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Synthesis and Reactivity of the First (Hydrosulfido)gold(III) Complex. Crystal Structure of the Derivatives $NBu_4[\{Au(C_6F_5)_3\}_2SR]$ with the Isolobal Fragments R = H, $AuPPh_3$, $AgPPh_3$[†]

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The treatment of $NBu_4[AuBr(C_6F_5)_3]$ with NaSH affords the (hydrosulfido)gold(III) complex $NBu_4[Au(C_6F_5)_3SH]$. The latter compound reacts with $[Au(C_6F_5)_3OEt_2]$ to give the dinuclear species $NBu_4[\{Au(C_6F_5)_3\}_2SH]$. The isolobal analogy between H, $AuPPh_3$, and $AgPPh_3$ can be recognized in the complexes $NBu_4[\{Au(C_6F_5)_3\}_2S(MPPh_3)]$ (M = Au, Ag) synthesized by reaction of $NBu_4[\{Au(C_6F_5)_3\}_2SH]$ with $[Au(OClO_3)(PPh_3)]$ or $[Ag(O_3SCF_3)(PPh_3)]$ in the presence of Na_2CO_3. The structures of complexes $NBu_4[\{Au(C_6F_5)_3\}_2SR]$ (R = H, $AuPPh_3$, $AgPPh_3$) have been established by X-ray diffraction studies and show a trigonal-pyramidal geometry at sulfur with no short gold−gold or gold−silver interactions between the metallic centers.

Introduction

There is much current interest in the chemistry of transition-metal hydrosulfido complexes, mainly because these are useful in understanding many catalytic processes such as hydrogenation and hydrodesulfuration.[1,2] These species are still quite rare. (Hydrosulfido)gold complexes, for example, are very poorly represented; to the best of our knowledge only the gold(I) compounds $[N(PPh_3)_2][Au(SH)_2]$[3] and Q[AuR(SH)] (R = C_6F_5, 2-$(NO_2)C_6H_4$, 2,4,6-$(NO_2)_3C_6H_2$)[4] have been reported and no gold(III) derivatives have been described thus far.

We are currently studying gold complexes with bridging sulfido ligands and have reported on the ability of $[S(AuPR_3)_2]$ and $[S\{Au_2(\mu\text{-dppf})\}]$ to coordinate further gold(I) or gold(III) centers. These polynuclear derivatives show weak metal−metal interactions between the closed-shell d^{10} metal centers, termed aurophilic attractions,[5−9] that cannot be explained in terms of the classical theory of chemical bonding, but only in theoretical studies when considered as a correlation effect, strengthened by relativistic effects.[10−13] We have also investigated this type of interaction between gold(I) and gold(III) centers, showing it to be possible, although weaker than a gold(I)−gold(I) interaction.[9]

In this paper we have used a different approach to synthesize sulfur-centered gold complexes: we have prepared the convenient gold(III) starting material $NBu_4[Au(C_6F_5)_3(SH)]$, which represents the first example of a (hydrosulfido)gold(III) derivative. This complex can be used to coordinate further metallic fragments. In some of the complexes described here it is possible to envisage the isolobal analogy existing between the hydrogen atom and the fragments $AuPR_3$ and $AgPR_3$.

Results and Discussion

The reaction of $NBu_4[AuBr(C_6F_5)_3]$ with NaSH in an acetone/water mixture gives after workup the (hydrosulfido)gold(III) derivative $NBu_4[Au(C_6F_5)_3SH]$ (**1**) in high yield (96%) (see Scheme 1). The IR spectrum of **1** is very similar to that of the starting material, with the exception of a weak band at 313 cm^{-1} assignable to the vibration ν(Au−S); also present are the absorptions of the pentafluorophenyl groups bonded to a gold(III) center at 1507 (vs) and 966 (vs) cm^{-1}. The IR-active

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[†] Dedicated to Professor P. Royo on the occasion of his 60th birthday.

