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Complexes with S-Donor Ligands. 5.[†] Syntheses of the First (Hydrosulfido)- and Anionic Sulfidoorganogold(I) Complexes. Crystal and Molecular Structure of (Et₄N)₂[{Au(C₆F₅)₃(μ₃-S)]·0.5MeC(O)Et

José Vicente,^{*,‡} María-Teresa Chicote,^{*} Pablo González-Herrero, and Claus Grünwald[§]

Grupo de Química Organometálica, Departamento de Química Inorgánica, Facultad de Química, Universidad de Murcia, Apartado 4021, Murcia, 30071 Spain

Peter G. Jones^{*,||}

Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany

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Complexes Q[Au(R)Cl] react with H₂S in the presence of diethylamine to give the corresponding organo(hydrosulfido)gold(I) complexes Q[Au(R)(SH)] [R = C₆F₅, Q = Ph₃P=N=PPh₃ = PNP, Bu₄N; Q = PNP, R = C₆H₄NO₂-2, C₆H₂(NO₂)₃-2,4,6]. Under the same reaction conditions, Me₄N[Au(C₆F₅)Cl] gives the bridging organo(μ₃-sulfido)gold(I) complex (Me₄N)₂[{Au(C₆F₅)₃(μ₃-S)], whereas Et₄N[Au(C₆F₅)Cl] gives Et₄N[Au(C₆F₅)SH] or (Et₄N)₂[{Au(C₆F₅)₃(μ₃-S)] depending on the workup procedure. The crystal structure of Et₄N-[(Au(C₆F₅)₃(μ₃-S)]·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 biological³ or hydrodesulfuration^{4–6} processes, and their use as models in theoretical studies⁷ 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 = Ph₃P=N=PPh₃) 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 [(AuPR₃)_n(μ_n-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 [(Au₂(dppf))₂(μ₂-S)] [dppf = 1,1'-bis(diphenylphosphino)ferrocene] or [(AuPPh₃)₂(μ₂-S)] has allowed the synthesis of the mixed complexes [(Au₂-

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[‡] E-mail: jvs@fcu.um.es.

[§] On leave from the Institut für Anorganische Chemie der Universität Würzburg, Germany.

^{||} E-mail: jones@xray36.anchem.nat.tu-bs.de.

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(dppf)}(AuC₆F₅)(μ₃-S)] or [{Au₂(dppf)}(AuCH₂PPh₃)(μ₃-S)] or [(Au₂L₂){Au(C₆F₅)₃}(μ₄-S)] (L = PPh₃, L₂ = 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, [(AuC₆F₅)₃(μ₃-S)]²⁻, which is, along with [Au₁₂S₈]⁴⁻, [Au₂S₈]²⁻, and [AuS₉]⁻,³⁰ the only anionic sulfidogold(I) complex.

The formation of complexes [(AuPR₃)_n(μ_n-S)]⁽ⁿ⁻²⁾⁺, including the hypercoordinated species with *n* = 5 and 6, is an example of the tendency of AuPR₃⁺ 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(μ_n-S)]²⁻) should be more prone to act as ligands than the cationic complexes [(AuPPh₃)_n(μ_n-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 ¹³C{¹H}] or CFCl₃ (¹⁹F). 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 ¹³C resonances of PNP⁺ (PNP = Ph₃P=N=PPh₃) 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{C₆H₂(NO₂)₃-2,4,6}₂]₂,³⁹ [Au(C₆F₅)(tht)] (tht = tetrahydrothiophene), Et₄N[Au(C₆F₅)Cl], and Bu₄N[Au(C₆F₅)Cl] were prepared as previously described.⁴⁰

Synthesis of [Hg(C₆H₄NO₂-2)₂]. To a suspension of HO₂-CC₆H₄NO₂-2 (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(O₂CC₆H₄NO₂-2)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 C₁₂H₈HgN₂O₄: C, 32.40; H, 1.81; N, 6.23. Found: C, 32.44; H, 1.75; N, 6.28.

