Complexes with S-Donor Ligands. 5.[†] Syntheses of the First (Hydrosulfido)- and Anionic Sulfidoorganogold(I) Complexes. Crystal and Molecular Structure of $(Et_4N)_2[\{Au(C_6F_5)\}_3(\mu_3\text{-}S)]\cdot 0.5MeC(O)Et$

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Complexes Q[Au(R)Cl] react with H_2S in the presence of diethylamine to give the corresponding organo(hydrosulfido)gold(I) complexes Q[Au(R)(SH)] [R = C_6F_5, Q = $Ph_3P{=}N{=}PPh_3$ = PNP, Bu_4N; Q = PNP, R = $C_6H_4NO_2$-2, $C_6H_2(NO_2)_3$-2,4,6]. Under the same reaction conditions, $Me_4N[Au(C_6F_5)Cl]$ gives the bridging organo(μ_3-sulfido)gold(I) complex $(Me_4N)_2[\{Au(C_6F_5)\}_3(\mu_3\text{-}S)]$, whereas $Et_4N[Au(C_6F_5)Cl]$ gives $Et_4N[Au(C_6F_5)SH]$ or $(Et_4N)_2[\{Au(C_6F_5)\}_3(\mu_3\text{-}S)]$ depending on the workup procedure. The crystal structure of Et_4N-$[\{Au(C_6F_5)\}_3(\mu_3\text{-}S)]\cdot 0.5MeC(O)Et$ has been determined. The Au⋯Au contacts are 3.1844, 3.2773, and 3.4772 Å, with corresponding angles 86.68, 90.31, and 97.65° at sulfur.

Introduction

Transition-metal hydrosulfido complexes are under intensive investigation mainly because of the reactivity they exhibit toward organic substrates,[1,2] their implication in catalytic biological[3] or hydrodesulfuration[4−6] processes, and their use as models in theoretical studies[7] and as a source of complexes containing terminal sulfido ligands.[8] About 100 such complexes have been described, the most common being those of Mo[9−11] and Ru.[12−14] We have described the synthesis and crystal structure of the first homoleptic hydrosulfido metal complex, $PNP[Au(SH)_2]$,[15] (PNP = $Ph_3P{=}N{=}PPh_3$) which is thought to be involved in the geological transport of gold.[16−19] In this paper we report the first organogold(I) hydrosulfido complexes, Q[Au(R)(SH)], whose stability/reactivity depends on the nature of the counterion Q.

A large number of transition-metal complexes with sulfide ligands have been reported. These complexes have found applications as catalysts.[4,5,20,21] However, the number of sulfidogold complexes is very limited. Thus, a family of complexes $[(AuPR_3)_n(\mu_n\text{-}S)]^{(n-2)+}$ is known for $n = 2-6$ and various phosphine or diphosphine ligands.[22−28] The further coordinating ability of the sulfido ligand in $[\{Au_2(dppf)\}(\mu_2\text{-}S)]$ [dppf = 1,1′-bis(diphenylphosphino)ferrocene] or $[(AuPPh_3)_2(\mu_2\text{-}S)]$ has allowed the synthesis of the mixed complexes [{Au₂-

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(dppf)}$(AuC_6F_5)(\mu_3\text{-}S)$] or [{$Au_2$(dppf)}$(AuCH_2PPh_3)(\mu_3\text{-}S)$] or [$(Au_2L_2)\{Au(C_6F_5)_3\}_2(\mu_4\text{-}S)$] (L = PPh_3, L_2 = dppf).[22,29] As far as we are aware, these are the only sulfido complexes involving organogold moieties. We report here the first fully organogold sulfido complex, $[(AuC_6F_5)_3(\mu_3\text{-}S)]^{2-}$, which is, along with $[Au_{12}S_8]^{4-}$, $[Au_2S_8]^{2-}$, and $[AuS_9]^{-}$,[30] the only anionic sulfidogold(I) complex.

The formation of complexes $[(AuPR_3)_n(\mu_n\text{-}S)]^{(n-2)+}$, including the hypercoordinated species with $n = 5$ and 6, is an example of the tendency of $AuPR_3^+$ moieties to aggregate at interstitial atoms (C, P, N) to give interesting compounds with unusual structure and bonding, whose stability is attributed to a relativistic effect on Au(I) energy levels termed "aurophilicity".[31−38] It should be borne in mind that the successive aggregation of each AuL^+ unit at sulfur causes the charge of the resulting complex to increase by one unit, with concomitant increases in electrostatic repulsion effects and instability. Therefore, the aurophilic effect, which has been quantified to about 33 kJ/mol, must play an important role in these reactions.[33] It seemed of interest to establish whether neutral AuR units could show some tendency to aggregate at small interstitial atoms. According to electronic and steric effects the resulting anionic complexes (*e.g.* $[(AuR)_n(\mu_n\text{-}S)]^{2-}$) should be more prone to act as ligands than the cationic complexes $[(AuPPh_3)_n(\mu_n\text{-}S)]^{n+}$ and should therefore aggregate AuR or AuL^+ units more readily.

Experimental Section

All reactions were carried out in normal laboratory conditions. Technical grade solvents were purified by standard procedures. Infrared spectra were recorded in the range 4000−200 cm^{-1} on a Perkin-Elmer 16F PC FT-IR spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured on *ca.* 5×10^{-4} M acetone solutions with a Philips PW9501 conductimeter. Melting points were determined on a Reichert apparatus and are uncorrected. C, H, N, and S analyses were carried out with a Carlo Erba 1106 microanalyzer. NMR spectra were measured in a Varian Unity 300 spectrometer. Chemical shifts are referred to TMS [^1H and $^{13}C\{^1H\}$] or $CFCl_3$ (^{19}F). The integration of the signal corresponding to the SH proton is always less than expected, probably because of its greater relaxation time with respect to the other protons. The ^{13}C resonances of PNP^+ (PNP = $Ph_3P{=}N{=}PPh_3$) appear, with little differences between the various complexes, at δ 127 (dd of an AA′XX′ system, J_{CP} = 108 and 0.8 Hz, *i*-C), 130 (m, *o*-C), 132 (m, *m*-C) and 134 (s, *p*-C) and are not given below. $[Hg\{C_6H_2(NO_2)_3\text{-}2,4,6\}_2]$,[39] $[Au(C_6F_5)(tht)]$ (tht = tetrahydrothiophene), $Et_4N[Au(C_6F_5)Cl]$, and $Bu_4N[Au(C_6F_5)Cl]$ were prepared as previously described.[40]

Synthesis of $[Hg(C_6H_4NO_2\text{-}2)_2]$. To a suspension of $HO_2CC_6H_4NO_2$-2 (2.01 g, 12.02 mmol) in water (60 mL) was added $Hg(OAc)_2$ (2.30 g, 7.22 mmol). Immediately, a bulky white precipitate of $Hg(O_2CC_6H_4NO_2\text{-}2)_2$ formed, which was stirred for 0.5 h, filtered off, washed with water (20 mL), and dried *in vacuo* at 110 °C for 1 h. This product was decarboxylated by heating at 190 °C for 5 h in an open tube. After the mixture was cooled to room temperature, the resulting off-white solid was extracted with dichloromethane (5 × 25 mL). The combined extracts were filtered through Celite, the solvent was evaporated to dryness, and the residue was stirred in diethyl ether (40 mL) for 0.5 h to give the title compound as a pale yellow solid, which was filtered off and air dried. Yield: 753 mg, 28%. The melting point and IR spectrum coincide with those previously described.[41] Anal. Calcd for $C_{12}H_8HgN_2O_4$: C, 32.40; H, 1.81; N, 6.23. Found: C, 32.44; H, 1.75; N, 6.28.