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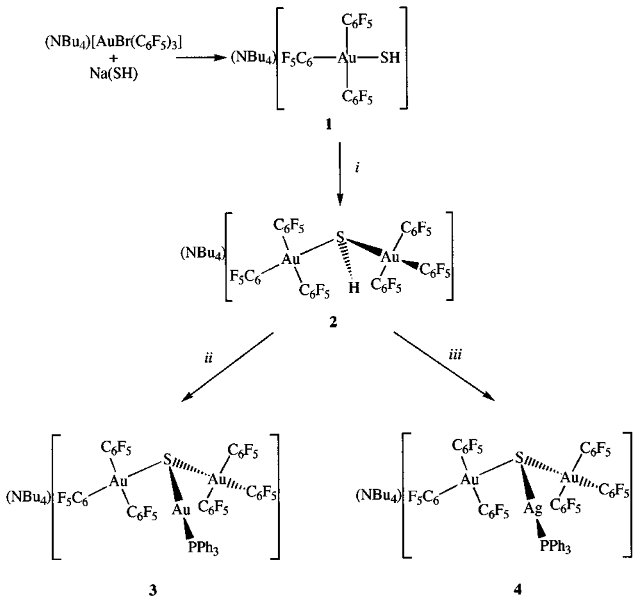
Scheme 1 [a]



[a] Legend: (*i*) [Au(C_6F_5)$_3$(OEt$_2$)]; (*ii*) [Au(OClO$_3$)PPh$_3$] + Na$_2$CO$_3$; (*iii*) [Ag(O$_3$SCF$_3$)PPh$_3$] + Na$_2$CO$_3$.

band corresponding to the ν(SH) mode that usually appears in the range 2300−2600 cm^{-1} is not observed; its weakness is a common feature of most SH complexes.

The ^{1}H NMR spectrum shows the signals assigned to the protons of the NBu$_4$ group and a singlet at −0.45 ppm, which corresponds to the SH proton. In the ^{19}F NMR spectrum the typical pattern of a tris(pentafluorophenyl)gold(III) unit appears; each pentafluorophenyl unit presents two multiplets and one triplet for the different fluorine nuclei; thus, six resonances appear in a 2:1 ratio because of the equivalence of the mutually trans C_6F_5 groups.

In the negative liquid secondary ion mass spectrum (LSIMS−) the anionic peak [Au(C_6F_5)$_3$SH]$^-$ appears at *m*/*z* 731 (60%), the peak assigned to [Au(C_6F_5)$_4$]$^-$ appears at *m*/*z* 865, and the association peaks [{Au(C_6F_5)}{Au(C_6F_5)$_3$}SH]$^-$ and [{Au(C_6F_5)$_3$}$_2$SH]$^-$ appear at *m*/*z* 1095 and 1429, respectively.

This indicated to us that the hydrosulfido ligand bonded to gold(III) could easily coordinate other metallic fragments. Taking this into account, we have studied the reaction of **1** with [Au(C_6F_5)$_3$OEt$_2$] in the molar ratio 1:1. The weakly coordinated ether molecule is displaced by the hydrosulfido group, and the complex NBu$_4$[{Au(C_6F_5)$_3$}$_2$SH] (**2**) can be isolated.

The ^{1}H and ^{19}F NMR spectra of **2** have patterns similar to those of **1**, although with a different chemical shift. The SH proton is not observed in the ^{1}H NMR spectrum, perhaps because it is overlapped by the NBu$_4$ protons. In the LSIMS− the anionic peak appears at *m*/*z* 1429 (42%).

