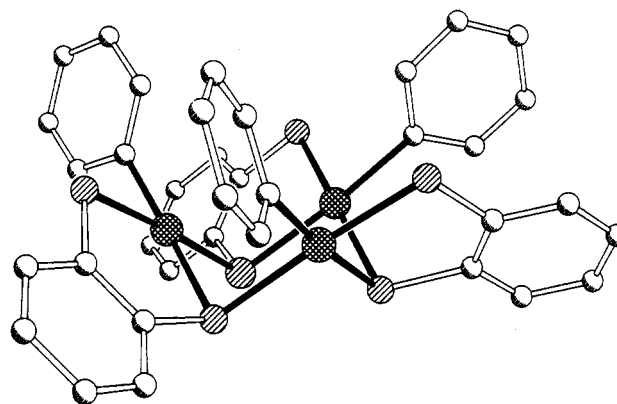
Figure 2. Molecule of compound **1** in the crystal (side view, arbitrary radii, H and F atoms omitted for clarity).

Table 1. Details of X-ray Structure Analyses for Compounds 1 and 8

	compd	
	1	**8·2CH₂Cl₂**
formula	$C_{36}H_{12}Au_3F_{15}S_6$	$C_{38}H_{27}AuCl_4F_5PS_4$
M_r	1512.72	1076.57
cryst habit	dark red tablet	pink platelet
cryst size (mm)	0.60 × 0.27 × 0.12	0.25 × 0.15 × 0.02
space group	$P\bar{3}$	$P\bar{1}$
temp (°C)	−130	−100
cell constants		
a (Å)	16.005(2)	12.677(3)
b (Å)	16.005(2)	13.288(3)
c (Å)	9.384(2)	13.534(3)
α (deg)	90	72.02(2)
β (deg)	90	82.19(2)
γ (deg)	120	67.72(2)
V (Å³)	2081.8(6)	2006.1(8)
Z	2	2
D_x (Mg m⁻³)	2.413	1.782
$F(000)$	1392	1052
μ (mm⁻¹)	10.9	4.23
transm factors	0.44−0.98	0.38−0.73
$2\theta_{max}$ (deg)	55	50
no. of reflcns		
measd	5848	7087
indpdt	3190	6727
R_{int}	0.052	0.117
$wR(F_2$, all reflcns)	0.098	0.114
$R(F, F > 4\sigma(F))$	0.039	0.066
no. of params	181	228
no. of restraints	160	107
S	1.05	0.76
max Δ/σ	0.001	<0.001
max $\Delta\rho$ (e Å⁻³)	1.9	1.4

The molecule displays crystallographic 3-fold symmetry. The immediate environment of each gold atom consists of one carbon atom and three sulfur atoms in a slightly distorted square-planar arrangement (root-mean-square deviation of five atoms 0.04 Å). One sulfur atom (S(1)) of each benzenedithiolate ligand bridges a pair of gold atoms and is thus three-coordinate, whereas the other (S(2)) only coordinates to one gold. The central six-membered Au_3S_3 ring adopts a chair configuration (Figure 2) analogous to that reported in [Au(CH₃)₂-NH₂]₃;[18] all three C_6F_5 groups lie on one side of the ring and all three dithiolate rings on the other side. The gold−gold distance is 3.515 Å, very similar to the 3.563 and 3.545 Å in [Au(CH₃)₂NH₂]₃[18] and longer than in dinuclear gold(III) derivative [Au₂(μ-CH₂)(μ-CH₂PPh₂-

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Table 2. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for Compound 1

	x	y	z	U(eq)[a]
Au	4720.7(2)	6955.6(2)	2811.9(3)	17.5(1)
S(1)	3629.3(11)	5634.5(12)	4202(2)	18.7(3)
S(2)	5113.8(13)	5961.1(13)	1587(2)	25.1(4)
C(11)	3973(5)	4764(5)	3783(7)	20.1(13)
C(12)	4627(5)	4929(5)	2659(8)	23.0(14)
C(13)	4870(5)	4225(5)	2384(8)	25.4(14)
C(14)	4494(6)	3406(5)	3208(8)	33(2)
C(15)	3854(6)	3250(5)	4315(8)	31(2)
C(16)	3600(5)	3936(5)	4605(7)	23.8(14)
C(21)	5671(5)	8007(5)	1483(7)	24.7(14)
C(22)	6604(5)	8655(5)	1890(8)	26.6(15)
C(23)	7275(5)	9326(6)	989(9)	34(2)
C(24)	7024(6)	9357(6)	−416(8)	38(2)
C(25)	6105(6)	8719(5)	−857(8)	32(2)
C(26)	5442(5)	8065(5)	89(8)	27.3(15)
F(1)	6903(3)	8604(3)	3228(5)	34.2(10)
F(2)	8179(3)	9937(4)	1420(6)	52.1(14)
F(3)	7670(4)	9976(4)	−1334(6)	57(2)
F(4)	5846(4)	8732(3)	−2213(5)	44.0(13)
F(5)	4543(3)	7448(3)	−398(5)	34.1(10)

[a] U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compound 1[a]

Au−C(21)	2.035(7)	Au−S(2)	2.292(2)
Au−S(1)	2.352(2)	Au−S(1′)	2.395(2)
S(1)−C(11)	1.779(7)	S(2)−C(12)	1.750(7)
C(21)−Au−S(2)	85.2(2)	C(21)−Au−S(1)	174.6(2)
S(2)−Au−S(1)	89.55(6)	C(21)−Au−S(1′)	95.7(2)
S(2)−Au−S(1′)	176.73(6)	S(1)−Au−S(1′)	89.70(8)
C(11)−S(1)−Au	101.5(2)	C(11)−S(1)−Au″	108.1(2)
Au−S(1)−Au″	95.53(6)	C(12)−S(2)−Au	102.7(2)

[a] Symmetry transformations used to generate equivalent atoms: (′) $-y + 1, x - y + 1, z$; (″) $-x + y, -x + 1, z$.