Syntheses of $Q[Au(C_6F_5)Cl]$ [Q = PNP (1·PNP), Me_4N (1·Me_4N)]. To a solution of $[Au(C_6F_5)(tht)]$ (tht = tetrahydrothiophene) (*ca.* 1 mmol) in acetone (10 mL) was added an equimolar amount of QCl, and the resulting solution or suspension was stirred for 0.5 (**1·PNP**) or 1 (**1·Me_4N**) h and then filtered through anhydrous $MgSO_4$. The filtrate was concentrated (3 mL) and diethyl ether (15 mL) added to precipitate **1·PNP** or **1·Me_4N** as white solids which were filtered off, washed with diethyl ether (25 mL) and dried in a nitrogen stream. **1·PNP**: Yield: 79%. Mp: 136 °C dec Λ_M: 94 Ω^{-1} cm^2 mol^{-1}. IR: ν(AuCl) 328 (vs) cm^{-1}. ^{19}F NMR ($CDCl_3$, δ): −164.78 (m, 2 F, *m*-F), −163.56 (m, 1 F, *p*-F), −115.30 (m, 2 F, *o*-F). Anal. Calcd for $C_{42}H_{30}AuClF_5NP_2$: C, 53.78; H, 3.22; N, 1.49. Found: C, 53.94; H, 3.07; N, 1.50. **1·Me_4N**: Yield: 90%. Mp: 186 °C dec Λ_M: 135 Ω^{-1} cm^2 mol^{-1}. IR: ν(AuCl) 318 (vs) cm^{-1}. ^{19}F-NMR ($CDCl_3$, δ): −164.41 (m, 2 F, *m*-F), −163.55 (m, 1 F, *p*-F), −115.14 (m, 2 F, *o*-F). Anal. Calcd for $C_{10}H_{12}AuClF_5N$: C, 25.36; H, 2.55; N, 2.96. Found: C, 25.38; H, 2.44; N, 2.91.

Synthesis of $PNP[Au(C_6H_4NO_2\text{-}2)Cl]$ (2). A mixture of $PNP[AuCl_2]$ (834 mg, 1.04 mmol), $[Hg(C_6H_4NO_2\text{-}2)_2]$ (298 mg, 0.67 mmol), and Me_4NCl (270 mg, 2.46 mmol) in acetone (50 mL) was refluxed for 5 h. After the mixture was cooled to room temperature, the solvent was evaporated to dryness and the black residue refluxed in dichloromethane for 0.5 h. The suspension was filtered through anhydrous $MgSO_4$ and the clear yellow filtrate concentrated to 3 mL under vacuum. Addition of ethanol (20 mL) led to slow precipitation of **2** as a pale yellow solid which was filtered off and air dried. The product was recrystallized from dichloromethane and diethyl ether. Yield: 303 mg, 33%. Mp: 147 °C dec Λ_M: 92 Ω^{-1} cm^2 mol^{-1}. IR: ν(AuCl) 314 (m); $\nu_{asym}(NO_2)$ 1504 (s) cm^{-1}. NMR ($CDCl_3$, δ): ^1H, 6.96 (m, 1 H, $C_6H_4NO_2$-2), 7.17 (m, 1 H, $C_6H_4NO_2$-2), 7.41−7.69 (m, 31 H, $C_6H_4NO_2$-2 + PNP), 7.71 (m, 1 H, $C_6H_4NO_2$-2); $^{13}C\{^1H\}$ 122.63 (s), 123.16 (s), 130.80 (s), 142.48 (s, C3-C6, $C_6H_4NO_2$-2), 150.36 (s, C1, $C_6H_4NO_2$-2), 158.13 (s, C2, $C_6H_4NO_2$-2). Anal. Calcd for $C_{42}H_{34}AuClN_2O_2P_2$: C, 56.48; H, 3.84; N, 3.14. Found: C, 56.32; H, 3.81; N, 3.23.

Synthesis of $PNP[Au\{C_6H_2(NO_2)_3\text{-}2,4,6\}Cl]$ (3). A mixture of $PNP[AuCl_2]$ (478 mg, 0.59 mmol), $[Hg\{C_6H_2(NO_2)_3\text{-}2,4,6\}_2]$ (203 mg, 0.33 mmol), and $(Me_4N)Cl$ (220 mg, 2.01 mmol) in acetone (20 mL) was refluxed for 5 h. After the mixture was cooled to room temperature, the solvent was evaporated to dryness and the black residue refluxed in dichloromethane (20 mL) for 15 min. The suspension was filtered through anhydrous $MgSO_4$ and the clear red filtrate concentrated to 3 mL. Addition of ethanol (20 mL) led to slow precipitation of **3** as a greenish-yellow solid which was filtered off, washed with ethanol (9 mL) and diethyl ether (6 mL), and air dried. The product was recrystallized from dichloromethane and ethanol. Yield: 520 mg, 89%. Mp: 132 °C. Λ_M: 85 Ω^{-1} cm^2 mol^{-1}. IR: ν(AuCl) 326 (m); $\nu_{asym}(NO_2)$ 1530

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(vs), 1518 (vs) cm^{-1}. NMR (CDCl$_3$, δ): ^{1}H, 7.4−7.7 (m, 30 H, PNP), 8.65 (s, 2H, $C_6H_2(NO_2)_3$-2,4,6); ^{13}C{^{1}H} 120.38 (s, C3, $C_6H_2(NO_2)_3$-2,4,6), 143.71 (s, C1, $C_6H_2(NO_2)_3$-2,4,6), 155.94 and 159.59 (s, C2 and C4, $C_6H_2(NO_2)_3$-2,4,6). Anal. Calcd for $C_{42}H_{32}AuClN_4O_6P_2$: C, 51.31; H, 3.28; N, 5.70. Found: C, 51.44; H, 3.36; N, 5.62.