The structure of complex **2** has been determined by X-ray diffraction studies of its dichloromethane solvate; the anion is shown in Figure 1, with a selection of bond lengths and angles in Table 1. The hydrogen atom of the SH$^-$ ligand could be located with reasonable certainty (see below), and the geometry can be considered as triangular pyramidal at sulfur, or tetrahedral if we take into account the lone pair. The gold(III)−gold(III) distance, 3.984(1) Å, is too long to be considered an interaction; furthermore, the Au−S−Au angle is even wider than that expected for an ideal tetrahedron (113.76(13)°). The Au−S distances, 2.390(3) and 2.367(3) Å, are very similar to those found in other gold(III) complexes triply bonded to a sulfur atom such as [S(Au$_2$dppf){Au(C_6F_5)$_3$}][9] (dppf = 1,1′-bis(diphenylphosphino)ferrocene) (2.374(4) Å) or [{S(Au$_2$dppf)}$_2${Au(C_6F_5)$_2$}](CF$_3$SO$_3$)[9] (2.387(4), 2.397(4) Å), but they are also of the same order as those found in complexes with a μ_4-sulfur moiety such as [S(Au$_2$dppf){Au(C_6F_5)$_3$}$_2$][8] (2.380(3), 2.385(3) Å) and [S(AuPPh$_3$)$_2${Au(C_6F_5)$_3$}$_2$].[8] The Au−C bond lengths vary depending on the position of the C_6F_5 group; the shortest distances correspond to the carbon atoms trans to the sulfur atom, 2.042(13) and 2.051(13) Å, and the others are typical values for tris(pentafluorophenyl)gold(III) complexes. The SH hydrogen is directed toward a chlorine atom of the dichloromethane molecule; this may represent a weak S−H···Cl hydrogen bond (H···Cl = 2.66 Å, S···Cl = 3.79 Å, S−H···Cl = 143°).

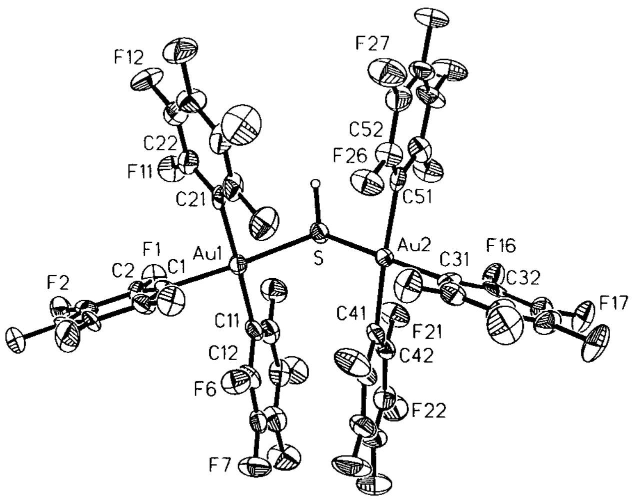


Figure 1. Structure of the anion of complex **2** in the crystal. Displacement parameter ellipsoids represent 50% probability surfaces. The H atoms (except SH) are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 2

Au(1)−C(1)	2.042(13)	Au(1)−C(11)	2.064(14)
Au(1)−C(21)	2.080(14)	Au(1)−S	2.390(3)
Au(2)−C(31)	2.051(13)	Au(2)−C(41)	2.086(14)
Au(2)−C(51)	2.102(14)	Au(2)−S	2.367(3)
C(1)−Au(1)−C(11)	89.4(5)	C(1)−Au(1)−C(21)	88.6(5)
C(11)−Au(1)−C(21)	177.5(5)	C(1)−Au(1)−S	175.8(4)
C(11)−Au(1)−S	92.3(4)	C(21)−Au(1)−S	89.7(4)
C(31)−Au(2)−C(41)	86.9(5)	C(31)−Au(2)−C(51)	91.0(5)
C(41)−Au(2)−C(51)	176.5(5)	C(31)−Au(2)−S	173.7(4)
C(41)−Au(2)−S	92.1(4)	C(51)−Au(2)−S	89.6(4)
Au(2)−S−Au(1)	113.76(13)	C(2)−C(1)−Au(1)	118.8(10)
C(6)−C(1)−Au(1)	122.7(10)	C(12)−C(11)−Au(1)	122.6(11)
C(16)−C(11)−Au(1)	123.9(11)	C(26)−C(21)−Au(1)	121.7(11)
C(22)−C(21)−Au(1)	120.6(11)	C(36)−C(31)−Au(2)	126.3(10)
C(32)−C(31)−Au(2)	117.9(10)	C(42)−C(41)−Au(2)	122.1(11)
C(46)−C(41)−Au(2)	120.9(12)	C(52)−C(51)−Au(2)	124.5(11)
C(56)−C(51)−Au(2)	118.2(11)		