$CH_2)_2(C_6F_5)_2]^{19}$ at 3.113 Å. Although metal−metal interactions with gold(III)−gold(I) distances of 3.470 Å[20] (av) have been postulated, we believe that in our complex the mentioned Au···Au distance is imposed by the six-membered ring.

The three Au−S bond lengths differ significantly. As expected, those to the bridging S (Au−S(1) and Au−S(1′)) are longer (2.352(2) and 2.395(2) Å) than Au−S(2) (2.292(2) Å). It is surprising that Au−S(1′) (*trans* to S) is longer than Au−S(1) (*trans* to C) in view of the appreciable expected *trans* influence of carbon ligands at gold; however, a comparison of Au−S bond lengths in $[Au(dmit)_2]^{-}$ [21,22] and $[Au(dmit)(C_6F_5)_2]^{-}$ [23] shows no significant differences. The shorter distance Au−S(2) is very similar to those observed in other dithiolate gold(III) complexes with two-coordinate sulfur, such as $[Au(C_6F_5)(1,2\text{-}S_2C_6H_4)(PPh_3)]^{17}$ (2.314(1) and 2.299(1) Å) and $[Au(1,2\text{-}S_2C_6H_4)_2]$ (2.305 Å),[6] and shorter than in related gold(I) derivatives, e.g. $[Au_2(1,2\text{-}S_2C_6H_4)(PPh_3)_2]$ (2.325(3) and 2.316(3) Å).[10,11] The Au−C bond of 2.035 Å is similar to those in $[Au(1,2\text{-}S_2C_6H_4)(C_6F_5)(PPh_3)]^{17}$ (2.061(4) Å) or $[Au(C_6F_5)_2\{S_2CN(CH_2Ph)_2\}]^{24}$ (2.047(6) and 2.049(6) Å].
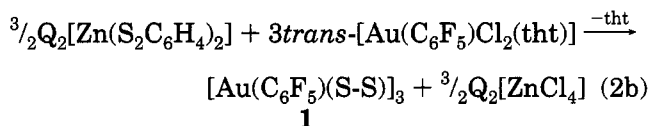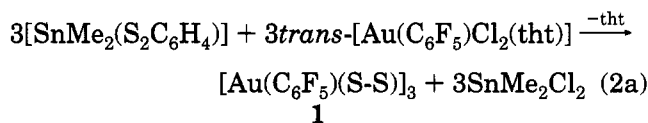
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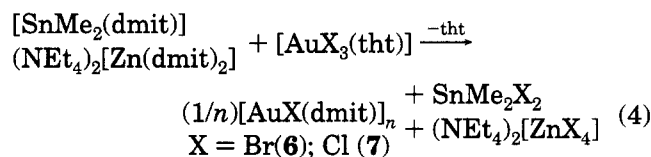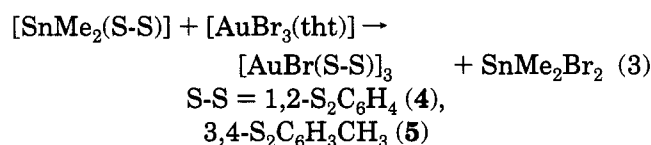(23) Cerrada, E.; Jones, P. G.; Laguna, A.; Laguna, M. Unpublished results.

The formation of **1** can be represented as shown in process 2.

$$3[SnMe_2(S_2C_6H_4)] + 3\textit{trans-}[Au(C_6F_5)Cl_2(tht)] \xrightarrow{-tht}$$
$$[Au(C_6F_5)(S\text{-}S)]_3 + 3SnMe_2Cl_2 \quad (2a)$$
$$\mathbf{1}$$

$$^3/_2Q_2[Zn(S_2C_6H_4)_2] + 3\textit{trans-}[Au(C_6F_5)Cl_2(tht)] \xrightarrow{-tht}$$
$$[Au(C_6F_5)(S\text{-}S)]_3 + {}^3/_2Q_2[ZnCl_4] \quad (2b)$$
$$\mathbf{1}$$

When reaction 2 is carried out with the toluene analog $3,4\text{-}S_2C_6H_3CH_3$, a brown complex **2** is formed, for which analysis and mass spectra indicate the same type of trinuclear derivative $[Au(C_6F_5)(S_2C_6H_3CH_3)]_3$; however ¹H NMR (two singlets for the Me groups) and ¹⁹F NMR (two types of nonrotating C_6F_5 groups) show that probably it is a mixture of isomers, because the dithiolate ligand is not symmetrical. The mass spectrum shows the trinuclear parent peak at m/z 1554 (55%) and the loss of 1, 2, or 3 C_6F_5 groups at m/z 1387 (55%), 1220 (20%), and 1066 (20%), respectively.

Reaction 2 proceeds in a similar way with 2-thioxo-1,3-dithiole-4,5-dithiolate (dmit) as ligand, affording a dark purple product $[Au(C_6F_5)(dmit)]_n$ (**3**) that has an uninformative mass spectrum, with no peaks assignable to $[Au(C_6F_5)(dmit)]_n^+$. Its ¹⁹F NMR shows one type of C_6F_5 group, for which only three signals are present because both *ortho*-F and *meta*-F are equivalent. Although the reactivity of complex **3** (see below) is very similar to that shown by complexes **1** and **2**, we do not have conclusive data to propose a trinuclear structure for complex **3**.