Syntheses of Q[Au(C₆F₅)Cl] [Q = PNP (1-PNP), Me₄N (1-Me₄N)]. To a solution of [Au(C₆F₅)(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-Me₄N) h and then filtered through anhydrous MgSO₄. The filtrate was concentrated (3 mL) and diethyl ether (15 mL) added to precipitate 1-PNP or 1-Me₄N 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 cm² mol⁻¹. IR: ν(AuCl) 328 (vs) cm⁻¹. ¹⁹F NMR (CDCl₃, 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 C₄₂H₃₀AuClF₅NP₂: C, 53.78; H, 3.22; N, 1.49. Found: C, 53.94; H, 3.07; N, 1.50. **1-Me₄N:** Yield: 90%. Mp: 186 °C dec Λ_M : 135 Ω⁻¹ cm² mol⁻¹. IR: ν(AuCl) 318 (vs) cm⁻¹. ¹⁹F-NMR (CDCl₃, 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 C₁₀H₁₂AuClF₅N: C, 25.36; H, 2.55; N, 2.96. Found: C, 25.38; H, 2.44; N, 2.91.

Synthesis of PNP[Au(C₆H₄NO₂-2)Cl] (2). A mixture of PNP[AuCl₂] (834 mg, 1.04 mmol), [Hg(C₆H₄NO₂-2)₂] (298 mg, 0.67 mmol), and Me₄NCl (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 MgSO₄ 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 cm² mol⁻¹. IR: ν(AuCl) 314 (m); ν_{asym}(NO₂) 1504 (s) cm⁻¹. NMR (CDCl₃, δ): ¹H, 6.96 (m, 1 H, C₆H₄NO₂-2), 7.17 (m, 1 H, C₆H₄NO₂-2), 7.41–7.69 (m, 31 H, C₆H₄NO₂-2 + PNP), 7.71 (m, 1 H, C₆H₄NO₂-2); ¹³C{¹H} 122.63 (s), 123.16 (s), 130.80 (s), 142.48 (s, C3-C6, C₆H₄NO₂-2), 150.36 (s, C1, C₆H₄NO₂-2), 158.13 (s, C2, C₆H₄NO₂-2). Anal. Calcd for C₄₂H₃₄AuClN₂O₂P₂: C, 56.48; H, 3.84; N, 3.14. Found: C, 56.32; H, 3.81; N, 3.23.

Synthesis of PNP[Au{C₆H₂(NO₂)₃-2,4,6}Cl] (3). A mixture of PNP[AuCl₂] (478 mg, 0.59 mmol), [Hg{C₆H₂(NO₂)₃-2,4,6}₂] (203 mg, 0.33 mmol), and (Me₄N)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 MgSO₄ 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 cm² mol⁻¹. IR: ν(AuCl) 326 (m); ν_{asym}(NO₂) 1530

