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Unexpected Ring-Opening Reaction to a New Cyanamide-Thiolate Ligand Stabilized as a Dinuclear Gold Complex

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We have synthesized the gold complexes [Au(C_6F_5)$_3$(2-amt)], **1**, [Au(C_6F_5)(2-amt)], **2**, and [Au(2-amt)(PPh_3)](CF_3SO_3), **3**, where 2-amt = 2-aminothiazoline (2-amino-4,5-dihydrothiazole) by displacement of labile ligands from corresponding gold(III) and gold(I) precursors. The reaction of 2-amt with [Au(acac)(PPh_3)] evolves to an unprecedented ring-opening reaction to give the new ligand (2-cyanamide)ethylthiolate, stabilized as a dinuclear gold(I) coordination derivative, [($AuPPh_3$)$_2$(μ-SCH_2CH_2N-CN)], **4**. The molecular structure of complexes **1** and **4** has been confirmed by X-ray diffraction studies. Complex **4** displays short gold−gold distances of 3.0821(3), 3.17618(19), and 3.2867(2) Å (three different molecules in two different crystal forms) and secondary sulfur−gold or nitrogen−gold bonds. Complexes **3** and **4** luminesce intensely in the solid state at low temperature.

Introduction

The synthesis of monocyclic and condensed thiazoles has attracted much attention because of their biological, synthetic, and pharmaceutical importance.[1] However, ring-opening reactions of thiazoles are not common, although some have been well studied, such as the hydrolysis of thiazolidines (tetrahydrothiazoles) to give aldehydes and amino-thiols by cleavage of C−S bonds.[1,2]

Metal complexes of thiazoles have been utilized as models to investigate the relationship between medicinal effectiveness and coordination properties to metal centers.[3] Gold complexes have also been synthesized because of their established activity against rheumatoid arthritis and tumors.[4]

Here we report the synthesis of mononuclear gold(III) and gold(I) complexes of 2-aminothiazoline (2-amino-4,5-dihydrothiazole or 2-amt). We further report the unprecedented ring-opening reaction of 2-amino-4,5-dihydrothiazole (2-amt) to give the new ligand (2-cyanamide)ethylthiolate stabilized as a dinuclear gold(I) coordination derivative, which moreover shows very short gold−gold distances. It has been shown that these contacts play an important role, for instance, in the stabilization of hypercoordinated phosphinogold(I) derivatives around oxygen, sulfur, nitrogen, or carbon centers.[5] In addition we have demonstrated that some of the new derivatives are photoluminescent in the solid state at low temperature.

Results and Discussion

As outlined in Scheme 1, 2-amt displaces the labile tetrahydrothiophene or triflate ligands in gold(III) and gold(I) precursors to give the mononuclear gold complexes **1**−**3**.

IR spectroscopy clearly established the presence of N−H and pentafluorophenyl in organometallic complexes **1** and **2** and triflate anion in complex **3**. ^{19}F NMR spectroscopy of **1** and **2** showed the presence of a unique Au−(C_6F_5)$_3$ or Au−C_6F_5 unit. The ^{31}P{^{1}H} NMR spectrum of **3** showed a singlet at 33.3 ppm. In the proton

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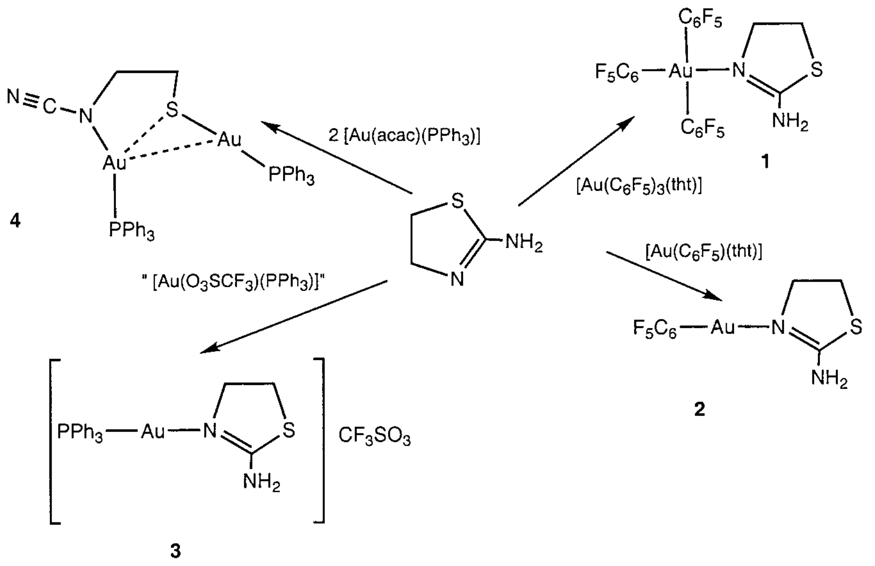
Scheme 1