Synthesis of PNP[Au(C_6F_5)(SH)] (4·PNP). H_2S was bubbled through a stirred solution of **1·PNP** (705 mg, 0.75 mmol) in a mixture of dichloromethane (10 mL) and diethylamine (0.3 mL) for 3 min. The solvent was then evaporated to *ca.* 5 mL and diethyl ether (10 mL) added to give a white precipitate of (Et_2NH_2)Cl, which was removed by filtration through anhydrous $MgSO_4$. The clear filtrate was concentrated (3 mL) to precipitate **4·PNP** as a white solid which was filtered off, washed with diethyl ether (10 mL), and dried in a nitrogen stream. Yield: 605 mg, 86%. Mp: 136 °C. Λ_M: 102 Ω^{-1} cm^2 mol^{-1}. IR: ν(Au−S) 338 (m); ν(C_6F_5) 1500 (vs), 948 (vs), 790 (s) cm^{-1}. NMR (CDCl$_3$, δ): ^{1}H −1.16 (s, 1H, SH), 7.3−7.7 (m, 30 H, PNP); ^{19}F −164.58 (m, 2 F *m*-F), −163.95 (m, 1 F *p*-F), −115.66 (m, *o*-F). Anal. Calcd for $C_{42}H_{31}AuF_5NP_2S$: C, 53.91; H, 3.34; N, 1.50; S, 3.43. Found: C, 53.68; H, 3.23; N, 1.56; S, 3.77.

Synthesis of Bu_4N[Au(C_6F_5)(SH)] (4·Bu_4N). H_2S was bubbled through a stirred solution of Bu_4N[Au(C_6F_5)Cl] (200 mg, 0.31 mmol) in a mixture of dichloromethane (4 mL) and diethylamine (0.1 mL) for 3 min. The solvent was then evaporated to *ca.* 3 mL and diethyl ether (15 mL) added to give a white precipitate of (Et_2NH_2)Cl, which was removed by filtration through anhydrous $MgSO_4$. The clear filtrate was concentrated (3 mL) to precipitate **4·Bu_4N** as a white solid. *n*-Pentane (15 mL) was added to complete the precipitation of **4·Bu_4N**, which was filtered off and dried in a nitrogen stream. Yield: 178 mg, 89%. M.p.: 73 °C. Λ_M: 112 Ω^{-1} cm^2 mol^{-1}. IR: ν(Au−S) 334 (m); ν(C_6F_5) 1500 (vs), 950 (vs), 790 (s) cm^{-1}. NMR (CDCl$_3$, δ): ^{1}H −1.19 (s, 1H, SH), 0.99 (t, 12 H, Me, Bu_4N), 1.42 (m, 8 H, CH_2, Bu_4N), 1.67 (m, 8 H, CH_2, Bu_4N), 3.27 (m, 8 H, CH_2, Bu_4N); ^{19}F −163.83 (m, 2 F, *m*-F), −162.63 (m, 1 F, *p*-F), −116.30 (m, 2 F, *o*-F). Anal. Calcd for $C_{22}H_{37}AuF_5NS$: C, 41.32; H, 5.83; N, 2.19; S, 5.01. Found: C, 41.18; H, 5.99; N, 2.26; S, 4.75.

Synthesis of Et_4N[Au(C_6F_5)(SH)] (4·Et_4N). H_2S was bubbled through a stirred solution of Et_4N[Au(C_6F_5)Cl] (151 mg, 0.28 mmol) in a mixture of acetone (5 mL) and diethylamine (0.1 mL) for 3 min. A small amount of (Et_2NH_2)SH formed as a white precipitate. Addition of diethyl ether (25 mL) caused the precipitation of (Et_2NH_2)Cl, which was removed along with (Et_2NH_2)SH by filtration through anhydrous $MgSO_4$. The clear filtrate was concentrated (3 mL) and *n*-pentane (20 mL) added to give a white precipitate of **4·Et_4N**, which was filtered off and dried in a nitrogen stream. Yield: 81 mg, 80%. Mp: 60 °C. IR: ν(Au−S) 332 (m); ν(C_6F_5) 1506 (vs), 952 (vs), 792 (s) cm^{-1}. NMR (CDCl$_3$, δ): ^{1}H −1.17 (s, 1 H, SH), 1.38 (tt, Me, 12 H, $^3J_{HH}$ = 7.2 Hz, $^3J_{HN}$ = 2.0 Hz), 3.39 (q, 8 H, CH_2); ^{19}F −163.67 (m, 2 F, *m*-F), −162.23 (m, 1 F, *p*-F), −116.66 (m, 2 F, *o*-F). Anal. Calcd for $C_{14}H_{21}AuF_5NS$: C, 31.89; H, 4.01; N, 2.66; S, 6.08. Found: C, 31.66; H, 4.00; N, 2.64; S, 5.25.

Synthesis of PNP[Au($C_6H_4NO_2$-2)(SH)] (5). H_2S was bubbled through a stirred solution of **2** (120 mg, 0.13 mmol) in a mixture of dichloromethane (4 mL) and diethylamine (0.2 mL) for 4 min. Immediate addition of diethyl ether (20 mL) to the resulting yellow solution led to the precipitation of a yellow solid which was filtered off, washed with water (2 × 1 mL) and diethyl ether (2 × 5 mL), and air dried to give **5**. Yield: 101 mg, 85%. Mp: 135 °C. Λ_M: 91 Ω^{-1} cm^2 mol^{-1}. IR: ν(AuS) 330 (m); ν_{asym}(NO_2) 1504 (s) cm^{-1}. NMR (CDCl$_3$, δ): ^{1}H −1.30 (s, 1H, SH), 6.96 (m, 1H, $C_6H_4NO_2$-2), 7.22 (m, 1H, $C_6H_4NO_2$-2), 7.3−7.7 (m, 31H, PNP + $C_6H_4NO_2$-2), 7.78 (m, 1H, $C_6H_4NO_2$-2); ^{13}C{^{1}H} 122.71 (s), 122.95 (s), 130.86 (s), 142.19 (s, C3-C6, $C_6H_4NO_2$-2), 158.16 (s, C1, $C_6H_4NO_2$-2), 163.20 (s, C2, $C_6H_4NO_2$-2). Anal. Calcd for $C_{42}H_{35}AuN_2O_2P_2S$: C, 56.63; H, 3.96; N, 3.15; S, 3.60. Found: C, 56.34; H, 4.34; N, 3.04; S, 3.70.