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(vs), 1518 (vs) cm^{-1} . NMR (CDCl_3 , δ): ^1H , 7.4–7.7 (m, 30 H, PNP), 8.65 (s, 2H, $\text{C}_6\text{H}_2(\text{NO}_2)_{3-2,4,6}$); $^{13}\text{C}\{^1\text{H}\}$ 120.38 (s, C3, $\text{C}_6\text{H}_2(\text{NO}_2)_{3-2,4,6}$), 143.71 (s, C1, $\text{C}_6\text{H}_2(\text{NO}_2)_{3-2,4,6}$), 155.94 and 159.59 (s, C2 and C4, $\text{C}_6\text{H}_2(\text{NO}_2)_{3-2,4,6}$). Anal. Calcd for $\text{C}_{42}\text{H}_{32}\text{AuClN}_4\text{O}_6\text{P}_2$: 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 $(\text{Et}_2\text{NH}_2)\text{Cl}$, 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} : $102\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$. IR: $\nu(\text{Au}-\text{S})$ 338 (m); $\nu(\text{C}_6\text{F}_5)$ 1500 (vs), 948 (vs), 790 (s) cm^{-1} . NMR (CDCl_3 , δ): ^1H -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 $\text{C}_{42}\text{H}_{31}\text{AuF}_5\text{NP}_2\text{S}$: 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 Bu₄N[Au(C_6F_5)(SH)] (4-Bu₄N). H_2S was bubbled through a stirred solution of $\text{Bu}_4\text{N}[\text{Au}(\text{C}_6\text{F}_5)\text{Cl}]$ (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 $(\text{Et}_2\text{NH}_2)\text{Cl}$, which was removed by filtration through anhydrous MgSO_4 . The clear filtrate was concentrated (3 mL) to precipitate **4-Bu₄N** as a white solid. *n*-Pentane (15 mL) was added to complete the precipitation of **4-Bu₄N**, which was filtered off and dried in a nitrogen stream. Yield: 178 mg, 89%. M.p.: 73°C . Λ_{M} : $112\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$. IR: $\nu(\text{Au}-\text{S})$ 334 (m); $\nu(\text{C}_6\text{F}_5)$ 1500 (vs), 950 (vs), 790 (s) cm^{-1} . NMR (CDCl_3 , δ): ^1H -1.19 (s, 1H, SH), 0.99 (t, 12 H, Me, Bu₄N), 1.42 (m, 8 H, CH₂, Bu₄N), 1.67 (m, 8 H, CH₂, Bu₄N), 3.27 (m, 8 H, CH₂, Bu₄N); ^{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 $\text{C}_{22}\text{H}_{37}\text{AuF}_5\text{NS}$: 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 Et₄N[Au(C_6F_5)(SH)] (4-Et₄N). H_2S was bubbled through a stirred solution of $\text{Et}_4\text{N}[\text{Au}(\text{C}_6\text{F}_5)\text{Cl}]$ (151 mg, 0.28 mmol) in a mixture of acetone (5 mL) and diethylamine (0.1 mL) for 3 min. A small amount of $(\text{Et}_2\text{NH}_2)\text{SH}$ formed as a white precipitate. Addition of diethyl ether (25 mL) caused the precipitation of $(\text{Et}_2\text{NH}_2)\text{Cl}$, which was removed along with $(\text{Et}_2\text{NH}_2)\text{SH}$ 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-Et₄N**, which was filtered off and dried in a nitrogen stream. Yield: 81 mg, 80%. Mp: 60°C . IR: $\nu(\text{Au}-\text{S})$ 332 (m); $\nu(\text{C}_6\text{F}_5)$ 1506 (vs), 952 (vs), 792 (s) cm^{-1} . NMR (CDCl_3 , δ): ^1H -1.17 (s, 1 H, SH), 1.38 (tt, Me, 12 H, $^3J_{\text{HH}} = 7.2\text{ Hz}$, $^3J_{\text{HN}} = 2.0\text{ Hz}$), 3.39 (q, 8 H, CH₂); ^{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 $\text{C}_{14}\text{H}_{21}\text{AuF}_5\text{NS}$: 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($\text{C}_6\text{H}_4\text{NO}_2$)(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 ($2 \times 1\text{ mL}$) and diethyl ether ($2 \times 5\text{ mL}$), and air dried to give **5**. Yield: 101 mg, 85%. Mp: 135°C . Λ_{M} : $91\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$. IR: $\nu(\text{AuS})$ 330 (m); $\nu_{\text{asym}}(\text{NO}_2)$ 1504 (s) cm^{-1} . NMR (CDCl_3 , δ): ^1H -1.30 (s, 1H, SH), 6.96 (m, 1H, $\text{C}_6\text{H}_4\text{NO}_2$), 7.22 (m, 1H, $\text{C}_6\text{H}_4\text{NO}_2$), 7.3–7.7 (m, 31H, PNP + $\text{C}_6\text{H}_4\text{NO}_2$), 7.78 (m, 1H, $\text{C}_6\text{H}_4\text{NO}_2$); $^{13}\text{C}\{^1\text{H}\}$ 122.71 (s), 122.95 (s), 130.86 (s), 142.19 (s, C3-C6, $\text{C}_6\text{H}_4\text{NO}_2$), 158.16 (s, C1, $\text{C}_6\text{H}_4\text{NO}_2$), 163.20 (s, C2, $\text{C}_6\text{H}_4\text{NO}_2$). Anal. Calcd for $\text{C}_{42}\text{H}_{35}$ -