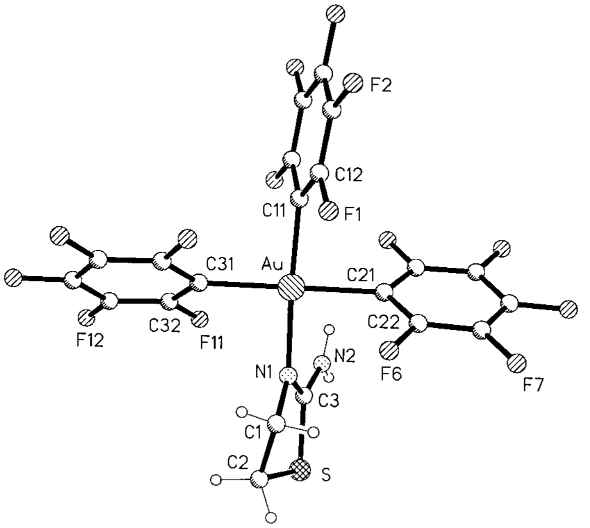


Figure 1. Molecular structure of complex **1**.

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

Au–C(11)	2.016(2)	S–C(2)	1.821(3)
Au–C(21)	2.063(2)	N(1)–C(3)	1.301(3)
Au–N(1)	2.0664(18)	N(1)–C(1)	1.470(3)
Au–C(31)	2.068(2)	N(2)–C(3)	1.336(3)
S–C(3)	1.751(2)	C(1)–C(2)	1.518(3)
C(11)–Au–C(21)	87.93(8)	C(3)–N(1)–Au	124.91(15)
C(11)–Au–N(1)	176.63(7)	C(1)–N(1)–Au	121.17(14)
C(21)–Au–N(1)	89.23(8)	N(1)–C(1)–C(2)	107.79(19)
C(11)–Au–C(31)	92.26(8)	C(1)–C(2)–S	104.59(17)
C(21)–Au–C(31)	179.18(8)	N(1)–C(3)–N(2)	124.6(2)
N(1)–Au–C(31)	90.61(8)	N(1)–C(3)–S	115.47(16)
C(3)–S–C(2)	90.03(11)	N(2)–C(3)–S	119.94(17)
C(3)–N(1)–C(1)	113.16(18)		

NMR spectra the methylene protons of 2-amt are seen as triplets and the amino group as a broad singlet. The LSI MS mass spectra show the peaks at *m*/*z* (complex, % abundance, assignment): 799 (**1**, 13, $[M - H]^+$), 401 (**2**, 15, $[Au(2\text{-amt})_2]^+$), 561 (**3**, 12, $[M - CF_3SO_3]^+$).

We have confirmed the molecular structure of the gold(III) complex **1** by X-ray diffraction studies (see Figure 1). Suitable crystals were obtained from dichloromethane–hexane. Selected bonds and angles are shown in Table 1. The main features are (a) the gold(III) center displays a slightly distorted square planar coordination with CAuC and CAuP angles ranging from 87.93(8)° to 92.26(8)°; (b) 2-amt is coordinated through the ring nitrogen atom with an Au–N distance of 2.0664(18) Å; (c) the amino C–N bond length of 1.336(3) Å indicates a C–N bond order intermediate between 1 (for instance N(1)–C(1) is 1.470(3) Å) and 2 (for instance N(1)–C(3) is 1.301(3) Å) but closer to a double bond, which implies some electron density delocalization as reported for similar complexes;[3] (d) the Au–C bond length trans to 2-amt (2.016(2) Å) is shorter than that trans to pentafluorophenyl (2.063(2) and 2.068(2) Å), as expected because of the stronger trans influence of pentafluorophenyl. Within the molecule, the contacts N(2)–H(01)···F(10) (2.61 Å, 158°) and, possibly, ···Au (2.91 Å, 110°) might be classified as hydrogen bonds. The intermolecular contact N(1)–H(02)···F(5) (2.22 Å, 151°) is more clear-cut.