It is well-known that the AuPR$_3$ group is isolobal with the hydrogen atom and mostly uses the 6s orbital of gold for bonding. This isolobal relationship explains the often close structural analogy between various homo- and heteronuclear compounds containing AuPR$_3$ groups and those of the related hydrido derivatives. This isolobal analogy also extends to the AgPPh$_3$ group; thus,

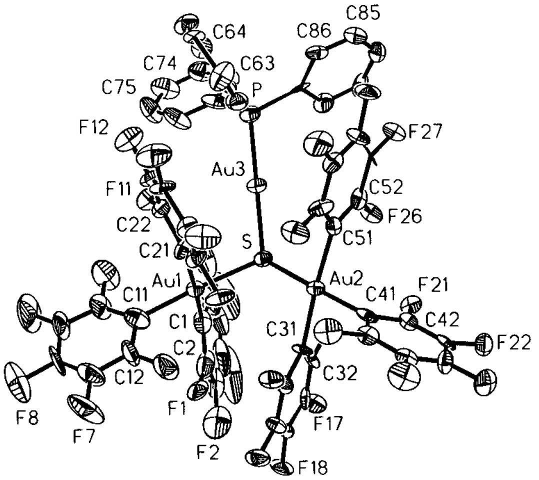


Figure 2. Perspective view of the anion of complex **3**. Displacement parameter ellipsoids represent 50% probability surfaces. H atoms are omitted for clarity.

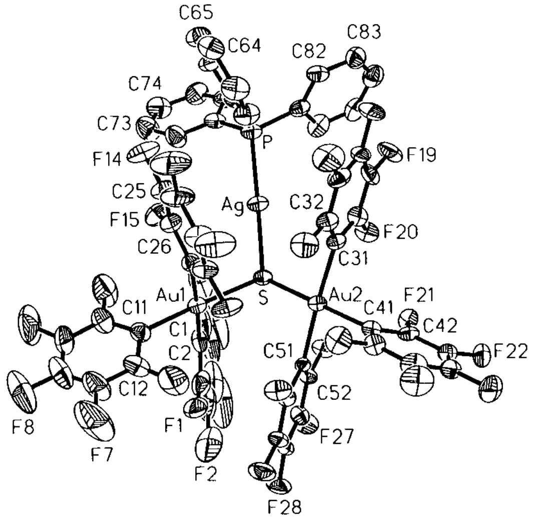


Figure 3. Structure of the anion of complex **4** in the crystal. Displacement parameter ellipsoids represent 50% probability surfaces. The H atoms are omitted for clarity.

we have synthesized the complexes $NBu_4[\{Au(C_6F_5)_3\}_2SR]$ (R = $AuPPh_3$ (**3**), $AgPPh_3$ (**4**)), which are isolobal with complex **2**.

Complexes **3** and **4** are white solids, stable to moisture and air. They behave as 1:1 electrolytes in acetone. In the IR spectra the bands arising from the pentafluorophenyl groups, the PPh_3 ligand, and the vibration ν(Au−S) appear. The vibration ν(Ag−S) is not observed, possibly because it is too weak or is below the instrumental limit of 200 cm^{-1}. In the $^{31}P\{^1H\}$ NMR spectra the phosphorus bonded to gold appears as a singlet, whereas that bonded to silver appears as a broad signal at room temperature that sharpens into two doublets because of the coupling with the silver nuclei ^{107}Ag and ^{109}Ag.

The negative liquid secondary ion mass spectra of complexes **3** and **4** show the anionic peaks at *m/z* 1887 (**3**; 23%) and 1799 (**4**; 7%) with coincident experimental and calculated isotopical distribution.