$\text{AuN}_2\text{O}_2\text{P}_2\text{S}$: 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($\text{C}_6\text{H}_2(\text{NO}_2)_{3-2,4,6}$)(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 ($2 \times 1\text{ mL}$) and diethyl ether (20 mL), and air dried to give **6**. Yield: 87 mg, 79%. Mp: 116°C . Λ_{M} : $91\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$. IR: $\nu(\text{AuS})$ 334 (m); $\nu_{\text{asym}}(\text{NO}_2)$ 1530 (s), 1514 (s) cm^{-1} . NMR (CDCl_3 , δ): ^1H -1.09 (s, 1 H, SH), 7.4–7.7 (m, 30 H, PNP), 8.70 (s, 2H, $\text{C}_6\text{H}_2(\text{NO}_2)_{3-2,4,6}$). $^{13}\text{C}\{^1\text{H}\}$ 120.65 (s, C3, $\text{C}_6\text{H}_2(\text{NO}_2)_{3-2,4,6}$), 143.42 (s, C1, $\text{C}_6\text{H}_2(\text{NO}_2)_{3-2,4,6}$), 159.27 and 166.58 (s, C2 and C4, $\text{C}_6\text{H}_2(\text{NO}_2)_{3-2,4,6}$). Anal. Calcd for $\text{C}_{42}\text{H}_{33}\text{AuN}_4\text{O}_6\text{P}_2\text{S}$: 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 (Me₄N)₂[{Au(C_6F_5)₃(μ_3 -S)] (7-Me₄N). H_2S was bubbled through a stirred suspension of **1-Me₄N** (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-Me₄N** as a white solid, which was filtered off and air dried. Yield: 98 mg, 66%. Mp: 231°C dec . Λ_{M} : $204\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$. IR: $\nu(\text{Au}-\text{S})$ 366 (m), 312 (w); $\nu(\text{C}_6\text{F}_5)$ 1504 (vs), 950 (vs), 790 (s) cm^{-1} . NMR [$(\text{CD}_3)_2\text{CO}$, δ]: ^1H , 3.45 (t, NMe₄, $^2J_{\text{HN}} = 6.0\text{ Hz}$); ^{19}F -164.35 (m, 3 F, *m-F* + *p-F*), -114.36 (m, 2 F, *o-F*). Anal. Calcd for $\text{C}_{26}\text{H}_{24}\text{Au}_3\text{F}_{15}\text{N}_2\text{S}$: 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 (Et₄N)₂[{Au(C_6F_5)₃(μ_3 -S)] (7-Et₄N). H_2S was bubbled through a stirred solution of $\text{Et}_4\text{N}[\text{Au}(\text{C}_6\text{F}_5)\text{Cl}]$ (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-Et₄N** as a white solid which was filtered off and air dried. Yield: 700 mg, 80%. Mp: 176°C dec . Λ_{M} : $186\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$. IR: $\nu(\text{Au}-\text{S})$ 360 (m), 312 (w); $\nu(\text{C}_6\text{F}_5)$ 1496 (vs), 952 (vs), 790 (s) cm^{-1} . NMR [$(\text{CD}_3)_2\text{CO}$, δ]: ^1H , 1.35 (tt, Me, 3 H, $^3J_{\text{HH}} = 7.2\text{ Hz}$, $^3J_{\text{HN}} = 2.0\text{ Hz}$), 3.47 (q, CH₂, 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 ($[\text{Au}(\text{C}_6\text{F}_5)_2]$, 100), 760 ($[\{\text{Au}(\text{C}_6\text{F}_5)_2\}_2(\mu_2\text{-S})]$, 71), 761 (31), 957 (65), 1124 (M, 42), 1254 (51). Anal. Calcd for $\text{C}_{34}\text{H}_{40}\text{Au}_3\text{F}_{15}\text{N}_2\text{S}$: 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-Et₄N**.