Process 2 can be extended to the synthesis of halo−gold derivatives starting from $[AuX_3(tht)]$ (X = Cl, Br), but in these cases the reaction is not a general procedure; only with the dmit ligand does the reaction work as intended with the tin and zinc derivatives and X = Cl or Br. In contrast, when $1,2\text{-}S_2C_6H_4$ or $3,4\text{-}S_2C_6H_3\text{-}CH_3$ are used, only the bromide derivatives can be isolated by the reaction of the tin complex (eqs 3 and 4)

$$[SnMe_2(S\text{-}S)] + [AuBr_3(tht)] \rightarrow$$
$$[AuBr(S\text{-}S)]_3 + SnMe_2Br_2 \quad (3)$$
$$S\text{-}S = 1,2\text{-}S_2C_6H_4 \textbf{ (4)},$$
$$3,4\text{-}S_2C_6H_3CH_3 \textbf{ (5)}$$

$$\begin{matrix}[SnMe_2(dmit)] \\ (NEt_4)_2[Zn(dmit)_2]\end{matrix} + [AuX_3(tht)] \xrightarrow{-tht}$$
$$\begin{matrix}(1/n)[AuX(dmit)]_n & + SnMe_2X_2 \\ & + (NEt_4)_2[ZnX_4]\end{matrix} \quad (4)$$
$$X = Br \textbf{(6)}; Cl \textbf{(7)}$$

¹H NMR of complexes **4** and **5** shows only dithiolate resonances, in accordance with their formulation. We have only analytical data for complexes **6** and **7**, because their insolubility precludes spectroscopic techniques. Only the mass spectrum of **4** shows the trinuclear parent peak (m/z 1512, 15%); complexes **5**−**7** give a very poor ionization pattern with the lack of signals of the trinuclear species. We presume that complexes **4** and

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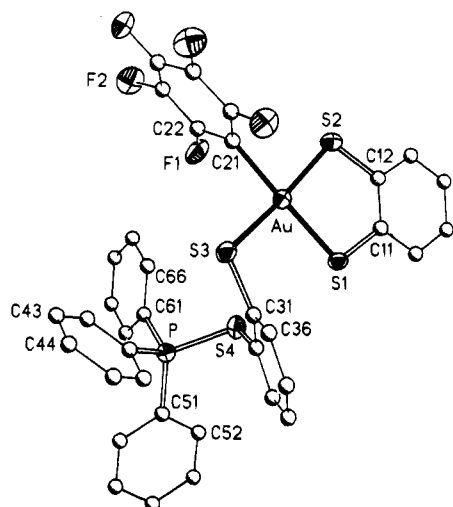
Figure 3. Molecule of compound **8** in the crystal. Ellipsoids correspond to 50% probability levels. Hydrogen and carbon radii are arbitrary.

(probably) **5** present trinuclear structures similar to **1**, but in the case of the dmit derivatives, **6** and **7**, only polynuclear structures can be proposed.

Complexes **1–3** react under very mild conditions (diethyl ether, room temperature, reaction times of the order of minutes) with neutral ligands such as PPh$_3$ (gold/ligand ratio 1:1) to give the previously known complexes [Au(C$_6$F$_5$)(S-S)(PPh$_3$)].[17] When complex **2** is involved, the resulting product shows one ^{31}P NMR signal, one ^{1}H NMR resonance for the methyl group, and three resonances in the ^{19}F NMR spectra, as reported for [Au(C$_6$F$_5$)(S$_2$C$_6$H$_3$CH$_3$)(PPh$_3$)][17] in accordance with a formulation of **2** as a mixture of isomers. When S-S = S$_2$C$_6$H$_4$ is used, a small quantity of a pink complex **8** precipitates and can be easily recovered. Analytical data and the mass spectrum are in accordance with the composition "[Au(C$_6$F$_5$)(S$_2$C$_6$H$_4$)$_2$-(PPh$_3$)]" (*m/z* = 906 [M$^+$], 32%). The apparent presence of two dithiolate ligands and a pentafluorophenyl group would indicate five negative charges; however, the base peak (SC$_6$H$_4$SPPh$_3$) (*m/z* = 403) in the spectrum suggested that this modified ligand might be present in the complex.

The molecular structure of complex **8** was resolved by an X-ray study of its bis(dichloromethane) solvate (Figure 3), confirming its formulation as [Au(C$_6$F$_5$)-(S$_2$C$_6$H$_4$)(SC$_6$H$_4$SPPh$_3$)]. Atomic coordinates are given in Table 4 and selected bond lengths and angles in Table 5. The complex is mononuclear and exhibits square-planar geometry (mean deviation of five atoms 0.04 Å); one benzenedithiolate acts as a chelating anion, and a new thiolate ligand is observed, formed by an unprecedented coupling of triphenylphosphine and one S terminus of dithiolate. It is noteworthy that the [Au-(C$_6$F$_5$)(S$_2$C$_6$H$_4$)] fragment in this complex is very similar to the recently reported [Au(C$_6$F$_5$)(S$_2$C$_6$H$_4$)(PPh$_3$)].[17] The Au–S(dithiolate) bond lengths are Au–S(1) = 2.314(4) and Au–S(2) = 2.299(4) Å, the longer being *trans* to the C$_6$F$_5$, but Au–S(3), the bond to the new ligand, is longer again at 2.338(4) Å. The P–S(4) bond length of 2.058-(5) Å is consistent with its formulation as a formally