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

Au(1)−C(21)	2.05(2)	Au(1)−C(11)	2.05(2)
Au(1)−C(1)	2.07(2)	Au(1)−S	2.374(5)
Au(2)−C(41)	2.00(2)	Au(2)−C(51)	2.04(2)
Au(2)−C(31)	2.05(2)	Au(2)−S	2.374(5)
Au(3)−P	2.250(5)	Au(3)−S	2.303(5)
C(21)−Au(1)−C(11)	89.3(7)	C(21)−Au(1)−C(1)	173.4(5)
C(11)−Au(1)−C(1)	90.2(7)	C(21)−Au(1)−S	93.6(5)
C(11)−Au(1)−S	176.5(5)	C(1)−Au(1)−S	87.1(5)
C(41)−Au(2)−C(51)	89.4(6)	C(41)−Au(2)−C(31)	87.8(6)
C(51)−Au(2)−C(31)	176.3(6)	C(41)−Au(2)−S	172.4(3)
C(51)−Au(2)−S	92.6(5)	C(31)−Au(2)−S	89.8(5)
P−Au(3)−S	173.6(2)	Au(3)−S−Au(1)	107.4(2)
Au(3)−S−Au(2)	113.0(2)	Au(1)−S−Au(2)	108.4(2)
C(61)−P−Au(3)	113.3(5)	C(81)−P−Au(3)	113.3(6)
C(71)−P−Au(3)	112.6(6)	C(2)−C(1)−Au(1)	125.4(14)
C(6)−C(1)−Au(1)	120.0(13)	C(12)−C(11)−Au(1)	122.5(13)
C(16)−C(11)−Au(1)	123.5(13)	C(26)−C(21)−Au(1)	125.4(11)
C(22)−C(21)−Au(1)	121.1(10)	C(32)−C(31)−Au(2)	121.4(10)
C(36)−C(31)−Au(2)	125.3(10)	C(42)−C(41)−Au(2)	121.5(10)
C(46)−C(41)−Au(2)	127.5(11)	C(56)−C(51)−Au(2)	123.2(11)
C(52)−C(51)−Au(2)	122.0(10)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 4

Au(1)−C(11)	2.038(8)	Au(1)−C(1)	2.050(8)
Au(1)−C(21)	2.058(7)	Au(1)−S	2.374(2)
Au(2)−C(41)	2.046(7)	Au(2)−C(51)	2.058(7)
Au(2)−C(31)	2.062(7)	Au(2)−S	2.361(2)
Ag−P	2.355(2)	Ag−S	2.357(2)
P−C(61)	1.811(8)	P−C(71)	1.819(8)
P−C(81)	1.823(9)		
C(11)−Au(1)−C(1)	91.1(3)	C(11)−Au(1)−C(21)	88.5(3)
C(1)−Au(1)−C(21)	173.5(3)	C(11)−Au(1)−S	177.8(2)
C(1)−Au(1)−S	87.7(2)	C(21)−Au(1)−S	92.9(2)
C(41)−Au(2)−C(51)	87.9(2)	C(41)−Au(2)−C(31)	90.0(2)
C(51)−Au(2)−C(31)	177.0(3)	C(41)−Au(2)−S	172.1(2)
C(51)−Au(2)−S	89.6(2)	C(31)−Au(2)−S	92.2(2)
P−Ag−S	171.78(7)	Ag−S−Au(2)	111.84(8)
Ag−S−Au(1)	107.79(8)	Au(2)−S−Au(1)	108.23(7)
C(61)−P−C(71)	105.6(3)	C(61)−P−C(81)	105.6(3)
C(71)−P−C(81)	106.1(3)	C(61)−P−Ag	112.3(2)
C(71)−P−Ag	113.3(2)	C(81)−P−Ag	113.3(2)
C(2)−C(1)−Au(1)	125.4(7)	C(6)−C(1)−Au(1)	119.5(6)
F(1)−C(2)−C(1)	120.0(8)	C(12)−C(11)−Au(1)	122.5(6)
C(16)−C(11)−Au(1)	122.8(6)	C(42)−C(41)−Au(2)	118.8(5)
C(46)−C(41)−Au(2)	125.0(5)	C(52)−C(51)−Au(2)	121.4(5)
C(56)−C(51)−Au(2)	124.1(5)	C(66)−C(61)−P	121.4(6)
C(62)−C(61)−P	117.1(6)		