Synthesis of (Bu₄N)₂[{Au(C_6F_5)₃(μ_3 -S)] (7-Bu₄N). Complex **7-Me₄N** (106 mg, 0.08 mmol) and $(\text{Bu}_4\text{N})\text{Cl}$ (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 $(\text{Me}_4\text{N})\text{Cl}$. 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-Bu₄N** as a white solid which was filtered off and dried in a nitrogen stream. Yield: 58 mg, 43%. Mp: 123°C . Λ_{M} : $142\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$. IR: $\nu(\text{Au}-\text{S})$ 364 (m), 310 (w); $\nu(\text{C}_6\text{F}_5)$ 1500 (vs), 950 (vs), 788 (s) cm^{-1} . NMR [$(\text{CD}_3)_2\text{CO}$, δ]: ^1H , 0.94 (t, Me, Bu₄N, 3 H), 1.42 (m, CH₂, Bu₄N, 2 H), 1.79 (m, CH₂, Bu₄N, 2 H), 3.44 (m, CH₂, Bu₄N, 2 H); ^{19}F -164.63 (m, *m-F*, *p-F*), -113.95 (m, *o-F*). Anal. Calcd for $\text{C}_{50}\text{H}_{72}\text{Au}_3\text{F}_{15}\text{N}_2\text{S}$: 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.

Table 1. Crystal Data for 7-Et₄N·0.5MeC(O)Et

molecular formula	C ₃₆ H ₄₄ Au ₃ F ₁₅ N ₂ O _{0.5} S
molecular weight	1420.69
source	liquid diffusion MeC(O)Et/Et ₂ O
description	prism
colour	colorless
crystal system	orthorhombic
<i>a</i> , Å	30.346(5)
<i>b</i> , Å	47.526(9)
<i>c</i> , Å	12.009(2)
<i>V</i> , Å ³	17319(5)
<i>Z</i>	16
radiation (λ, Å)	Mo Kα (0.710 73)
temperature, K	173(2)
monochromator	graphite
space group	<i>Fdd2</i>
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
<i>hkl</i> limits	–36 < <i>h</i> < 0 –56 < <i>k</i> < 0 –14 < <i>l</i> < 14
reflections measured	7616
independent reflections	7615
<i>R</i> _{int}	0.007
<i>R</i> 1 [<i>I</i> > 2σ(<i>I</i>), <i>wR</i> 2 ^a	0.0411, 0.0806

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

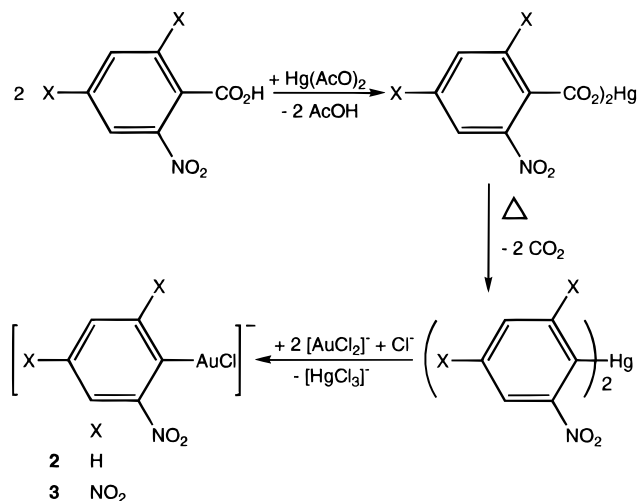
Synthesis of (PNP)₂[Au(C₆F₅)₃(μ₃-S)] (7-PNP). Complex 7-Me₄N (75 mg, 0.06 mmol) and PNPdCl (71 mg, 0.12 mmol) were mixed in dichloromethane (8 mL). The resulting suspension was stirred for 1 h and filtered through anhydrous MgSO₄ to remove the white precipitate of (Me₄N)Cl. Partial evaporation of the 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 cm² mol⁻¹. Mp: 64 °C. IR: ν(Au–S) 362 (w); ν(C₆F₅) 1494 (vs), 950 (vs), 786 (s) cm⁻¹. NMR [(CD₃)₂CO, δ]: ¹H, 7.5–7.8 (m, PNP⁺); ¹⁹F –165.16 (m, *p*-F), –164.71 (m, *m*-F), –113.89 (m, *o*-F). Anal. Calcd for C₉₀H₆₀Au₃F₁₅N₂P₄S: 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-Et₄N·0.5MeC(O)Et. **Crystal data:** C₃₆H₄₄Au₃F₁₅N₂O_{0.5}S, *M_r* = 1420.69, orthorhombic, *Fdd2*, *a* = 30.346(5) Å, *b* = 47.526(9) Å, *c* = 12.009(2) Å, *V* = 17 319 Å³, *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. Δρ 0.90 e Å⁻³. See Table 1.