Table 4. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for Compound 8

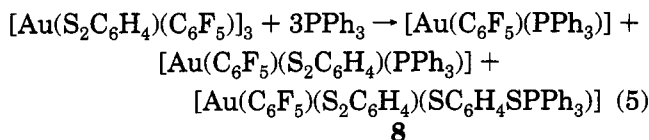|	*x*	*y*	*z*	*U*(eq)^a
Au	8874.2(6)	3305.6(7)	2629.0(6)	24.8(2)
P	4399(3)	5919(3)	2934(3)	25.6(10)
S(1)	8901(3)	4310(3)	3745(3)	26.9(10)
S(2)	10257(3)	1723(4)	3573(3)	34.8(12)
S(3)	7554(4)	4829(4)	1495(3)	33.7(12)
S(4)	5989(3)	5377(3)	3539(3)	30.4(10)
C(11)	9863(7)	3244(7)	4710(6)	27(4)
C(12)	10458(8)	2162(8)	4605(6)	32(4)
C(13)	11210(7)	1355(6)	5367(7)	37(4)
C(14)	11366(7)	1629(7)	6234(6)	41(4)
C(15)	10771(7)	2711(8)	6339(5)	35(4)
C(16)	10019(7)	3519(6)	5577(7)	23(4)
C(21)	8869(11)	2350(12)	1679(10)	37(5)
C(22)	8200(10)	1704(10)	1900(10)	28(4)
C(23)	8167(11)	1052(11)	1275(10)	34(4)
C(24)	8745(11)	1126(13)	350(11)	41(4)
C(25)	9464(12)	1724(12)	119(12)	45(5)
C(26)	9500(11)	2308(12)	811(10)	32(4)
F(1)	7551(7)	1627(7)	2782(6)	45(2)
F(2)	7470(7)	452(7)	1515(6)	50(3)
F(3)	8708(7)	550(7)	−268(6)	55(3)
F(4)	10061(7)	1780(7)	−779(6)	55(3)
F(5)	10157(7)	2989(7)	468(6)	47(3)
C(31)	7258(7)	6093(5)	1859(7)	15(3)
C(32)	6567(7)	6352(6)	2702(6)	23(4)
C(33)	6291(6)	7407(7)	2865(5)	31(4)
C(34)	6707(7)	8202(6)	2183(7)	25(4)
C(35)	7398(7)	7943(6)	1340(6)	33(4)
C(36)	7673(6)	6888(7)	1177(5)	34(4)
C(41)	4357(7)	6404(7)	1540(5)	24(4)
C(42)	4050(7)	5838(6)	984(7)	30(4)
C(43)	4026(7)	6218(7)	−95(7)	47(5)
C(44)	4309(8)	7164(8)	−617(5)	41(4)
C(45)	4616(7)	7729(6)	−61(7)	40(4)
C(46)	4640(7)	7349(7)	1017(7)	26(4)
C(51)	3352(7)	7030(7)	3396(7)	30(4)
C(52)	3480(6)	7169(7)	4344(7)	28(4)
C(53)	2622(8)	7984(8)	4731(6)	40(4)
C(54)	1636(7)	8660(7)	4169(7)	47(5)
C(55)	1508(6)	8522(7)	3221(7)	42(5)
C(56)	2366(8)	7707(8)	2834(6)	34(4)
C(61)	4058(8)	4661(6)	3454(6)	24(4)
C(62)	3074(7)	4658(6)	4048(7)	30(4)
C(63)	2857(6)	3658(8)	4456(6)	32(4)
C(64)	3623(8)	2659(6)	4268(7)	34(4)
C(65)	4607(7)	2662(6)	3673(7)	38(4)
C(66)	4824(6)	3662(8)	3266(6)	40(5)
C(98)	3242(22)	508(22)	2804(20)	146(11)
Cl(1)	3594(6)	296(6)	1561(7)	154(3)
Cl(2)	4322(6)	−1(6)	3592(7)	156(3)
C(99)	8697(15)	5485(15)	8550(14)	77(6)
Cl(3)	7296(4)	6491(4)	8549(4)	75(2)
Cl(4)	8817(4)	4426(4)	8086(4)	72(2)

^{a} *U*(eq) is defined as one-third of the trace of the orthogonalized **U**$_{ij}$ tensor.

single bond (cf. standard P=S bond length of ca. 1.95 Å), although there are few examples of P–S single bonds at four-coordinate phosphorus (2.0737(9) Å in a recently measured NC$_2$PS system[25]).
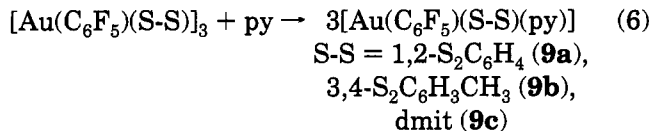
The yield of complex **8** can be increased using a higher gold/PPh$_3$ ratio; the best result (11%) is obtained with the ratio 1:1.5. Neither other phosphines as PPh$_2$Me or PPhMe$_2$ nor AsPh$_3$ give coupling thiolate-ligand complexes; only the known[17] [Au(C$_6$F$_5$)(S$_2$C$_6$H$_4$)L] (L = PPh$_2$Me, PPhMe$_2$, AsPh$_3$) are obtained. Complex **8** is only formed when the reaction takes place in diethyl ether, probably because of its insolubility in this solvent. When the reaction is done in dichloromethane, the ^{31}P NMR shows that [Au(C$_6$F$_5$)(S$_2$C$_6$H$_4$)(PPh$_3$)] is the only gold product containing PPh$_3$. Complex **8** is not an

(25) Pinchuk, V. A.; Müller, C.; Fischer, A.; Thönnessen, H.; Jones, P. G.; Schmutzler, R.; Markowsky, L. N.; Shermolovich, Y. G.; Pinchuk, A. M. *Phosphorus, Sulfur Silicon*, submitted for publication.

intermediate in the formation of $[Au(C_6F_5)(S_2C_6H_4)-(PPh_3)]$ because when a solution is stirred in diethyl ether or dichloromethane, the starting complex is recovered without change. We do not have the evidence of the formation mechanism of complex **8**, but a way could be the attack of PPh_3 on one nonbridging S atom and the reduction of one gold center giving rise with one extra triphenylphosphine to $[Au(C_6F_5)(PPh_3)]$, which can be detected by ^{31}P and ^{19}F NMR in the reaction solvent, and complex **8**. The third Au appears as $[Au(C_6F_5)(S_2C_6H_4)(PPh_3)]$. A possible reaction is presented in eq 5.

$$[Au(S_2C_6H_4)(C_6F_5)]_3 + 3PPh_3 \rightarrow [Au(C_6F_5)(PPh_3)] +$$
$$[Au(C_6F_5)(S_2C_6H_4)(PPh_3)] +$$
$$[Au(C_6F_5)(S_2C_6H_4)(SC_6H_4SPPh_3)] \quad (5)$$
$$\mathbf{8}$$