Synthesis of PNP[Au{$C_6H_2(NO_2)_3$-2,4,6}(SH)] (6). To a yellow solution of **3** (110 mg, 0.11 mmol) in dichloromethane (4 mL) was added diethylamine (0.05 mL). H_2S was bubbled through the resulting red solution until the color changed to bright orange. Immediate addition of diethyl ether (40 mL) led to slow precipitation of a bright orange solid which was filtered off, washed with water (2 × 1 mL) and diethyl ether (20 mL), and air dried to give **6**. Yield: 87 mg, 79%. Mp: 116 °C. Λ_M: 91 Ω^{-1} cm^2 mol^{-1}. IR: ν(AuS) 334 (m); ν_{asym}(NO_2) 1530 (s), 1514 (s) cm^{-1}. NMR (CDCl$_3$, δ): ^{1}H −1.09 (s, 1 H, SH), 7.4−7.7 (m, 30 H, PNP), 8.70 (s, 2H, $C_6H_2(NO_2)_3$-2,4,6). ^{13}C{^{1}H} 120.65 (s, C3, $C_6H_2(NO_2)_3$-2,4,6), 143.42 (s, C1, $C_6H_2(NO_2)_3$-2,4,6), 159.27 and 166.58 (s, C2 and C4, $C_6H_2(NO_2)_3$-2,4,6). Anal. Calcd for $C_{42}H_{33}AuN_4O_6P_2S$: C, 51.44; H, 3.39; N, 5.71; S, 3.27. Found: C, 51.55; H, 3.36; N, 5.74; S, 3.84.

Synthesis of (Me_4N)$_2$[{Au(C_6F_5)}$_3$(μ_3-S)] (7·Me_4N). H_2S was bubbled through a stirred suspension of **1·Me_4N** (165 mg, 0.35 mmol) in a mixture of acetone (5 mL) and diethylamine (0.1 mL) for 4 min. Addition of diethyl ether (15 mL) to the resulting solution gave a white precipitate which was removed by filtration through anhydrous $MgSO_4$. Partial evaporation of the clear filtrate (3 mL) and addition of diethyl ether (15 mL) led to slow precipitation of **7·Me_4N** as a white solid, which was filtered off and air dried. Yield: 98 mg, 66%. Mp: 231 °C dec Λ_M: 204 Ω^{-1} cm^2 mol^{-1}. IR: ν(Au−S) 366 (m), 312 (w); ν(C_6F_5) 1504 (vs), 950 (vs), 790 (s) cm^{-1}. NMR [$(CD_3)_2CO$, δ]: ^{1}H, 3.45 (t, NMe_4, $^2J_{HN}$ = 6.0 Hz); ^{19}F −164.35 (m, 3 F, *m*-F + *p*-F), −114.36 (m, 2 F, *o*-F). Anal. Calcd for $C_{26}H_{24}Au_3F_{15}N_2S$: C, 24.54; H, 1.90; N, 2.20; S, 2.52. Found: C, 24.57; H, 2.09; N, 2.45; S, 3.06.

Synthesis of (Et_4N)$_2$[{Au(C_6F_5)}$_3$(μ_3-S)] (7·Et_4N). H_2S was bubbled through a stirred solution of Et_4N[Au(C_6F_5)Cl] (1002 mg, 1.89 mmol) in a mixture of dichloromethane (10 mL) and diethylamine (0.5 mL) for 5 min. Diethyl ether (35 mL) was added to precipitate a white solid which was filtered off, washed with water (10 mL), and air dried. The product was then dissolved in acetone (15 mL) and the resulting solution filtered through anhydrous $MgSO_4$. Evaporation of the solvent (*ca.* 6 mL) and addition of diethyl ether (30 mL) led to the precipitation of **7·Et_4N** as a white solid which was filtered off and air dried. Yield: 700 mg, 80%. Mp: 176 °C dec Λ_M: 186 Ω^{-1} cm^2 mol^{-1}. IR: ν(Au−S) 360 (m), 312 (w); ν(C_6F_5) 1496 (vs), 952 (vs), 790 (s) cm^{-1}. NMR [$(CD_3)_2CO$, δ]: ^{1}H, 1.35 (tt, Me, 3 H, $^3J_{HH}$ = 7.2 Hz, $^3J_{HN}$ = 2.0 Hz), 3.47 (q, CH_2, 2 H); ^{19}F −164.50 (m, 3 F, *m*-F + *p*-F), −114.19 (m, 2 F, *o*-F). Mass spectrum (FAB): *m/z* 383 (21), 531 ([Au(C_6F_5)$_2$], 100), 760 ([{Au(C_6F_5)}$_2$(μ_2-S)], 71), 761 (31), 957 (65), 1124 (M, 42), 1254 (51). Anal. Calcd for $C_{34}H_{40}Au_3F_{15}N_2S$: C, 29.49; H, 2.91; N, 2.02; S, 2.32. Found: C, 29.62; H, 2.93; N, 2.03; S, 2.50. Single crystals were grown by slow diffusion of diethyl ether into a MeC(O)Et solution of **7·Et_4N**.

Synthesis of (Bu_4N)$_2$[{Au(C_6F_5)}$_3$(μ_3-S)] (7·Bu_4N). Complex **7·Me_4N** (106 mg, 0.08 mmol) and (Bu_4N)Cl (48 mg, 0.17 mmol) were mixed in dichloromethane (8 mL). The resulting suspension was stirred for 1 h and filtered through anhydrous $MgSO_4$ to remove the white precipitate of (Me_4N)Cl. Partial evaporation of the filtrate (3 mL) and addition of diethyl ether (20 mL) gave a small amount of a white solid, which was removed by filtration through anhydrous $MgSO_4$. Partial evaporation of the clear filtrate (5 mL) led to the precipitation of **7·Bu_4N** as a white solid which was filtered off and dried in a nitrogen stream. Yield: 58 mg, 43%. Mp: 123 °C. Λ_M: 142 Ω^{-1} cm^2 mol^{-1}. IR: ν(Au−S) 364 (m), 310 (w); ν(C_6F_5) 1500 (vs), 950 (vs), 788 (s) cm^{-1}. NMR [$(CD_3)_2CO$, δ]: ^{1}H, 0.94 (t, Me, Bu_4N, 3 H), 1.42 (m, CH_2, Bu_4N, 2 H), 1.79 (m, CH_2, Bu_4N, 2 H), 3.44 (m, CH_2, Bu_4N, 2 H); ^{19}F −164.63 (m, *m*-F, *p*-F), −113.95 (m, *o*-F). Anal. Calcd for $C_{50}H_{72}Au_3F_{15}N_2S$: C, 37.32; H, 4.51; N, 1.74; S, 1.99. Found: C, 37.69; H, 4.59; N, 1.79; S, 2.26.

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Table 1. Crystal Data for 7·Et$_4$N·0.5MeC(O)Et

molecular formula	$C_{36}H_{44}Au_3F_{15}N_2O_{0.5}S$
molecular weight	1420.69
source	liquid diffusion MeC(O)Et/Et$_2$O
description	prism
colour	colorless
crystal system	orthorhombic
a, Å	30.346(5)
b, Å	47.526(9)
c, Å	12.009(2)
V, Å^3	17319(5)
Z	16
radiation (λ, Å)	Mo Kα (0.710 73)
temperature, K	173(2)
monochromator	graphite
space group	*Fdd*2
crystal size, mm^3	0.40 × 0.25 × 0.20
μ, mm^{-1}	10.882
absorption correction	Psi scans
max. transmission, %	0.91
min. transmission, %	0.63
diffractometer type	Siemens P4
data collection method	ω scans
2θ range, min.−max.	6.1−50.0
hkl limits	$-36 < h < 0$ $-56 < k < 0$ $-14 < l < 14$
reflections measured	7616
independent refelctions	7615
R_{int}	0.007
R1($I > 2\sigma I$), wR2^a	0.0411, 0.0806

^{a} $R1 = \sigma||F_o| - |F_c||/\sigma|F_o|$. $wR2 = [\sigma[w(F_o^2 - F_c^2)^2]/\sigma[w(F_o^2)^2]]^{0.5}$.