We have also carried out reactions of 2-amt with $[Au(acac)(PPh_3)]$, which were intended to provide its conjugate base, where the imino tautomer becomes important, in a complex involving the phosphino-gold(I) fragment. Surprisingly, a mixture was obtained containing free 2-amt and complex **4**; the reaction in the 1:2 molar ratio led to pure complex **4** (see Scheme 1), which is formed by cleavage of the heterocyclic C–S bond and subsequent rearrangement to give a 2-cyanamide-ethylthiolate bridging ligand. As a first reaction step, we propose that the amt conjugate base is obtained and the phosphino-gold unit coordinates to the exocyclic nitrogen; a search in the Cambridge Structural Database shows that metals are often coordinated by both nitrogen atoms of the amt conjugate base, but gold could be coordinated by the exocyclic nitrogen and the sulfur because it is a soft metal with a high affinity for sulfur. Thus gold could promote the cleavage of the C–S bond and the formation of an –N=C=NH unit, which could be deprotonated and rearranged to the more stable cyanamide group, stabilized by a second phosphino-gold. We have monitored our reaction by NMR at −90 °C; the phosphorus spectrum shows several resonances

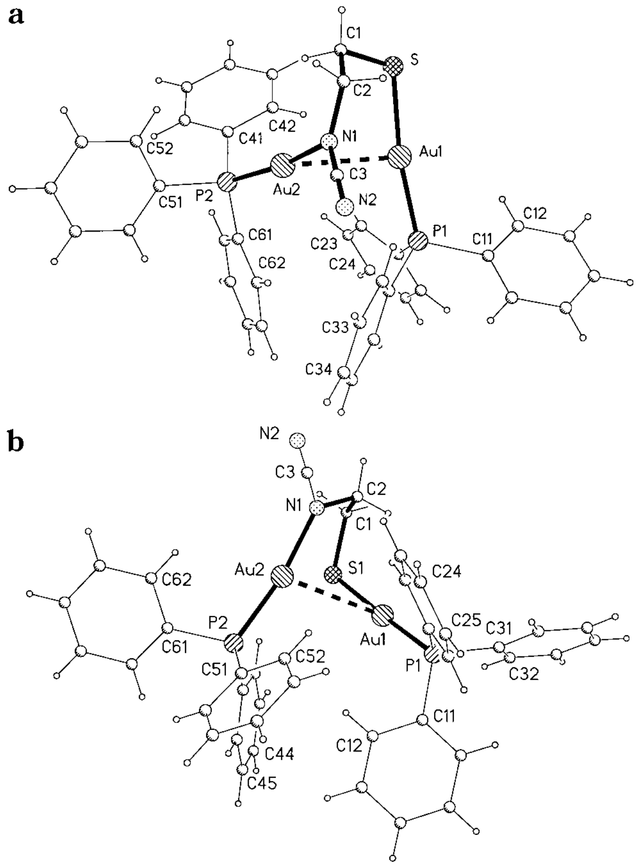


Figure 2. Molecular structure of complex **4**: (a) **4a** (acetone solvate); (b) **4b** (one independent molecule).

apart from the final product, whereas at −30 °C only complex **4** is observed.

We have repeated the reaction in acetone in 1:1 molar ratio, and rapidly a white precipitate was formed. The solution contained free ligand and a small amount of complex **4**, while the solid was complex **4**. The well-known higher stability of thiolato gold(I) versus imino gold(I) derivatives and the formation of the cyanamide group should be the driving force of the reaction and the reason we have not obtained a mononuclear imino gold(I) complex.

The IR spectrum of derivative **4** shows no N−H absorption, whereas an absorption at 2145 cm^{-1} associated with the cyano group is clearly seen. The proton NMR spectrum shows methylene resonances as pseudotriplets with a smaller coupling constant than in the previous 2-amt derivatives (5 Hz, cf. 7.5 Hz), and no amino resonance is seen even at −90 °C. In the phosphorus NMR spectrum only a singlet is observed at 35.2 ppm, which broadens on lowering the temperature to −90 °C but does not split into the two expected signals. The mass spectrum shows peaks at 1019 (5%) corresponding to $[M + H]^+$ and 1409 (8%) due to $[S(AuPPh_3)_3]^+$; the base peak at 459 is $[AuPPh_3]^+$. Acetone solutions are nonconducting.