The reaction of polynuclear complexes **1–3** with pyridine, a ligand with limited affinity for gold(III), breaks the dithiolate bridge, affording mononuclear complexes **9a–c** (eq 6).

$$[Au(C_6F_5)(S\text{-}S)]_3 + py \rightarrow 3[Au(C_6F_5)(S\text{-}S)(py)] \quad (6)$$
$$S\text{-}S = 1,2\text{-}S_2C_6H_4 \ (\mathbf{9a}),$$
$$3,4\text{-}S_2C_6H_3CH_3 \ (\mathbf{9b}),$$
$$\text{dmit} \ (\mathbf{9c})$$

The analytical data and spectroscopic properties of complexes **9a–c** are in accordance with their formulation. ^{1}H NMR shows pyridine protons in a 1:1 ratio, and ^{19}F NMR show in all cases three signals indicating one type of C_6F_5 group with free rotation around the C-*ipso* atom. The mass spectra show the parent peak as follows: **9a** (*m/z* 583, 50%) and **9b** (*m/z* 597, 45%).

The reaction with pyridine to give complexes **9a–c** demonstrates the ease of breaking the sulfur bridges. This makes the complexes **1–3** an excellent starting point to extend gold(III) dithiolate chemistry. As an example we have carried out reactions with various halides and pseudohalogenides affording anionic complexes **10–12** (eq 7).

$$[Au(C_6F_5)(S\text{-}S)]_3 + 3XQ \rightarrow$$
$$Q[Au(C_6F_5)(S\text{-}S)X]$$
$$X = Br, \ Q = NBu_4 \ (\mathbf{10a\text{-}c}) \quad (7)$$
$$X = Cl, \ Q = PPN \ (\mathbf{11a\text{-}c})$$
$$X = SCN, \ Q = PPN \ (\mathbf{12a\text{-}c})$$
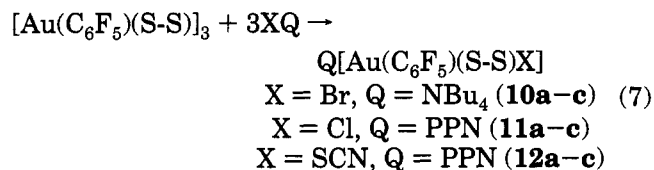
Complexes **10a,b**, **11a,b**, and **12a,b** are violet, and **10c**, **11c**, and **12c** are yellow-green solids. They show conductivities of 95–110 Ω^{-1} cm^2 mol^{-1} characteristic of 1:1 electrolytes, in agreement with their formulation. The ^{1}H NMR spectra show the ligand and cation resonances in the expected ratio. ^{19}F NMR again shows three resonances assignable to one C_6F_5 group, as expected for the monuclear complexes. The toluenedithiolate complexes **10b**, **11b**, and **12b** only show one absorption assignable to the Me group, as is usual in mononuclear complexes, although the two isomers should be present. Their mass spectra (FAB−) show peaks assignable to the parent anions as follows (*m/z*): **10a** (583, 100%), **10b** (598, 50%), **10c** (640, 15%), **11a** (539, 55%), **11b** (533, 5%), **12a** (562, 55%), **12b** (576,

100%), **12c** (618, 15%). **11c** does not show the parent anion, but $[M - Cl]^-$ is present at *m/z* = 560 (10%).

Experimental Section

Syntheses. $[Au(C_6F_5)(S\text{-}S)]_3$ [S-S = 1,2-$S_2C_6H_4$ (1), 3,4-$S_2C_6H_3CH_3$ (2)]. Method a. To a dichloromethane (30 cm^3) solution of $[Sn(CH_3)_2(1,2\text{-}S_2C_6H_4)]$ (0.029 g, 0.1 mmol) or $[Sn(CH_3)_2(3,4\text{-}S_2C_6H_3CH_3)]$ (0.030 g, 0.1 mmol) was added $[Au(C_6F_5)Cl_2(tht)]$ (0.052 g, 0.1 mmol), and the resulting solution was stirred for 1 h. Evaporation of the solvent to 5 cm^3 and addition of hexane (20 cm^3) resulted in the precipitation of brown complexes. Yield (%): 84 (**1**), 86 (**2**). **Method b.** To a dichloromethane (30 cm^3) solution of $(PPN)_2[Zn(1,2\text{-}S_2C_6H_4)_2]$ (0.076 g, 0.05 mmol) or $(PPN)_2[Zn(3,4\text{-}S_2C_6H_3CH_3)_2]$ (0.077 g, 0.05 mmol) was added $[Au(C_6F_5)Cl_2(tht)]$ (0.052 g, 0.1 mmol). After being stirred for 3 h, the solution was concentrated to 5 cm^3. Addition of diethyl ether (15 cm^3) gave a white precipitate $(PPN)_2[ZnCl_4]$. The solution was filtered through 1 cm of diatomaceous earth and the solvent removed to 5 cm^3. Addition of hexane (20 cm^3) led to the precipitation of brown solids. Yield (%): 84 (**1**), 86 (**2**). Data for **1** are as follows. Anal. Calcd for $C_{36}H_{12}Au_3F_{15}S_6$: C, 28.6; H, 0.8; S, 12.7. Found: C, 28.4; H, 0.85; S, 12.3. Λ_M: 5 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR: $\delta = 7.42$ and 7.04 (m, 4H, S$_2$C$_6$H$_4$). ^{19}F NMR: $\delta = -111.4$ (m, 1F, F$_o$), -120.65 (m, 1F, F$_o$), -155.5 (t, $^3J_{F_pF_m} = 23.6$ Hz, 1F, F$_p$), -158.15 (m, 1F, F$_m$), -158.7 (m, 1F, F$_m$). Data for **2** are as follows. Anal. Calcd for $C_{39}H_{18}Au_3F_{15}S_6$: C, 30.15; H, 1.2; S, 12.35. Found: C, 30.35; H, 1.25; S, 12.3. Λ_M: 22 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR: $\delta = 7.20$ and 6.82 (m, 3H, S$_2$C$_6$H$_3$CH$_3$), 2.28 (s, 3H, S$_2$C$_6$H$_3$CH$_3$). ^{19}F NMR: $\delta = -111.7$ (m, 1F, F$_o$), -120.5 (m, 1F, F$_o$), -122.1 (m, F$_o$), -156.2 (t, $^3J_{F_pF_m} = 20.0$ Hz, F$_p$), -157.1 (t, $^3J_{F_pF_m} = 19.3$ Hz, 1F, F$_p$), -159.15 (m, 1F, F$_m$), -159.5 (m, 1F, F$_m$), -159.7 (m, F$_m$).