Synthesis of (PNP)$_2$[{Au(C$_6$F$_5$)}$_3$(μ_3-S)] (7·PNP). Complex **7·Me$_4$N** (75 mg, 0.06 mmol) and PNPCl (71 mg, 0.12 mmol) were mixed in dichloromethane (8 mL). The resulting suspension was stirred for 1 h and filtered through anhydrous MgSO$_4$ to remove the white precipitate of (Me$_4$N)Cl. Partial evaporation of the filtrate (3 mL) and addition of diethyl ether (20 mL) gave a colorless oil. After decantation of the mother liquor, the oil was dried *in vacuo* to give **7·PNP** as a white solid. Yield: 103 mg, 81%. Λ_M: 187 Ω^{-1} cm^2 mol^{-1}. Mp: 64 °C. IR: ν(Au−S) 362 (w); ν(C$_6$F$_5$) 1494 (vs), 950 (vs), 786 (s) cm^{-1}. NMR [(CD$_3$)$_2$CO, δ]: ^{1}H, 7.5−7.8 (m, PNP$^+$); ^{19}F −165.16 (m, *p*-F), −164.71 (m, *m*-F), −113.89 (m, *o*-F). Anal. Calcd for $C_{90}H_{60}Au_3F_{15}N_2P_4S$: C, 49.11; H, 2.75; N, 1.27; S, 1.46. Found: C, 49.22; H, 2.84; N, 1.48; S, 1.47.

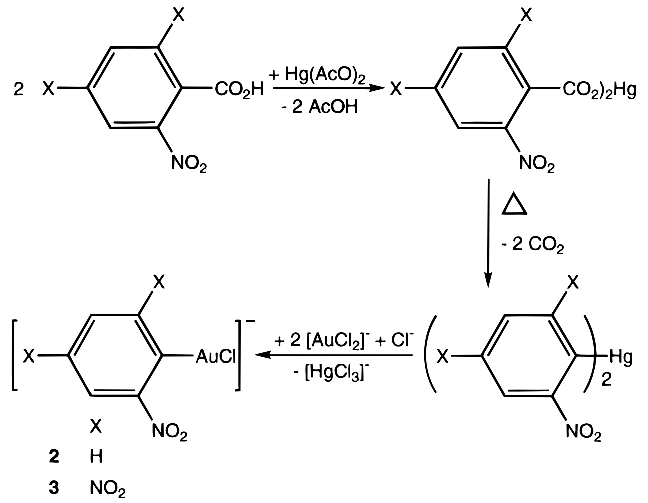
X-Ray Structure Determination of 7·Et$_4$N·0.5MeC(O)Et. Crystal data: $C_{36}H_{44}Au_3F_{15}N_2O_{0.5}S$, M_r = 1420.69, orthorhombic, *Fdd*2, *a* = 30.346(5) Å, *b* = 47.526(9) Å, *c* = 12.009(2) Å, *V* = 17 319 Å^3, *Z* = 16, D_x = 2.179 mg m^{-3}, λ(Mo Kα) = 0.710 73 Å, μ = 10.3 mm^{-1}, *F*(000) = 10 656, *T* = −100 °C. **Data collection and reduction:** Colorless prism 0.45 × 0.25 × 0.2 mm, Siemens P4 diffractometer, ω scans, 7615 independent reflections to 2θ 50°, absorption correction with ψ-scans (transmissions 0.63−0.91). **Structure solution:** direct methods. **Structure refinement:** Anisotropic on F^2 (program SHELXL-93, G. M. Sheldrick, University of Göttingen), H atoms using riding model, 357 restraints to local ring symmetry, and *U* components of neighboring light atoms, MeC(O)Et molecule disordered over a 2-fold axis. Absolute structure with "*x*" refinement [$x = -0.027(11)$[42]]. Final *R*w(F^2) 0.081 for all reflections, 343 parameters, conventional *R*(*F*) 0.041, *S* 0.86, max. $\Delta\rho$ 0.90 e Å^{-3}. See Table 1.

The programs use the neutral atom scattering factors, $\Delta f'$ and $\Delta f''$ and absorption coefficients from *International Tables for Crystallography* (Volume C, 1992; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht; Tables 6.1.1.4 (pp 500−502), 4.2.6.8 (pp 219−222) and 4.2.4.2 (pp 193−199), respectively.

Results and Discussion

Synthesis of the Arylgold(I) Complexes [Au(R)Cl]$^-$. The synthesis of [Hg(C$_6$H$_4$NO$_2$-2)$_2$] has been previously described.[41] However, it involves a tedious multistep procedure starting from *o*-nitroaniline, which in our hands gives yields no higher than 18%. Taking advantage of the procedure described by Kharash for the synthesis of the analogous complex [Hg{C$_6$H$_2$(NO$_2$)$_3$-2,4,6}$_2$],[39] we have prepared [Hg(C$_6$H$_4$NO$_2$-2)$_2$] by decarboxylation of the corresponding mercury(II) *o*-nitrobenzoate (Scheme 1), this procedure being not only much simpler but also allowing a higher yield.

Scheme 1



Complexes Q[Au(C$_6$F$_5$)Cl] [Q = Ph$_3$P=N=PPh$_3$ = PNP (**1·PNP**), Me$_4$N (**1·Me$_4$N**)] have been prepared by displacement of the labile tetrahydrothiophene (tht) ligand present in [Au(C$_6$F$_5$)(tht)] with the corresponding QCl salt, according to the procedure previously described by one of us for the syntheses of the analogous **1·NEt$_4$** and **1·NBu$_4$** salts.[40] The preparation of complexes PNP[Au(R)Cl] [R = C$_6$H$_4$NO$_2$-2 (**2**), C$_6$H$_2$(NO$_2$)$_3$-2,4,6 (**3**)] (Scheme 1) has been achieved by transmetalation reactions from the corresponding [HgR$_2$] and [AuCl$_2$]$^-$ complexes. This method has been previously described by us for the syntheses of the corresponding PhCH$_2$PPh$_3$$^+$ salts (R = C$_6$H$_5$NO$_2$-2,[43] C$_6$H$_2$(NO$_2$)$_3$-2,4,6,[44] C$_6$F$_5$[45]).