The programs use the neutral atom scattering factors, Δ⁺ and Δ⁺ 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(C₆H₄NO₂-2)₂] has been

Scheme 1

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{C₆H₂(NO₂)₃-2,4,6}]₂,³⁹ we have prepared [Hg(C₆H₄NO₂-2)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.

Complexes Q[Au(C₆F₅)Cl] [Q = Ph₃P=N=PPh₃ = PNP (1-PNP), Me₄N (1-Me₄N)] have been prepared by displacement of the labile tetrahydrothiophene (tht) ligand present in [Au(C₆F₅)(tht)] with the corresponding QCl salt, according to the procedure previously described by one of us for the syntheses of the analogous 1-NEt₄ and 1-NBu₄ salts.⁴⁰ The preparation of complexes PNP[Au(R)Cl] [R = C₆H₄NO₂-2 (2), C₆H₂(NO₂)₃-2,4,6 (3)] (Scheme 1) has been achieved by transmetalation reactions from the corresponding [HgR₂] and [AuCl₂][–] complexes. This method has been previously described by us for the syntheses of the corresponding PhCH₂PPh₃⁺ salts (R = C₆H₅NO₂-2,⁴³ C₆H₂(NO₂)₃-2,4,6,⁴⁴ C₆F₅⁴⁵).

Reactions of [Au(R)Cl][–] Complexes with SH₂. We have studied the reactions of H₂S with complexes [Au(R)Cl][–] [R = C₆F₅ (1), C₆H₄NO₂-2 (2), C₆H₂(NO₂)₃-2,4,6 (3)] containing various cations in attempts to obtain single crystals of the products. However, bubbling H₂S through solutions of Q[Au(R)Cl] complexes in a mixture of dichloromethane or acetone and diethylamine gives complexes Q[Au(R)(SH)] [R = C₆F₅ (4-PNP, 4-Bu₄N, 4-Et₄N), C₆H₄NO₂-2 (5), C₆H₂(NO₂)₃-2,4,6 (6)] or Q₂[{Au(C₆F₅)₃(μ₃-S)] (7-Me₄N, 7-Et₄N) depending on the reaction conditions and, to our surprise, also on Q. Thus, whereas complexes containing the PNP or Bu₄N cations lead always to hydrosulfido complexes 5, 6, 4-PNP, 4-Bu₄N, complex 1-Me₄N gives always the sulfido complex 7-Me₄N. When the cation is Et₄N, the product obtained is 4-Et₄N or 7-Et₄N, depending on the reaction conditions.