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[Au(C₆F₅)(dmit)]ₙ (3). Method a. To an acetone (30 cm³) solution of [Sn(dmit)(CH₃)₂] (0.034 g, 0.1 mmol) was added [Au-(C₆F₅)Cl₂(tht)] (0.052 g, 0.1 mmol), and the resulting solution was stirred for 4 h. Evaporation of the solvent to 5 cm³ and addition of hexane (20 cm³) resulted in the precipitation of the dark purple complex **3**. Yield: 65%. **Method b.** To an acetone (30 cm³) solution of (NEt₄)₂[Zn(dmit)₂] (0.071 g, 0.1 mmol) under dinitrogen was added [Au(C₆F₅)Cl₂(tht)] (0.104 g, 0.2 mmol). After being stirred for 3 h, the solution was concentrated to 1 cm³. Addition of diethyl ether (15 cm³) left a white solid (PPN)₂[ZnCl₄]; the solution was filtered through 1 cm of diatomaceous earth and solvent removed to 5 cm³. Addition of hexane (20 cm³) led to the precipitation of dark purple solid **3**, which was washed with water and dried *in vacuo*. Yield: 65%. Anal. Calcd for C₉AuF₅S₅: C, 19.3; S, 29.3. Found: C, 19.45 ; S, 28.6. ¹⁹F NMR: δ = −121.0 (m, 2F, F$_o$), −154.1 (t, $^3J_{F_pF_m}$ = 19.8Hz, 1F, F$_p$), −159.7 (m, 2F, F$_m$).

[AuBr(S-S)]₃ [S-S = 1,2-S₂C₆H₄ (4), 3,4-S₂C₆H₃CH₃ (5)]. Method a. To a dichloromethane (30 cm³) solution of [Sn(CH₃)₂(1,2-S₂C₆H₄)] (0.029 g, 0.1 mmol) or [Sn(CH₃)₂(3,4-S₂C₆H₃CH₃)] (0.030 g, 0.1 mmol) was added [AuBr₃(tht)] (0.052 g, 0.1 mmol), and the resulting solution was stirred for 1 h. Evaporation of the solvent to 5 cm³ and addition of diethyl ether (20 cm³) resulted in the precipitation of dark brown complexes. Yield (%): 55 (**4**), 48 (**5**). Data for **4** are as follows. Anal. Calcd for C₁₈H₁₂Au₃Br₃S₆: C, 17.3; H, 0.95; S, 15.35. Found: C, 17.5; H, 1.0; S, 16.0. ¹H NMR: δ = 7.70−7.04 (m, 4H, S₂C₆H₄). Data for **5** are as follows. Anal. Calcd for C₂₁H₁₈Au₃Br₃S₆: C, 19.5; H, 1.4; S, 14.9. Found: C, 19.8; H, 1.6; S, 15.5. ¹H NMR: δ = 7.62, 7.34 and 6.82 (m, 3H, S₂C₆H₃-CH₃), 2.21(s, 3H, S₂C₆H₃CH₃).

[Au(X)(dmit)]ₙ [X = Br (6), Cl (7)]. Method a. To an acetone (30 cm³) solution of [Sn(dmit)(CH₃)₂] (0.034 g, 0.1 mmol) was added [AuCl₃(tht)] (0.039 g, 0.1 mmol) or [AuBr₃-(tht)] (0.052 g, 0.1 mmol). Immediately black solids **6** and **7** precipitated, which were filtered off and dried *in vacuo*. Yield (%): 90 (**6**), 74 (**7**). **Method b.** To an acetone solution under dinitrogen of (NEt₄)₂[Zn(dmit)₂] (0.071 g, 0.1 mmol) was added [AuCl₃(tht)] (0.078 g, 0.2 mmol) or [AuBr₃(tht)] (0.104 g, 0.2 mmol). Black solids **6** and **7** appeared immediately, which were filtered off, washed with water, and dried *in vacuo*. Yield (%): 97 (**6**), 90 (**7**). Anal. Calcd for C₃AuBrS₅: C, 7.6; S, 33.8. Found: C, 7.7; S, 31.55.Anal. Calcd for C₃AuClS₅: C, 8.4; S, 37.3. Found: C, 9.0; S, 36.45.

[Au(C₆F₅)(S₂C₆H₄)(SC₆H₄SPPh₃)] (8). To a diethyl ether (30 cm³) solution of **1** (0.015 g, 0.05 mmol) was added PPh₃ (0.059 g, 0.225 mmol), and the resulting solution was stirred for 1 h. A pink solid appeared, which was filtered off and washed with diethyl ether (2 × 5 cm³). Yield: 11%. Anal. Calcd for C₃₆H₂₃AuF₅PS₄: C, 47.7; H, 2.55; S, 14.1. Found: C, 47.9; H, 2.6; S, 14.6. Λ$_M$: 7 Ω⁻¹ cm² mol⁻¹. ³¹P NMR: δ = 44.1 (s). ¹⁹F NMR: δ = −120.8 (m, 2F, Fo), −159.1 (t, $^3J_{F_pF_m}$ = 19.5 Hz, 1F, F$_p$), −162.7 (m, 2F, F$_m$).