Reactions of [Au(R)Cl]$^-$ Complexes with SH$_2$. We have studied the reactions of H$_2$S with complexes [Au(R)Cl]$^-$ [R = C$_6$F$_5$ (**1**), C$_6$H$_4$NO$_2$-2 (**2**), C$_6$H$_2$(NO$_2$)$_3$-2,4,6 (**3**)] containing various cations in attempts to obtain single crystals of the products. However, bubbling H$_2$S through solutions of Q[Au(R)Cl] complexes in a mixture of dichloromethane or acetone and diethylamine gives complexes Q[Au(R)(SH)] [R = C$_6$F$_5$ (**4·PNP**, **4·Bu$_4$N**, **4·Et$_4$N**), C$_6$H$_4$NO$_2$-2 (**5**), C$_6$H$_2$(NO$_2$)$_3$-2,4,6 (**6**)] or Q$_2$[{Au(C$_6$F$_5$)}$_3$(μ_3-S)] (**7·Me$_4$N**, **7·Et$_4$N**) depending on the reaction conditions and, to our surprise, also on Q. Thus, whereas complexes containing the PNP or Bu$_4$N cations lead always to hydrosulfido complexes **5**, **6**, **4·PNP**, **4·Bu$_4$N**, complex **1·Me$_4$N** gives always the sulfido complex **7·Me$_4$N**. When the cation is Et$_4$N, the product obtained is **4·Et$_4$N** or **7·Et$_4$N**, depending on the reaction conditions.

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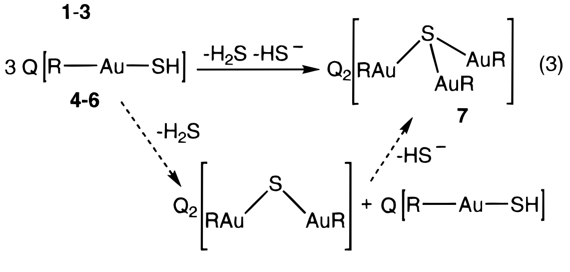
Scheme 2

$$H_2S + Et_2NH \longrightarrow [Et_2NH_2]^+ + HS^- \quad (1)$$

$$\underset{\mathbf{1\text{-}3}}{Q[Au(R)Cl]} + HS^- \longrightarrow Cl^- + Q[Au(R)(SH)] \quad (2)$$



	R	Q
1	C_6F_5	PNP, Bu_4N, Et_4N, Me_4N
2	$C_6H_4NO_2$-2	PNP
3	$C_6H_2(NO_2)_3$-2,4,6	PNP
4	C_6F_5	PNP, Bu_4N, Et_4N
5	$C_6H_4NO_2$-2	PNP
6	$C_6H_2(NO_2)_3$-2,4,6	PNP
7	C_6F_5	PNP, Bu_4N, Et_4N, Me_4N

PNP = $(PPh_3)_2N$

For the pentafluorophenyl complexes **4**, addition of diethyl ether to the resulting solutions causes selective precipitation of $(Et_2NH_2)Cl$, which is removed by filtration while $[Au(C_6F_5)(SH)]^-$ complexes remain in solution and are isolated by partial evaporation of the solvent (**4·PNP**) or addition of *n*-pentane (**4·Bu₄N, 4·Et₄N**). The synthesis and isolation of **4·Et₄N** must be rapid because it is rather unstable, even in the solid state, undergoing H_2S evolution. It was first obtained (33% yield) in a gram-scale reaction meant to prepare complex **7·Et₄N.** In the synthesis of complexes **5** and **6**, addition of diethyl ether causes the precipitation of these complexes along with $(Et_2NH_2)Cl$. These mixtures can be freed from the ammonium salt by washing with water. When Et_2NH is added to a yellow solution of $PNP[Au\{C_6H_2(NO_2)_3\text{-}2,4,6\}Cl]$, the solution color changes to red, probably associated with the presence of a new species that we have not been able to characterize. After a few minutes of bubbling H_2S through this red solution, the color turns to a bright orange. At this point immediate addition of diethyl ether is required to precipitate complex **6**. If the addition of diethyl ether is delayed, the color of the solution changes back to red and then addition of diethyl ether causes the precipitation of a mixture of unidentified products that does not contain **6** (by NMR).

Reaction Pathway. It is reasonable to assume that reactions 1 and 2 in Scheme 2 are common steps when bubbling H_2S through solutions containing Et_2NH and $Q[Au(R)Cl]$ complexes. When R = C_6F_5, the equilibrium 3 is displaced more or less to the right and is established more or less quickly, depending on the nature of Q. The major influence of the cation on this equilibrium is surprising. Thus, we have never observed the formation of trinuclear complexes **7** when starting from **1·PNP** or **1·Bu₄N**. We could obtain no evidence for the formation of the intermediate complex $Me_4N[Au(C_6F_5)(SH)]$; however, the existence of the equilibrium 3 is proved for **4·PNP** because if it is dissolved in acetone, the solvent evaporated after 2 h and this procedure repeated 10 times, the resulting mixture contains **7·PNP** in addition of **4·PNP** (by NMR). The reaction of **4·PNP** with Ag_2CO_3 (2:1) giving **7·PNP** and Ag_2S can also be understood using equilibrium 3. Similarly, an acetone solution of **4·Bu₄N** led to a mixture containing **4·Bu₄N** and **7·Bu₄N** and other unidentified products after stirring for 24 h. To prove the existence of **7·PNP** and **7·Bu₄N** in the above-mentioned mixtures, we prepared them independently by reacting **7·Me₄N** with the corresponding chloride salts. Chloroform or acetone solutions of **4·Et₄N** led to a white precipitate of **7·Et₄N** or, respectively, solutions containing **7·Et₄N** (^{19}F NMR).

Properties of $[Au(R)(SH)]^-$ and $[\{Au(C_6F_5)\}_2(\mu_2\text{-}S)]^{2-}$ Complexes. Although in the solid state all $Q[Au(R)(SH)]$ complexes here described smell of H_2S, the PNP salts are stable and can be stored at room temperature for several weeks, after which time a pale yellow color develops. Complex **4·Bu₄N** must be kept at −20 °C, because otherwise it decomposes to give an unidentified yellow oil after 1 day at room temperature. In the solid state, **4·Et₄N** changes into an orange solid after a few days, even when stored at −20 °C. However, when this orange material is dissolved in acetone-d^6, the $^{19}F\{^1H\}$ NMR spectrum shows only the presence of **7·Et₄N**. From the above comments it can be concluded that the stability of the $Q[Au(R)(SH)]$ complexes decreases with the size of the cation.