The crystal structures of complexes **3** and **4** have been established by X-ray diffraction, and the anions are shown in Figures 2 and 3 with selected bond lengths and angles in Tables 2 and 3, respectively. The complexes are isostructural and show the expected trigonal-pyramidal geometry with the sulfur at the vertex lying 0.78 (**3**) or 0.79 (**4**) Å out of the plane of the three metallic centers. The gold(III) centers have a very regular square planar geometry with angles that range from 87.8(6) to 92.6(5)° in **3** and from 87.7(2) to 92.9(2)° in **4**, whereas the gold(I) or silver(I) has a distorted linear geometry, S−Au(3)−P = 173.6(2)° and S−Ag−P = 171.78(7)°.

It is worth comparing these structures to those which have a sulfido ligand triply bridged to three gold(I) centers, $[S(AuPR_3)_3]^+$, and to two gold(I) and one gold(III) center, $[S(Au_2dppf)\{Au(C_6F_5)_3\}]$. In complexes of the type $[S(AuPR_3)]^+$ there are short Au···Au contacts of ca. 3 Å and usually the molecules are associated in pairs through intermolecular gold−gold interactions. In $[S(Au_2dppf)_2\{Au(C_6F_5)_3\}]$ there is a short intramolecular gold(I)−gold(I) contact and two different gold(I)−gold(III) distances (3.404(1) and 3.759(1) Å); in $[\{S(Au_2dppf)\}_2\{Au(C_6F_5)_2\}](CF_3SO_3)$, which has the same type of structure, the shorter Au(I)−Au(III) distance decreases to 3.2195(8) Å, a value that is of the same order as the longest gold(I)−gold(I) interactions in this type of complex and shows that gold(I)−gold(III) interactions, although weaker, are also possible. In complexes **3** and **4**, in contrast, there are no short metal−metal distances; in **3** the Au(I)−Au(III) distances are 3.770(1) and 3.900(1) Å, which, although they follow the pattern previously mentioned, are too long to be considered as interactions; the gold(III)−gold(III) distance is 3.852(1) Å. The corresponding Ag−Au(III) distances in **4** are longer, 3.882(1) and 3.907(1) Å, but the Au(III)−Au(III) distance is very similar, 3.836(1) Å.

Consistent with the long metal−metal distances, the Au−S−Au or Ag−S−Au angles are close to the ideal values for a tetrahedron. The Au^{III}−S distances are 2.374(5) Å (×2) in **3** and 2.374(2) and 2.357(2) Å in **4**, values that are shorter than those found in the starting material. The Au^{I}−S bond length is 2.303(5) Å, and the Ag−S length is 2.357(2) Å, which is in accordance with the observations[14−16] made by Schmidbaur et al. that the covalent radius of gold is smaller than that of silver, as was anticipated on the basis of data obtained in theoretical treatments including relativistic effects.

Table 4. Details of Data Collection and Structure Refinement for Complexes 2−4

compd	**2**·CH_2Cl_2	**3**·CH_2Cl_2	**4**·CH_2Cl_2
chem formula	$C_{53}H_{39}Au_2Cl_2F_{30}NS$	$C_{71}H_{53}Au_3Cl_2F_{30}NPS$	$C_{71}H_{53}AgAu_2Cl_2F_{30}NPS$
cryst habit	colorless prism	colorless prism	colorless tablet
cryst size/mm	0.25 × 0.20 × 0.20	0.15 × 0.15 × 0.11	0.50 × 0.25 × 0.10
cryst syst	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a/Å	12.3740(10)	12.442(2)	12.448(2)
b/Å	18.217(2)	13.084(3)	13.114(2)
c/Å	26.363(3)	23.125(4)	23.161(3)
α/deg		87.96(2)	86.968(10)
β/deg	98.848(7)	81.80(2)	81.152(10)
γ/deg		85.499(14)	85.320(10)
V/Å^3	5872.0(10)	3713.5(12)	3720.3(10)
Z	4	2	2
D_{calcd}/Mg m^{-3}	1.987	1.981	1.898
M_r	1756.75	2214.97	2125.88
F(000)	3368	2116	2052
T/°C	−100	−100	−100
$2\theta_{max}$/deg	45	45	50
μ(Mo $K\alpha$)/mm^{-1}	5.25	6.151	4.434
transmissn	0.705−0.919	0.682−0.960	0.696−0.982
no. of rflns measd	8796	10 260	13 130
no. of unique rflns	7517	9720	13 081
R_{int}	0.07	0.074	0.020
$R^a(F, F > 4\sigma(F))$	0.052	0.068	0.040
R_w (F^2, all rflns)^b	0.10	0.145	0.095
no. of rflns used	7505	9697	13 081
no. of params	794	892	999
no. of restraints	760	788	886
S^c	1.051	1.046	0.895
max $\Delta\rho$/e Å^{-3}	0.931	2.24	2.103