[Au(C₆F₅)(S-S)py] [S-S = 1,2-S₂C₆H₄ (9a), 3,4-S₂C₆H₃CH₃ (9b), dmit (9c)]. To a diethyl ether (30 cm³) solution of **1** (0.151 g, 0.04 mmol) or **2** (0.155 g, 0.04 mmol) or to an acetone (30 cm³) of **3** (0.168g, 0.1 mmol) was added excess pyridine. After being stirred for 2 h, the solutions were concentrated to 5 cm³. Addition of hexane (20 cm³) led to the precipitation of pink (**9a**, 33%; **9b**, 60%) or dark brown (**9c**, 65%) solids. Data for **9a** are as follows. Anal. Calcd for C₁₇H₉AuF₅NS₂: C, 35.0; H, 1.55; N, 2.4; S, 11.0. Found: C, 35.4; H, 1.3; N, 1.9; S, 11.7. Λ$_M$: 5 Ω⁻¹ cm² mol⁻¹. ¹H NMR: δ = 8.97 (m, 1H, py), 8.70 (m, 1H, py), 7.96 (m, 1H, py), 7.65 (m, 3H, py and S₂C₆H₄), 7.22 (m, 2H, S₂C₆H₄), 6.98 (m, 1H, S₂C₆H₄). ¹⁹F NMR: δ = −122.3 (m, 2F, F$_o$), −157.2 (t, $^3J_{F_pF_m}$ = 19.4 Hz, 1F, F$_p$), −161.7 (m, 2F, F$_m$). Data for **9b** are as follows. Anal. Calcd for C₁₈H₁₁AuF₅NS₂: C, 36.2; H, 1.85; N, 2.35; S, 10.75. Found: C, 36.4; H, 1.25; N, 2.35; S, 10.55. Λ$_M$: 3 Ω⁻¹ cm² mol⁻¹. ¹H NMR: δ = 8.95 (m, 1H, py), 8.60 (m, 1H, py), 7.94 (m, 1H, py), 7.50 (m, 2H, py), 7.05 (m, 2H, S₂C₆H₃CH₃), 6.80 (m, 1H, S₂C₆H₃CH₃), 2.25 (s, 3H, CH₃). ¹⁹F NMR: δ = −122.3 (m, 2F,

F$_o$), −157.3 (t, $^3J_{F_pF_m}$ = 19.5 Hz, 1F, F$_p$), −161.7 (m, 2F, F$_m$). Data for **9c** are as follows. Anal. Calcd for C₁₄H₅AuF₅NS₅: C, 26.3; H, 0.8; N, 2.2; S, 25.1. Found: C, 26.15; H, 0.8; N, 2.6; S, 23.85. ¹H NMR: δ = 7.35 (m, 2H), 7.75 (t, 2H), 8.7 (m, 1H). ¹⁹F NMR: δ = −121.0 (m, 2F, F$_o$), −154.1 (t, $^3J_{F_pF_m}$ = 19Hz, 1F, F$_p$), −159.7 (m, 2F, F$_m$).