Given that complexes **4** and **7** are white solids, the yellow or orange materials formed by decomposition of solid complexes **4** could contain the intermediate in the decomposition process **4** → **7** that we assume to be the $Q_2[\{Au(C_6F_5)\}_2(\mu_2\text{-}S)]$ complex (not isolated; see Scheme 2). This complex would decompose rapidly to **7** as shown in the case of **4·Et₄N**. The FAB spectrum of **4·Et₄N** shows the presence of this dinuclear species as the second strongest peak. Consistent with the postulated instability of $Q_2[\{Au(C_6F_5)\}_2(\mu_2\text{-}S)]$ complexes, we have failed in all attempts to prepare them independently. Thus, the reactions of $PNP[Au(C_6F_5)Cl]$ with Li_2S (2:1 in EtOH) gives **7·PNP** plus other unidentified products and that of $PNP[Au(C_6F_5)(SH)]$ with $PNP[Au(C_6F_5)Cl]$ + Tl(acac) (1:1:1 in acetone) gives **7·PNP**, $PNP[Au(C_6F_5)_2]$, and unreacted $PNP[Au(C_6F_5)(SH)]$.

The behavior of complexes $Q[Au(R)Cl]$ contrasts with that of $[AuCl(PR_3)]$ (R = Ph, PhMe-4, PhOMe-4) when they are reacted with H_2S in the presence of diethylamine. In the first case, complexes $Q[Au(R)(SH)]$ and/or $Q_2[\{Au(C_6F_5)\}_3(\mu_3\text{-}S)]$ are obtained and μ_2-S complexes cannot be isolated, whereas in the second case only $[(AuPR_3)_2(\mu_2\text{-}S)]$ complexes are obtained.

We have also failed in all attempts to prepare derivatives of complexes **4** and **7**. Thus, $[Au(C_6F_5)(tht)]$ reacts with **4·PNP** or **7·Et₄N** to give mainly Au_2S and $Q[Au(C_6F_5)_2]$. Complex $[Au(OClO_3)(PPh_3)]$ reacts with **7·Et₄N** (1:1) or (2:1) to give $[Et_4N][Au(C_6F_5)_2]$ + $[Au(C_6F_5)(PPh_3)]$ + Au_2S or, respectively, an unstable product that decomposes into metallic gold. The inability of these hydrosulfido and sulfido complexes to aggregate AuC_6F_5 or $AuPPh_3^+$ units contrasts with the behavior observed in complexes $[(AuPR_3)_n(\mu_n\text{-}S)]^{(n-2)+}$ and with our expectations.

Complex **7·PNP** is obtained when **4·PNP** is reacted with ^tBuNC (1:1 acetone, 29 h) or with acetylene (1.5

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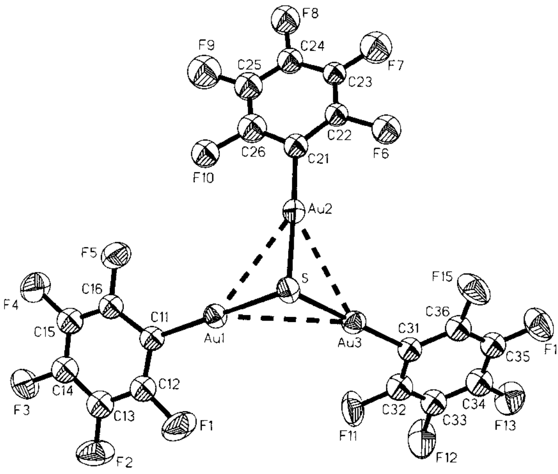

Figure 1. ORTEP plot of **7·Et$_4$N·0.5MeC(O)Et** with the labeling scheme. Selected bond lengths (Å) and angles (°): Au(1)−S, 2.301(4); Au(2)−S, 2.321(4); Au(3)−S, 2.319(4); Au(1)−Au(2), 3.2773(9); Au(1)−Au(3), 3.4772(9); Au(2)−Au(3), 3.1844(9); Au(1)−C(11), 2.017(14); Au(2)−C(21), 2.019(14); Au(3)−C(31), 2.042(13). Au(1)−S−Au(2), 90.31(13); Au(1)−S−Au(3), 97.65(13); Au(2)−S−Au(3), 86.68(12); C(11)−Au(1)−S, 176.6(4); C(21)−Au(2)−S, 177.7(3); C(31)−Au(3)−S, 177.0(3).

bar, CH_2Cl_2, 3 days; along with PNP[Au(C_6F_5)$_2$]). Complex mixtures (mainly containing PNP[Au(C_6F_5)Cl]) are always obtained when **4·PNP** is reacted with Cl_2IPh. The attempted reactions of **7·Et$_4$N** with an excess of CS_2, or yellow HgO or MeI, led to recovery of the starting material along with small amounts of Et$_4$N[Au(C_6F_5)$_2$].

After 3 days in $CDCl_3$ solution, the nitrophenyl complex **5** does not decompose, whereas the trinitrophenyl **6** does so only to a limited extent. The synthesis of complexes Q[Au($C_6H_5NO_2$-2)Cl], with Q = Et$_4$N, Me$_4$N, was attempted following the same method used with the PNP salt, but the products decompose to metallic gold. This is a new example of the influence of the size of the cation on the stability of an anionic complex. Et$_4$N[Au{$C_6H_2(NO_2)_3$-2,4,6}Cl] reacts with H_2S in CH_2Cl_2/Et_2NH to give a mixture of complexes that we could not separate.

Structure of Complexes: Crystal Structure of [NEt$_4$]$_2$[S(AuC$_6$F$_5$)$_3$]·0.5MeC(O)Et (see Figure 1). The sulfur atom is in a distorted trigonal pyramidal environment with short Au···Au contacts and, correspondingly, narrow Au−S−Au angles. Two of these pairs of parameters [Au···Au, 3.1844 (9), 3.2773 (9) Å; Au−S−Au, 86.68(12)°, 90.31(13)°] are in the normal range observed for related gold(I) complexes [(AuPR$_3$)$_3$(μ_3-S)]X (R = Ph, X = PF$_6$,[26] BF$_4$,[27] R = Me, ^{i}Pr, Ph$_2$Me, X = BF$_4$[46]) or [Au{(μ_3-S)(AuPPh$_3$)$_2$}$_2$]$^+$,[47] [Au···Au, 2.990(1)−3.420(1); Au−S−Au, 79.5(1)(6)−95.0(3)], whereas one pair lies outside the range [Au···Au, 3.4772 (9) Å; Au−S−Au, 97.65(13)°]. Therefore, it seems that the aurophilic interactions are similar or slightly weaker in **7·Et$_4$N** than in its homologues containing AuPPh$_3$$^+$ groups, in spite of the differences in charge and size of the groups attached to the gold atom. All of the above values of Au···Au, and Au−S−Au are similar to those calculated for S(AuPH$_3$)$_3$$^+$ using relativistic potentials [Au···Au, 3.05, 3.52 Å; Au−S−Au, 82.3, 98,5°].[48]

