Complexes with S-Donor Ligands. 7. New 1,1-Ethylenedithiolato Complexes of Thallium(I), Gold(I), and Gold(III): Syntheses, Structure, and Molecular Cubic Hyperpolarizabilities[†]

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β-Diketonato complexes [Tl{CH{C(O)R}$_2$}] or PPN[Au{CH{C(O)R}$_2$}$_2$] [where PPN = (Ph$_3$P)$_2$N] react with an excess of CS$_2$ to give, respectively, [Tl$_2${S$_2$C=C{C(O)R}$_2$}]$_n$ [R = Me (**1**) or Ph (**2**)] or (PPN)$_2$[Au$_2${μ-κ^2-S$_2$C=C{C(O)R}$_2$}$_2$] [R = Me (**3**·PPN) or Ph (**4**·PPN)]. The gold complexes **3**·PPN and **4**·PPN can also be obtained from PPN[AuCl$_2$] and the corresponding thallium 1,1-ethylenedithiolate. PPN[AuCl$_4$] reacts with **1** to give PPN[Au{κ^2-S$_2$C=C{C(O)Me}$_2$}$_2$] (**5**) which, in turn, reacts with PhICl$_2$, Br$_2$ or I$_2$ (1:1) to give PPN[AuX$_2${κ^2-S$_2$C=C{C(O)Me}$_2$}] [X = Cl (**6**), Br (**7**), or I (**8**)]. By reacting **6** with TlCF$_3$SO$_3$ and 1,10-phenanthroline (phen) in 1:2:1 molar ratio, the cationic complex [Au{κ^2-S$_2$C=C{C(O)Me}$_2$}(phen)]CF$_3$SO$_3$ (**9**) can be obtained. The crystal structures of **5** and **6**·0.5Me$_2$CO have been determined. Third-order nonlinearities of **3**·PPN, **3**·Pr$_4$N, **5**, and **6** have been evaluated by the Z-scan technique; an increase in nonlinearity upon extending the π-system is observed, with the anionic dimetallacycle containing two gold and four sulfur atoms in **3** responsible for the largest nonlinearities (approximately 100 × 10^{-36} esu).

Introduction

The interest in gold complexes with S-bonded ligands is mainly due to their potential use in medicine (chrysotherapy). The thiolatogold(I) complexes commercially known as Solganol and Auranofin are active against i.p. P388 leukemia,[2] are highly cytotoxic to some tumor cells,[3] and act as in vitro inhibitors of HIV-1.[4] In addition they are, along with Myocrisin and Allochrysine, among the most efficient antiarthritic drugs.[5−7]

2,2-Disubstituted 1,1-ethylenedithiolate salts, which are obtained from the reaction of methylene active compounds with carbon disulfide in a basic medium,[8,9] are precursors for the syntheses of ketenedithioacetals that, in turn, are versatile intermediates for the synthesis of a diversity of heterocycles.[9−15] In addition, ketene dithioacetals bearing electron-withdrawing substituents behave as push−pull polarized ethylenes and display interesting photophysical properties.[11,16−19]

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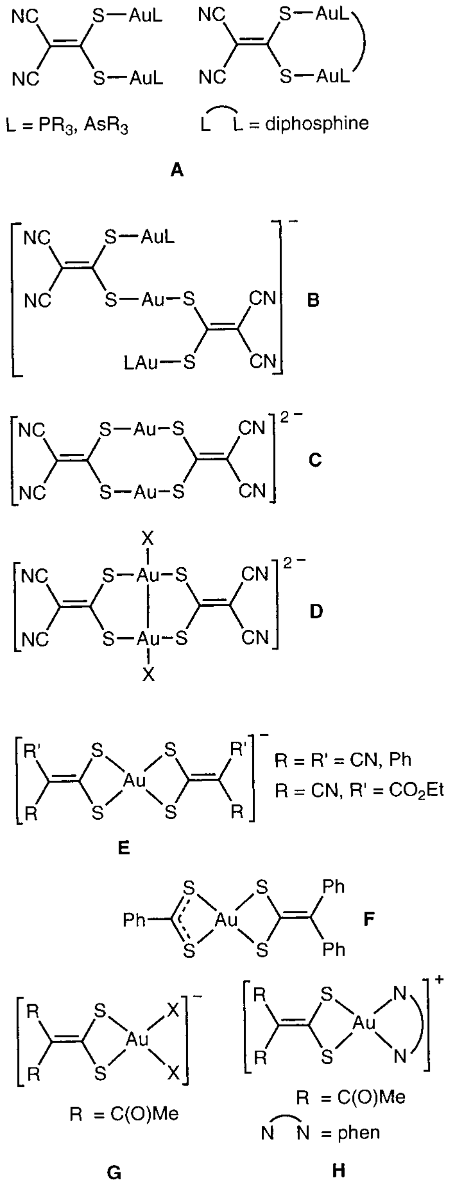
Metal complexes with 1,1-ethylenedithiolato ligands also display interesting properties related to their electronic structure. Thus, platinum(II) complexes with 2-ethoxycarbonyl-2-cyano-1,1-ethylenedithiolato (ecda) and 2,2-dicyano-1,1-ethylenedithiolato (*i*-mnt) are luminescent and their absorption and emission spectra have been studied.[20−29] Gold(I) complexes with *i*-mnt are also luminescent.[30−32] Additionally, 1,1-ethylenedithiolato complexes have received attention due to their ability to stabilize metal ions in high oxidation states, such as $\mathrm{Cu^{III}}$[33,34] or $\mathrm{Fe^{IV}}$,[35] and to form polynuclear complexes with interesting cluster structures.[36−39]