To confirm the structure of the new bridging cyanamide-thiolate ligand, we have determined the X-ray structure (see Figure 2). Suitable crystals were obtained from acetone−diethyl ether−petroleum ether (40:60). Complex **4** crystallizes as two different solvates; **4a** is an acetone monosolvate, and **4b** contains two independent molecules of **4** and a partially occupied water site.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex 4a

Au(1)−P(1)	2.2757(11)	S−C(1)	1.822(4)
Au(1)−S	2.3031(10)	N(1)−C(3)	1.313(5)
Au(1)−Au(2)	3.0821(3)	N(1)−C(2)	1.484(5)
Au(2)−N(1)	2.053(3)	C(1)−C(2)	1.519(6)
Au(2)−P(2)	2.2389(10)	C(3)−N(2)	1.169(5)
P(1)−Au(1)−S	170.14(4)	C(3)−N(1)−C(2)	114.6(3)
P(1)−Au(1)−Au(2)	102.17(3)	C(3)−N(1)−Au(2)	121.5(3)
S−Au(1)−Au(2)	87.44(3)	C(2)−N(1)−Au(2)	121.7(3)
N(1)−Au(2)−P(2)	172.02(10)	C(2)−C(1)−S	115.6(3)
N(1)−Au(2)−Au(1)	72.35(9)	N(1)−C(2)−C(1)	111.7(3)
P(2)−Au(2)−Au(1)	113.91(3)	N(2)−C(3)−N(1)	179.5(5)
C(1)−S−Au(1)	108.91(14)		

Selected bond and angles for **4a** and **4b** are summarized in Tables 2 and 3. All three molecules display two phosphino-gold units bonded to the new 2-cyanamide-ethyl-thiolate as bridging ligand, through an amide-thiolate bridge. The main difference between the three molecules are the angles at gold, the gold(I)···gold(I) distances, the presence or absence of a secondary sulfur−gold(I) bond, and the conformations of the ring Au(1)···Au(2)−N(1)−C(2)−C(1)−S. The geometry around the gold centers is linear, but with some distortions [**4a**: P(1)−Au(1)−S 170.14(4)°, N(1)−Au(2)−P(2) 172.02(10)°; **4b**: P(1)−Au(1)−S(1) 176.02(3)°, 178.75(3)°, N(1)−Au(2)−P(2) 167.51(7)°, 162.54(8)°] with short gold−gold distances of 3.0821(3), 3.17618(19), and 3.2867(2) Å, respectively, and a secondary sulfur−gold(I) contact of 3.764(1), 3.0485(7), and 2.9533(8) Å, respectively. Thus in **4a** the shorter gold−gold distances are associated with the much longer sulfur−gold distance, which is unlikely to represent a significant interaction; there is however in this case a short contact to nitrogen, Au(1)···N(1) 3.143(3) Å. The rings Au(1)···Au(2)−N(1)−C(2)−C(1)−S all display a distorted boat form, but in **4a** Au(2) and C(1) lie out of the plane of the other four atoms, whereas in **4b** Au(1) and C(2) lie out of the plane. This is clearly recognizable in the figures and correlates with the Au···S contacts. It is noteworthy that the thiolate ligand shows C−N bond lengths of ca. 1.16, 1.31, and 1.47 Å corresponding to the CN, N−CN, and N−CH_2 fragments, respectively.

The solid state emission and excitation spectra have been studied at 298 and 77 K. There is no emission at room temperature. At low temperature complexes **1** and **2** do not luminesce, while complexes **3** and **4** luminesce intensely. The dinuclear phosphino-thiolato complex **4** shows the emission maximum at 479 nm and the excitation maximum at 350 nm, which in similar complexes has been related (a) to the gold interactions, metal to metal centered transition; (b) sulfur to gold transition, ligand to metal charge transfer transition; (c) to the S−Au···Au unit, ligand to metal charge transfer modified by the gold−gold interactions.[6] The mononuclear amino-phosphino complex **3** displays the emission maximum at 444 nm with a shoulder at 515 nm and the excitation maximum at 333 nm. Luminescent mono-