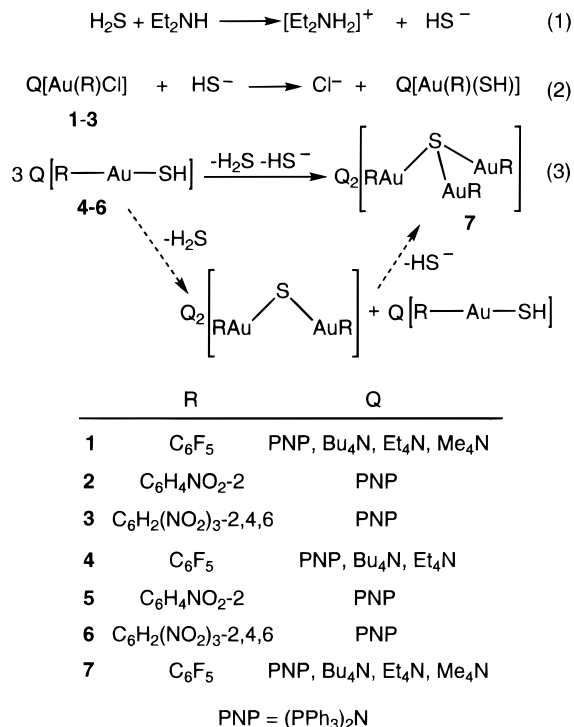
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Scheme 2



For the pentafluorophenyl complexes **4**, addition of diethyl ether to the resulting solutions causes selective precipitation of (Et₂NH₂)Cl, which is removed by filtration while [Au(C₆F₅)(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 H₂S 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 (Et₂NH₂)Cl. These mixtures can be freed from the ammonium salt by washing with water. When Et₂NH is added to a yellow solution of PNP[Au{C₆H₂(NO₂)₃-2,4,6}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 H₂S 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 H₂S through solutions containing Et₂NH and Q[Au(R)Cl] complexes. When R = C₆F₅, 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 Me₄N[Au(C₆F₅)(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 Ag₂CO₃ (2:1) giving **7**·PNP and Ag₂S 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 (¹⁹F NMR).

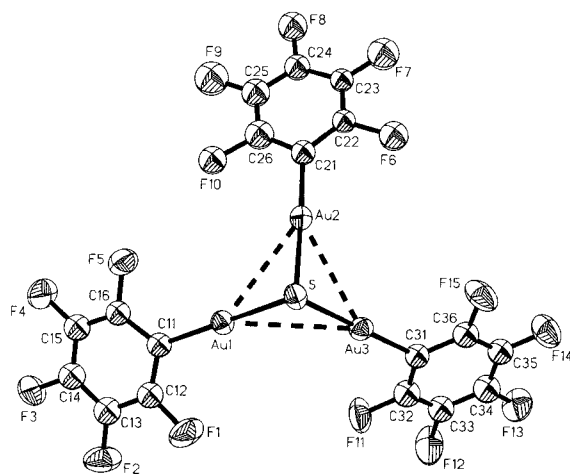
Properties of [Au(R)(SH)][−] and [{Au(C₆F₅)₂(μ₂-S)]^{2−} Complexes. Although in the solid state all Q[Au(R)(SH)] complexes here described smell of H₂S, the PNP salts are stable and can be stored at room temperature for several weeks, after which time a pale yellow color develops. Complex **4**·Bu₄N must 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 ¹⁹F{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 Q₂[{Au(C₆F₅)₂(μ₂-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 Q₂[{Au(C₆F₅)₂(μ₂-S)] complexes, we have failed in all attempts to prepare them independently. Thus, the reactions of PNP[Au(C₆F₅)Cl] with Li₂S (2:1 in EtOH) gives **7**·PNP plus other unidentified products and that of PNP[Au(C₆F₅)(SH)] with PNP[Au(C₆F₅)Cl] + Tl(acac) (1:1:1 in acetone) gives **7**·PNP, PNP[Au(C₆F₅)₂], and unreacted PNP[Au(C₆F₅)(SH)].

The behavior of complexes Q[Au(R)Cl] contrasts with that of [AuCl(PR₃)] (R = Ph, PhMe-4, PhOMe-4) when they are reacted with H₂S in the presence of diethylamine. In the first case, complexes Q[Au(R)(SH)] and/or Q₂[{Au(C₆F₅)₂(μ₂-S)] are obtained and μ₂-S complexes cannot be isolated, whereas in the second case only [(AuPR₃)₂(μ₂-S)] complexes are obtained.