The gold atoms are in essentially linear environments with CAuS angles of 176.6(4)°, 177.0(3)°, and 177.7(3)°. The Au(I)−S distances [2.319(4), 2.301(4), and 2.321(4) Å] are similar to those found for the above mentioned complexes [(AuPR$_3$)$_3$(μ_3-S)]X and [Au{(μ_3-S)(AuPPh$_3$)$_2$}$_2$]$^+$ [range 2.303(7)−2.342 (7) Å].[26,27,46,47] The Au(I)−S distances increase with the number of gold atoms attached to sulfur. Thus, for complex **7·Et$_4$N** they are intermediate between those found in [{Au(PPh$_3$)}$_2$(μ^2-S)] [2.161 (5) and 2.157 (5) Å][49] and in [{Au(PPh$_3$)}$_4$(μ^4-S)].[28] This fact can be related to the corresponding decrease in the energy observed for the corresponding ν(Au−S) IR bands (see below).[23]

The solid state IR spectra of the complexes Q[Au(R)(SH)] **4**−**6** are almost identical to those of the corresponding Q[Au(R)Cl)] derivatives used as starting materials, except for the absence of the strong absorption assigned to ν(Au−Cl) [**1·PNP**, 328; **1·Me$_4$N**, 318; Et$_4$N[Au(C_6F_5)Cl],[40] 318; **2**, 314; **3**, 326 cm^{-1}] and the presence of a new medium to weak band in the 330−340 cm^{-1} region (**4·PNP**, 338; **4·Bu$_4$N**, 334; **4·Et$_4$N**, 332; **5**, 330; **6**, 334 cm^{-1}) that can reasonably be assigned to ν(Au−S). The IR-active band in the 2300−2600 cm^{-1} region corresponding to the ν(SH) mode is not observed; its weakness is a common feature in most SH complexes, including PNP[Au(SH)$_2$].[15] The trinuclear complexes Q$_2$[S(AuC$_6$F$_5$)$_3$] (**7**) show bands assignable to ν(Au−S) at 362 (w) (**7·PNP**), 366 (m) and 312 (w) (**7·Me$_4$N**), 360 (m) and 312 (w) (**7·Et$_4$N**) or 364 (m) and 310 (w) (**7·Bu$_4$N**) cm^{-1} in agreement with data reported for some related [(AuL)$_3$(μ_3-S)]$^+$ complexes.[23]

Complexes **1**, **4**, and **7**, bearing the C_6F_5 group, show characteristic strong absorptions,[50] at around 1500, 950, and 790 cm^{-1} and nitrophenyl complexes **5** and **6** those corresponding to ν_{asym}(NO$_2$) absorptions at 1504 (**5**) or 1530, 1514 (**6**) cm^{-1}.[43] The corresponding ν_{sym}(NO$_2$) bands have diagnostic utility because they are sensitive to the coordination mode of the nitrophenyl ligands. They appear at around 1330 cm^{-1} for monocoordinate $O_2NC_6H_4$ ligands and shift to 1260 cm^{-1} when the ligand coordinates through carbon and oxygen. In complexes **5** and **6**, unfortunately, these bands cannot be assigned because they are obscured by the presence of strong bands in the 1320−1220 cm^{-1} region from the PNP cations. Although we have described complexes of Pd,[51] Pt,[52] and Rh[53] with monocoordinate or chelating nitrophenyl ligands, we have always failed in our attempts to coordinate the nitro group to gold(I) or -(III); thus, we assume that the nitrophenyl ligands are monodentate and that complexes **5** and **6** are linear two-coordinate, the most common geometry for gold(I) complexes. PNP salts show bands at around 1580 (m), 1320−1220 (s, br), 544 (s), 527 (s), 491 (s). The expected absorptions from the cations Me$_4$N, Bu$_4$N, and Et$_4$N

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around 950 cm^{-1} coincide with a very strong C_6F_5 band in complexes **4** and **7**.

The ^{1}H-NMR spectra of all the Q[Au(R)(SH)] complexes show the resonance due to the SH protons between −1.09 and −1.34 ppm [R = C_6F_5, Q = PNP (−1.16 ppm), Bu_4N (−1.19 ppm), Et_4N (−1.17 ppm); R = $C_6H_4NO_2$-2 (−1.34 ppm); R = $C_6H_2(NO_2)_3$-2,4,6 (−1.09 ppm)], suggesting that the withdrawing ability of the R group decreases in the sequence $C_6H_2(NO_2)_3$-2,4,6 > C_6F_5 > $C_6H_4NO_2$-2. This signal appears in PNP[Au(SH)$_2$] at $\delta = -1.22$ ppm and in most other hydrosulfido complexes between $\delta = +4$ and $\delta = -4$ ppm.[15] The ^{19}F NMR spectra of complexes **1** ($CDCl_3$), **4** ($CDCl_3$), and **7** (acetone-d^6) show multiplets corresponding to *o*-F (−113.89 to −116.66 ppm) and *m*-F (−163.67 to −165.16 ppm) at similar chemical shifts. The *p*-F multiplet appears in **1** ($CDCl_3$) and **4** ($CDCl_3$) at an intermediate frequency (−162.23 to −163.95 ppm) whereas in **7·PNP** ($CDCl_3$) it is observed at higher field overlapping with the *m*-F multiplet (−165.20 ppm). This overlapping is also observed in the spectra of **7·Bu$_4$N**, **7·Me$_4$N**, and **7·Et$_4$N** (acetone-d^6) while in **7·PNP** (acetone-d^6) the *p*-F multiplet appears at higher field (−165.20 ppm) than that of the *m*-F multiplet (−164.71 ppm).

Conclusions

Two types of complexes Q[Au(R)(SH)] and $Q_2[\{Au(C_6F_5)\}_3(\mu_3\text{-}S)]$ have been isolated by reacting H_2S, Et_2NH, and Q[Au(R)Cl]. The nature of Q and the reaction conditions influence the result. Complexes Q[Au(R)(SH)] are obtained for the larger cations [R = C_6F_5, Q = PNP, Bu_4N; Q = PNP, R = $C_6H_4NO_2$-2, $C_6H_2(NO_2)_3$-2,4,6], whereas $(Me_4N)_2[\{Au(C_6F_5)\}_3(\mu_3\text{-}S)]$ is obtained for the smallest cation. Et_4N[Au(R)(SH)] or $(Et_4N)_2[\{Au(C_6F_5)\}_3(\mu_3\text{-}S)]$ can be obtained for the intermediate cation. All attempts to prepare $(PNP)_2[\{Au(C_6F_5)\}_2(\mu_2\text{-}S)]$ gave $(PNP)_2[\{Au(C_6F_5)\}_3(\mu_3\text{-}S)]$. Other reactions, attempting to use these hydrosulfido or sulfido complexes as ligands to increase the coordination number of the sulfur, failed. Among the possible reasons for this could be the great stability of $[Au(C_6F_5)_2]^-$ or $[Au(C_6F_5)(PPh_3)]$ complexes.

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Supporting Information Available: A listing of both refined and calculated atomic coordinates, all the anisotropic thermal parameters, and full bond lengths and angles for compound **7·Et$_4$N·0.5MeC(O)Et** (7 pages). Ordering information is given on any current masthead page.

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