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

Au(1)−P(1)	2.2577(7)	Au(3)−P(101)	2.2650(7)
Au(1)−S(1)	2.3072(7)	Au(3)−S(101)	2.3128(7)
Au(1)−Au(2)	3.17618(19)	Au(3)−Au(4)	3.2867(2)
Au(2)−N(1)	2.066(2)	Au(4)−N(101)	2.071(2)
Au(2)−P(2)	2.2373(7)	Au(4)−P(102)	2.2327(7)
S(1)−C(1)	1.824(3)	S(101)−C(101)	1.824(3)
N(1)−C(3)	1.315(4)	N(101)−C(103)	1.318(4)
N(1)−C(2)	1.469(3)	N(101)−C(102)	1.464(4)
N(2)−C(3)	1.157(4)	N(102)−C(103)	1.151(4)
C(1)−C(2)	1.515(4)	C(101)−C(102)	1.509(5)
P(1)−Au(1)−S(1)	176.02(3)	P(101)−Au(3)−S(101)	178.75(3)
P(1)−Au(1)−Au(2)	112.12(2)	P(101)−Au(3)−Au(4)	118.225(19)
S(1)−Au(1)−Au(2)	65.328(19)	S(101)−Au(3)−Au(4)	60.75(2)
N(1)−Au(2)−P(2)	167.51(7)	N(101)−Au(4)−P(102)	162.54(8)
N(1)−Au(2)−Au(1)	84.04(7)	N(101)−Au(4)−Au(3)	87.03(8)
P(2)−Au(2)−Au(1)	107.326(19)	P(102)−Au(4)−Au(3)	107.91(2)
C(1)−S(1)−Au(1)	104.75(9)	C(101)−S(101)−Au(3)	104.76(10)
C(3)−N(1)−C(2)	115.5(2)	C(103)−N(101)−C(102)	116.7(3)
C(3)−N(1)−Au(2)	118.34(19)	C(103)−N(101)−Au(4)	120.5(2)
C(2)−N(1)−Au(2)	125.26(17)	C(102)−N(101)−Au(4)	122.6(2)
C(2)−C(1)−S(1)	114.61(18)	C(102)−C(101)−S(101)	114.7(2)
N(1)−C(2)−C(1)	113.4(2)	N(101)−C(102)−C(101)	112.6(3)
N(2)−C(3)−N(1)	178.8(3)	N(102)−C(103)−N(101)	178.7(4)

Table 4. Details of Crystal Data and Structure Refinement for Complexes 1 and 4

	1	**4a**	**4b**
empirical formula	$C_{21}H_6AuF_{15}N_2S$	$C_{42}H_{40}Au_2N_2OP_2S$	$C_{39}H_{34.36}Au_2N_2O_{0.18}P_2S$
fw	800.30	1076.69	1021.86
temperature/K	133	133	133
wavelength/Å	0.71073	0.71073	0.71073
cryst syst	triclinic	orthorhombic	monoclinic
space group	$P\bar{1}$	$P2_12_12_1$	$P2_1/n$
a/Å	9.4658(8)	10.0414(8)	16.4127(11)
b/Å	9.8107(8)	10.3564(8)	13.5924(8)
c/Å	12.8953(11)	37.010(3)	31.2528(18)
α/deg	75.409(3)	90	90
β/deg	80.164(3)	90	93.218(3)
γ/deg	88.393(3)	90	90
volume/Å^3	1141.74(17)	3848.8(5)	6961.1(7)
Z	2	4	8
density(calcd)/Mg/m^3	2.328	1.858	1.950
abs coeff/mm^{-1}	6.672	7.788	8.604
F(000)	752	2072	3902
cryst habit	colorless square prism	colorless needle	colorless tablet
cryst size/mm	0.33 × 0.19 × 0.18	0.45 × 0.08 × 0.04	0.35 × 0.26 × 0.11
θ range for data collection	1.66 to 30.03	2.04 to 30.04	1.31 to 30.03
index ranges	$-13 \le h \le 13, -13 \le k \le 13, -18 \le l \le 18$	$-14 \le h \le 14, -14 \le k \le 14, -52 \le l \le 52$	$-23 \le h \le 23, -19 \le k \le 19, -44 \le l \le 44$
no. of reflns collected	23 792	77 204	141 032
no. of ind reflns	6643 [R(int) = 0.0196]	11 265 [R(int) = 0.0684]	20 341 [R(int) = 0.0478]
max. and min. transmn	0.564 and 0.371	0.862 and 0.497	0.564 and 0.309
no. of data/restraints/params	6643/104/369	11265/133/454	20341/254/834
goodness-of-fit on F^2	1.047	0.957	0.983
R1 [$I > 2\sigma(I)$][a]	0.0177	0.0245	0.0224
wR2 (all data)[b]	0.0451	0.0471	0.0512
largest diff peak and hole/e Å^{-3}	3.398, −0.908	1.871 and −0.929	1.401 and −0.908

[a] $R1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2(F^2) = [\sum\{w(F_o^2 - F_c^2)2\}/\sum\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and a and b are constants adjusted by the program.

nuclear gold(I) complexes usually are three-coordinated or display short gold−gold distances.[6a] In addition, the 2-amt ligand displays an emission centered at 457 nm with the excitation maximum at 287 nm, which indicates that the emission of complex **3** could be ligand centered but modified by the phosphino-gold(I) unit.