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

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 and H 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 in $CDCl_3$ on a Varian Unity 300 spectrometer and a Bruker ARX 300 spectrometer. 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 $NBu_4[AuBr(C_6F_5)_3]$[17] and $[Au(C_6F_5)_3OEt_2]$[18] were prepared by published procedures. $[Au(OClO_3)PPh_3]$ was prepared from $[AuCl(PPh_3)]$[19] and $AgClO_4$ in dichloromethane, and $[Ag(O_3SCF_3)(PPh_3)]$ was obtained from $Ag(O_3SCF_3)$ and PPh_3 in dichloromethane.

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. $NBu_4[Au(C_6F_5)_3SH]$ (1). To a solution of $NBu_4[AuBr(C_6F_5)_3]$ (0.1 mmol; 0.102 g) in an acetone/water mixture (20/5 mL) was added NaSH (1 mmol, 0.056 g). The solution was stirred for 3 h, and then the solvent was evaporated to ca. 5 mL. The resulting solid was filtered off and washed several times with water. The solid was dissolved in dichloromethane and the solution filtered over $MgSO_4$. The resulting solution was concentrated to ca. 5 mL, and addition of hexane gave a white solid of **1**. Yield: 96%. $\Lambda_M = 121\ \Omega^{-1}$ cm^2 mol^{-1}. Anal. Found: C, 41.44; H, 3.31; N, 1.46; S, 3.21. Calcd for $C_{34}H_{37}AuF_{15}NS$: C, 41.94; H, 3.73; N, 1.44; S, 3.29. ^1H NMR: δ −0.45 (s) (SH) ppm. ^{19}F NMR: δ −120.9 (m, 4F, *o*-F), −122.6 (m, 2F, *o*-F), −164.1 (m, 4F, *m*-F), −164.2 (m, 2F, *m*-F), −161.1 [t, 2F, *p*-F, ^3J(FF) = 19.34 Hz], −161.2 [t, 1F, *p*-F, ^3J(FF) = 19.29 Hz] ppm.

$NBu_4[\{Au(C_6F_5)_3\}_2SH]$ (2). To a solution of $NBu_4[Au(C_6F_5)_3SH]$ (0.1 mmol, 0.097 g) in dichloromethane (20 mL) was added $NBu_4[AuBr(C_6F_5)_3]$ (0.1 mmol, 0.102 g), and the solution was stirred for 3 h. The solvent was evaporated to ca. 5 mL, and addition of hexane afforded a white solid of **2**. Yield: 90%. $\Lambda_M = 111.5\ \Omega^{-1}$ cm^2 mol^{-1}. Anal. Found: C, 37.16; H, 1.80; N, 0.73; S, 2.21. Calcd for $C_{52}H_{37}Au_2F_{30}NS$: C, 37.36; H, 2.23; N, 0.84; S, 1.92. ^{19}F NMR: δ −121.4 (m, 8F, *o*-F), −122.0 (m, 4F, *o*-F), −162.1 (m, 8F, *m*-F), −162.4 (m, 4F, *m*-F), −147.8 [t, 4F, *p*-F, ^3J(FF) = 19.29 Hz], −158.0 [t, 2F, *p*-F, ^3J(FF) = 19.98 Hz] ppm.