Q[Au(C₆F₅)X(S-S)] [Q = NBu₄, X = Br, S-S = 1,2-S₂C₆H₄ (10a), 3,4-S₂C₆H₃CH₃ (10b), dmit (10c); Q = PPN, X = Cl, S-S = 1,2-S₂C₆H₄ (11a), 3,4-S₂C₆H₃CH₃ (11b), dmit (11c); Q = PPN, X = SCN, S-S = 1,2-S₂C₆H₄ (12a), 3,4-S₂C₆H₃CH₃ (12b), dmit (12c)]. To an acetone (30 cm³) solution of **1** (0.151 g, 0.1 mmol), **2** (0.155 g, 0.1 mmol), or **3** (0.168 g, 0.1 mmol) was added NBu₄Br (0.096 g, 0.3 mmol), PPN(Cl) (0.172 g, 0.3 mmol) or PPN(SCN) (0.178 g, 0.3 mmol). After being stirred for 4 h, the solutions were concentrated to 5 cm³. Addition of hexane (20 cm³) led to the precipitation of violet (**10−12a,b**) or yellow-green (**10−12c**) solids. Data for **10a** are as follows. Yield: 41%. Anal. Calcd for C₂₈H₄₀AuBrF₅NS₂: C, 40.7; H, 4.9; N, 1.7; S, 7.75. Found: C, 40.9; H, 4.9; N, 1.9; S, 6.85. Λ$_M$: 111 Ω⁻¹ cm² mol⁻¹. ¹H NMR: δ = 7.06 and 6.76 (m, 4H, S₂C₆H₄), 3.07, 1.50, 1.36 and 0.94 (m, 9H, NBu₄). ¹⁹F NMR: δ = −120.7 (m, 2F, F$_o$), −158.8 (t, $^3J_{F_pF_m}$ = 19.9 Hz, 1F, F$_p$), −162.35 (m, 2F, F$_m$). Data for **10b** are as follows. Yield: 68%. Anal. Calcd for C₂₉H₄₂AuBrF₅NS₂: C, 41.45; H, 5.05; N, 1.65; S, 7.85. Found: C, 41.6; H, 5.25; N, 1.65; S, 7.0. Λ$_M$: 113 Ω⁻¹ cm² mol⁻¹. ¹H NMR: δ = 6.94 and 6.65 (m, 3H, S₂C₆H₃-CH₃), 3.02, 1.45, 1.31 and 0.91 (m, 9H, NBu₄), 2.19 (s, 3H, S₂C₆H₃CH₃). ¹⁹F NMR: δ = −120.7 (m, 2F, F$_o$), −158.85 (t, $^3J_{F_pF_m}$ = 19.9 Hz 1F, F$_p$), −162.35 (m, 2F, F$_m$), 2.19 (s, 3H, S₂C₆H₃CH₃). Data for **10c** are as follows. Yield: 85%. Anal. Calcd for C₂₅H₃₆AuBrF₅NS₅: C, 34.0; H, 4.1; N, 1.6; S, 18.2. Found: C, 34.6; H, 4.4; N, 1.7; S, 16.8. Λ$_M$: 123 Ω⁻¹ cm² mol⁻¹. ¹⁹F NMR: δ = −121.4 (m, 2F, F$_o$), −157.6 (t, $^3J_{F_pF_m}$ = 19.9 Hz, 1F, F$_p$), −162.0 (m, 2F, F$_m$). Data for **11a** are as follows. Yield: 60%. Anal. Calcd for C₄₈H₃₄AuClF₅NP₂S₂: C, 53.45; H, 3.2; N, 1.3; S, 5.95. Found: C, 53.65; H, 3.2; N, 1.2; S, 5.55. Λ$_M$: 94 Ω⁻¹ cm² mol⁻¹. ¹H NMR: δ = 7.63−7.41 (m, 30H, PPN), 7.06 and 6.76 (m, 4H, S₂C₆H₄). ¹⁹F NMR: δ = −120.3 (m, 2F, F$_o$), −160.1 (t, $^3J_{F_pF_m}$ = 20.05 Hz, 1F, F$_p$), −168.0 (m, 2F, F$_m$). Data for **11b** are as follows. Yield: 64%. Anal. Calcd for C₄₉H₃₆AuClF₅NP₂S₂: C, 53.9; H, 3.3; N, 1.3; S, 5.85. Found: C, 53.15; H, 3.45; N, 0.95; S, 5.65. Λ$_M$: 99 Ω⁻¹ cm² mol⁻¹. ¹H NMR: δ = 7.62−7.41 (m, 30H, PPN), 7.10 and 6.50 (m, 3H, S₂C₆H₃CH₃), 2.15 (s, 3H, S₂C₆H₃CH₃). ¹⁹F NMR: δ = −120.2 (m, 2F, F$_o$), −160.2 (t, $^3J_{F_pF_m}$ = 20.1 Hz, 1F, F$_p$), −163.0 (m, 2F, F$_m$). Data for **11c** are as follows. Yield: 70%. Anal. Calcd for C₄₅H₃₀AuClF₅NP₂S₅: C, 47,6; H, 2.7; N, 1.2; S, 14.1. Found: C, 47.6; H, 3.2; N, 1.5; S, 12.3. Λ$_M$: 120 Ω⁻¹ cm² mol⁻¹. ¹⁹F NMR: δ = −120.1 (m, 2F, F$_o$), −158.1 (t, 3$J_{F_pF_m}$ = 20Hz, 1F, F$_p$), −162.05 (m, 2F, F$_m$). Data for **12a** are as follows. Yield: 89%. Anal. Calcd for C₄₉H₃₄AuF₅N₂P₂S₃: C, 53.45; H, 3.1; N, 2.25; S, 8.75. Found: C, 53.4; H, 3.45; N, 2.1; S, 8.2. Λ$_M$: 115 Ω⁻¹ cm² mol⁻¹. ¹H NMR: δ = 7.72−7.30 (m, 30H, PPN) 7.10 and 6.80 (m, 4H, S₂C₆H₄). ¹⁹F NMR: δ = −119.7 (m, 2F, F$_o$), −158.5 (t, $^3J_{F_pF_m}$ = 20.5 Hz, 1F, F$_p$), −162.3 (m, 2F, F$_m$). Data for **12b** are as follows. Yield: 44%. Anal. Calcd for C₅₀H₃₆AuF₅N₂P₂S₃: C, 53.85; H, 3.25; N, 2.5; S, 8.65. Found: C, 53.4; H, 3.4; N, 2.2; S, 8.3. Λ$_M$: 107 Ω⁻¹ cm² mol⁻¹. ¹H NMR: δ = 7.65−7.33 (m, 30H, PPN), 6.94 and 6.63 (m, 3H, S₂C₆H₃CH₃). Data for **12c** are as follows. Yield: 83%. Anal. Calcd for C₄₆H₃₀AuF₅N₂P₂S₆: C, 47.75; H, 2.6; N, 2.4; S, 16.6. Found: C, 48.2; H, 2.4; N, 2.35; S, 14.4. Λ$_M$: 113 Ω⁻¹ cm² mol⁻¹. ¹⁹F NMR: δ = −120.7 (m, 2F, F$_o$), −157.0 (t, $^3J_{F_pF_m}$ = 20 Hz, 1F, F$_p$), −161.7 (m, 2F, F$_m$).

X-Ray Structure Determinations. Compound 1. *Data collection:* Data were measured with Mo Kα radiation on a Stoe STADI-4 diffractometer fitted with a Siemens LT-2 low-temperature device. Cell constants were refined from ±ω values of ca. 50 reflections in the 2θ range 20−23°. Absorption corrections were based on ψ-scans. *Structure solution:* heavy-atom method. *Structure refinement:* anisotropic on F^2 (program SHELXL-93, G. M. Sheldrick, Univ. of Göttingen) using

all reflections; H atoms using riding model. Other details are given in Tables 1–3.

Compound 8. The structure was determined as for compound **1** except for the following. *Data collection:* Siemens P4 diffractometer, cell constants refined from setting angles, absorption correction using SHELXA (G. M. Sheldrick, unpublished). *Structure refinement:* C atoms isotropic, phenyl rings idealized. Other details are in Tables 1, 4, and 5.

Supporting Information Available: Descriptions of the crystal structure determinations, including tables of crystal data, data collection, and solution and refinement parameters, hydrogen coordinates, bond distances and angles, and thermal parameters (8 pages). Ordering information is given on any current masthead page.

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