Experimental Section

General Procedures. All the reactions were carried out under an argon atmosphere at room temperature. IR spectra were recorded on a Perkin-Elmer 883 spectrophotometer, over the range 4000−200 cm^{-1}, by using Nujol mulls between polyethylene sheets. ^{1}H, ^{19}F, and ^{31}P{^{1}H} NMR spectra were recorded on a Brüker ARX·300 or GEMINI 2000 apparatus in $CDCl_3$ solutions (if no other solvent is stated); chemical shifts are quoted relative to $SiMe_4$ (external, ^{1}H), $CFCl_3$ (external, ^{19}F), and 85% H_3PO_4 (external, ^{31}P). C, H, N, and S analyses were performed with a Perkin-Elmer 2400 microanalyzer. Conductivities were measured in acetone solution with a Philips PW 9509 apparatus. Mass spectra were recorded on a VG Autospec using LSI MS technique (with a Cs gun) and 3-nitrobenzyl alcohol as matrix. The luminescence spectra were recorded on a Perkin-Elmer LS-50B spectrofluorometer.

Preparation of Compounds. [Au(C_6F_5)$_x$(2-amt)], x = 3 (1), x = 1 (2). To a 15 mL dichloromethane or diethyl ether solution of [Au(C_6F_5)$_x$(tht)][7,8] (tht = tetrahydrothiophene; 0.1

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g; $x = 3$, 0.13 mmol; $x = 1$, 0.22 mmol) was added the ligand 2-amt (13 mg, 0.13 mmol; 22 mg, 0.22 mmol). After stirring for 2 h, the solution was concentrated to ca. 3 mL. Addition of cold hexane afforded complexes **1** and **2** as white solids, which were washed with cold hexane. Yield of **1**: 80 mg (79%). Data for **1**: ^{1}H NMR δ 5.60 (s, 2H; NH_2), 3.98 (t, ^3J(H,H) = 7.6 Hz, 2H; CH_2), 3.47 (t, 2H; CH_2); ^{19}F NMR δ −123.43 (m, $2F_o$), −124.49 (m, $4F_o$), −156.91 (t, ^3J(F,F) = 20.1 Hz, $2F_p$), −157.79 (t, ^3J(F,F) = 20.1 Hz, $1F_p$), −161.27 (m, $4F_m$), −162.47 (m, $2F_m$); IR 3516, 3410 (N−H), 964, 816, 797 (C_6F_5) cm^{-1}. Anal. Calcd for $C_{21}H_6AuF_{15}N_2S$ (800.3): C, 31.5; H, 0.75; N, 3.5; S, 4.0. Found: C, 31.6; H, 0.8; N, 3.59; S, 3.75. LSI MS (*m*/*z* (%, assignment)): 799 (13, $[M - H]^+$), 466 (100, $[M - 2(C_6F_5)]^+$). Λ: 2.1 Ω^{-1} cm^2 mol^{-1}. Yield of **2**: 97 mg (95%). Data for **2**: ^{1}H NMR δ 5.68 (s, 2H; NH_2), 4.20 (t, ^3J(H,H) = 7.6 Hz, 2H; CH_2), 3.54 (t, 2H; CH_2); ^{19}F NMR δ −117.50 (m, $2F_o$), −160.74 (t, ^3J(F,F) = 20.1 Hz, $1F_p$), −164.16 (m, $2F_m$). IR: 3513, 3488, 3460, 3379, 3352 (N−H), 954, 806 (C_6F_5) cm^{-1}. Anal. Calcd for $C_9H_6AuF_5N_2S$ (466.2): C, 23.2; H, 1.3; N, 6.0; S, 6.9. Found: C, 23.05; H, 1.3; N, 6.05; S, 6.55. LSI MS (*m*/*z* (%, assignment)): 401 (15, $[Au(2\text{-amt})_2]^+$). Λ: 4.5 Ω^{-1} cm^2 mol^{-1}.