$NBu_4[\{Au(C_6F_5)_3\}_2S(MPPh_3)]$ (M = Au (3), Ag (4)). To a dichloromethane (20 mL) solution of **2** (0.1 mmol, 0.167 g) was added $[Au(OClO_3)PPh_3]$ (0.1 mmol, 0.056 g) or $[Ag(O_3SCF_3)PPh_3]$ (0.1 mmol, 0.052 g) and excess Na_2CO_3 (2 mmol, 0.212 g), and the suspension was stirred for 1 h. The solid sodium carbonate was filtered off and the solvent evaporated to ca. 5 mL. Addition of hexane (15 mL) led to white solid **3** or **4**. Complex **3**: yield 75%. $\Lambda_M = 107\ \Omega^{-1}$ cm^2 mol^{-1}. Anal. Found: C, 39.44; H, 1.98; N, 0.51; S, 1.94. Calcd for $C_{70}H_{52}Au_3F_{30}NPS$: C, 39.47; H, 2.41; N, 0.66; S, 1.51. $^{31}P\{^1H\}$ NMR, δ 36.5 ppm. ^{19}F: δ −121.1 (m, 8F, *o*-F), −121.7 (m, 4F, *o*-F), −163.3 (m, 8F, *m*-F), −163.4 (m, 4F, *m*-F), −160.2 [t, 4F, *p*-F, ^3J(FF) = 19.98 Hz], −159.9 [t, 2F, *p*-F, ^3J(FF) = 19.99 Hz] ppm. Complex **4**: Yield 51%. Λ_M 114 Ω^{-1} cm^2 mol^{-1}. Anal. Found: C, 40.69; H, 2.47; N, 0.68; S, 1.55. Calcd for $C_{70}H_{52}AgAu_2F_{30}NPS$: C, 40.45; H, 2.57; N, 0.70; S, 1.77. ^{19}F: δ −120.1 (m, 8F, *o*-F), −121.8 (m, 4F, *o*-F), −163.3 (m, 8F, *m*-F), −163.3 (m, 4F, *m*-F), −160.4 [t, 4F, *p*-F, ^3J(FF) = 20.6 Hz], −160.3 [t, 2F, *p*-F, ^3J(FF) = 20.2 Hz] ppm.

Crystal Structure Determinations. The crystals were

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mounted in inert oil on glass fibers and transferred to the cold gas stream of a Siemens P4 diffractometer equipped with an Oxford (**2**, **3**) or Siemens LT-2 (**4**) low-temperature attachment. Data were collected using monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The scan type was $\theta - 2\theta$ (**2**, **3**) or ω (**4**). Cell constants were refined from setting angles of ca. 60 reflections in the range $2\theta = 10-25°$. Absorption corrections were applied on the basis of ψ-scans. Structures were solved by direct methods and refined on F^2 using the program SHELXL-93.[20] All ordered non-hydrogen atoms were refined anisotropically (**2**, **4**). For complex **3**, with a weakly diffracting crystal, the carbon and nitrogen atoms of the NBu_4 cation were refined isotropically. Complexes **3** and **4** crystallized with a very ill-defined dichloromethane molecule, the carbon atom of which could not be located; the major residual electron density in these structures is found near the chlorine atoms of the dichloromethane. Hydrogen atoms were included using a riding model. A system of restraints to light-atom displacement-factor components and local ring symmetry was used. Further details are given in Table 4. Special features of refinement for **2**: Despite apparently reasonable data, the H atom of the SH ligand could not at first be located. Only when two butyl groups of the cation had been refined using a 2-fold disorder model (with appropriate restraints) could a peak of 0.73 e/Å^3 (the fifth largest at that stage) be located in a suitable position. It was refined using a restrained S−H bond length of 1.33(2) Å.

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Supporting Information Available: Tables giving crystal data and structure refinement details, positional and thermal parameters, and bond distances and angles for **2**−**4** (34 pages). Ordering information is given on any current masthead page.

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