We have also failed in all attempts to prepare derivatives of complexes **4** and **7**. Thus, [Au(C₆F₅)(tht)] reacts with **4**·PNP or **7**·Et₄N to give mainly Au₂S and Q[Au(C₆F₅)₂]. Complex [Au(OCIO₃)(PPh₃)] reacts with **7**·Et₄N (1:1) or (2:1) to give [Et₄N][Au(C₆F₅)₂] + [Au(C₆F₅)(PPh₃)] + Au₂S or, respectively, an unstable product that decomposes into metallic gold. The inability of these hydrosulfido and sulfido complexes to aggregate AuC₆F₅ or AuPPh₃⁺ units contrasts with the behavior observed in complexes [(AuPR₃)_n(μ_n-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



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

The ^1H -NMR spectra of all the $\text{Q}[\text{Au}(\text{R})(\text{SH})]$ complexes show the resonance due to the SH protons between -1.09 and -1.34 ppm [$\text{R} = \text{C}_6\text{F}_5$, $\text{Q} = \text{PNP}$ (-1.16 ppm), Bu_4N (-1.19 ppm), Et_4N (-1.17 ppm); $\text{R} = \text{C}_6\text{H}_4\text{NO}_2-2$ (-1.34 ppm); $\text{R} = \text{C}_6\text{H}_2(\text{NO}_2)_3-2,4,6$ (-1.09 ppm)], suggesting that the withdrawing ability of the R group decreases in the sequence $\text{C}_6\text{H}_2(\text{NO}_2)_3-2,4,6 > \text{C}_6\text{F}_5 > \text{C}_6\text{H}_4\text{NO}_2-2$. This signal appears in $\text{PNP}[\text{Au}(\text{SH})_2]$ 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_4N , **7**· Me_4N , and **7**· Et_4N (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 $\text{Q}[\text{Au}(\text{R})(\text{SH})]$ and $\text{Q}_2[\{\text{Au}(\text{C}_6\text{F}_5)\}_3(\mu_3\text{-S})]$ have been isolated by reacting H_2S , $\text{Et}_2\text{-}$

NH , and $\text{Q}[\text{Au}(\text{R})\text{Cl}]$. The nature of Q and the reaction conditions influence the result. Complexes $\text{Q}[\text{Au}(\text{R})(\text{SH})]$ are obtained for the larger cations [$\text{R} = \text{C}_6\text{F}_5$, $\text{Q} = \text{PNP}$, Bu_4N ; $\text{Q} = \text{PNP}$, $\text{R} = \text{C}_6\text{H}_4\text{NO}_2-2$, $\text{C}_6\text{H}_2(\text{NO}_2)_3-2,4,6$], whereas $(\text{Me}_4\text{N})_2[\{\text{Au}(\text{C}_6\text{F}_5)\}_3(\mu_3\text{-S})]$ is obtained for the smallest cation. $\text{Et}_4\text{N}[\text{Au}(\text{R})(\text{SH})]$ or $(\text{Et}_4\text{N})_2[\{\text{Au}(\text{C}_6\text{F}_5)\}_3(\mu_3\text{-S})]$ can be obtained for the intermediate cation. All attempts to prepare $(\text{PNP})_2[\{\text{Au}(\text{C}_6\text{F}_5)\}_2(\mu_2\text{-S})]$ gave $(\text{PNP})_2[\{\text{Au}(\text{C}_6\text{F}_5)\}_3(\mu_3\text{-S})]$. 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 $[\text{Au}(\text{C}_6\text{F}_5)_2]^-$ or $[\text{Au}(\text{C}_6\text{F}_5)(\text{PPh}_3)]$ 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_4N ·**0.5MeC(O)Et** (7 pages). Ordering information is given on any current masthead page.

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