[Au(2-amt)(PPh_3)]CF_3SO_3, 3. To a 15 mL dichloromethane solution [Au(PPh_3)(CF_3SO_3)] (0.2 mmol, prepared in situ by reaction of [AuCl(PPh_3)][9] with [Ag(CF_3SO_3)]) was added the ligand (21 mg, 0.2 mmol). After the mixture was stirred for 1 h, the solution was concentrated to ca. 2 mL and diethyl ether (15 mL) was added to obtain **3** as a white solid, which was washed with diethyl ether. Yield: 107 mg (75%). Data for **3**: ^{1}H NMR δ 7.5−7.3 (m, 15H; Ph), 6.43 (br, 2H; NH_2), 3.93 (t, ^3J(H,H) = 7.3 Hz, 2H; CH_2), 3.42 (t, 2H; CH_2). ^{19}F NMR δ −79.1 (s, CF_3); ^{31}P{^{1}H} NMR δ 33.3 (s). IR: 3312, 3167 (N−H), 1286, 1157, 637 (CF_3SO_3) cm^{-1}. Anal. Calcd. for $C_{22}H_{21}AuF_3N_2O_3PS_2$ (710.5): C, 37.2; H, 3.0; N, 3.95; S, 9.05. Found: C, 37.05; H, 2.95; N, 4.0; S, 8.8. LSI MS (*m*/*z* (%, assignment)): 459 (100, $[AuPPh_3]^+$), 561 (12, $[M - CF_3SO_3]^+$), 721 (60, $[Au(PPh_3)_2]^+$). Λ: 110 Ω^{-1} cm^2 mol^{-1}.

[($AuPPh_3$)$_2$(μ-kS,kN1−SCH_2CH_2N−CN)], 4. To a solution of 2-amt (10 mg, 0.1 mmol) was added [Au(acac)(PPh_3)][10] (112 mg, 0.2 mmol), and the mixture was stirred for about 1 h. The solution was concentrated to ca. 2 mL, and the addition of petroleum ether afforded **4** as a white solid. Yield: 82 mg (80%). ^{1}H NMR: δ 7.5−7.3 (m, 30H; Ph), 3.78 (‘t’, ^3N(H,H) = 5.0 Hz, 2H; CH_2), 3.27 (‘t’, 2H; CH_2). ^{1}H NMR (CD_2Cl_2, −90 °C): δ 7.5−7.3 (m, 30H; Ph), 3.79 (br, 2H; CH_2), 3.25 (br, 2H; CH_2). ^{31}P{^{1}H} NMR: δ 35.2 (s). ^{31}P{^{1}H} NMR (CD_2Cl_2, −90 °C): δ 34.9 (br). IR: 2145 cm^{-1} (CN). Anal. Calcd for $C_{39}H_{34}Au_2N_2P_2S$ (1018.7): C, 46.0; H, 3.35; N, 2.75; S, 3.15. Found: C, 45.7; H, 3.25; N, 2.65; S, 3.0. LSI MS (*m*/*z* (%, assignment)): 459 (100, $[AuPPh_3]^+$), 721 (47, $[Au(PPh_3)_2]^+$), 1019 (5, $[M + H]^+$), 1147 (16, $[S(AuPPh_3)_3 - PPh_3]^+$), 1409 (8, $[S(Au - PPh_3)_3]^+$). Λ: 5 Ω^{-1} cm^2 mol^{-1}.

Crystal Structure Determination of 1 and 4. Crystal data and details of data collection and structure refinement of [Au(C_6F_5)$_3$(2-amt)] **1** and [($AuPPh_3$)$_2$(μ-SCH_2CH_2N−CN)] **4** (**4a** is an acetone monosolvate, **4b** contains two independent molecules of **4** and a partially occupied water site) are given in Table 4. Data were measured on a Bruker SMART 1000 CCD diffractometer. Absorption corrections were based on multiple scans (program SADABS). The structures were refined anisotropically on F^2 (program SHELXL-97[11]) using a system of restraints (light-atom *U* values and local ring symmetry). H atoms were included using a riding model.

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Supporting Information Available: An X-ray crystallographic file in CIF format for the structure determination of complexes **1** and **4** (**4a** and **4b**). This material is available free of charge via the Internet at http://pubs.acs.org.

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