Although a few 1,1-ethylenedithiolato complexes of Cr,[40] Mn,[40] Fe,[35,40−42] Co,[36,41,42] Ir,[43] Ag,[38,39] and Zn[40,44,45] have been reported, the most abundant are those of Ni,[33,34,40,41,46−48] Pd,[40,41,46,48−50] Pt,[20−29,40,41,43,46,48−50] Cu,[33,37,40,41,44] and Au,[31−33,41,51−57] which, in the majority of cases, contain the *i*-mnt ligand. This is also the case for gold complexes. Thus, complexes with gold(I) {$[(\mathrm{AuL})_2(\mu\text{-}\kappa^2\text{-}i\text{-mnt})]$ (L = phosphine or arsine),[32,53] $[\mathrm{Au}_2(\mu\text{-}\kappa^2\text{-}i\text{-mnt})(\mu\text{-LL})]$ (LL = bidentate phosphine) (**A** in Chart 1),[55,57] $[\mathrm{Au}_3(\mu\text{-}\kappa^2\text{-}i\text{-mnt})_2(\mathrm{PEt}_3)_2]^-$ (**B**),[31] and $[\mathrm{Au}_2(\mu\text{-}\kappa^2\text{-}i\text{-mnt})_2]^{2-}$ (**C**),[54,56]}, with gold(II) {$[\mathrm{Au}_2\mathrm{X}_2(\mu\text{-}\kappa^2\text{-}i\text{-mnt})_2]^{2-}$ [X = Cl or Br] (**D**)}, and with gold(III) {$[\mathrm{Au}\{\kappa^2\text{-}(\mathrm{S_2C{=}CRR'})_2\}]^-$ [54] (R = R′ = CN or Ph; R = CN and R′ = $\mathrm{CO_2Et}$) (**E**)[33,51,54] and $[\mathrm{Au}(\kappa^2\text{-}\mathrm{S_2C{=}CPh_2})(\mathrm{S_2CPh})]$[51] (**F**)} have been reported.

Chart 1



Here we describe the synthesis and properties of thallium(I), gold(I), and gold(III) complexes containing the ligands 2,2-diacetyl- or 2,2-dibenzoyl-1,1-ethylenedithiolato. To the best of our knowledge, these are the first 1,1-ethylenedithiolato complexes of thallium, the first 2,2-dibenzoyl-1,1-ethylenedithiolato complexes of any metal, and the first 2,2-diacetyl-

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ethylene-1,1-dithiolato complexes of gold. Some are new types of 1,1-ethylenedithiolato complexes of gold(III), such as $[AuX_2(\kappa^2\text{-}S_2C{=}CR_2)]^-$ [X = Cl, Br, or I; R = C(O)Me] (**G** in Chart 1) and the first cationic 1,1-ethylenedithiolato gold complex, $[Au(\kappa^2\text{-}S_2C{=}CR_2)(phen)]^+$ [phen = 1,10-phenanthroline; R = C(O)Me] (**H**). 2,2-Diacetyl-1,1-ethylenedithiolato complexes of Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, and Cd^{II} have been reported, but their nature was only established by elemental analysis.[58]

Apart from a few 1,1-ethylenedithiolato complexes of Pt(II) and Ir(III) obtained by oxidative addition of $\{(CF_3)_2C{=}CS_2\}_2$ on Pt(0) or Ir(I) derivatives,[43] all the 1,1-ethylenedithiolato complexes previously reported have been prepared by use of the corresponding alkali metal salts. In this paper, we report two alternative syntheses: the direct reaction of CS_2 with the metal-substituted methylene active compound (acetylacetone or dibenzoylmethane in our case) and the use of a 1,1-ethylenedithiolato thallium complex.

The nonlinear optical (NLO) properties of both organic molecules and inorganic complexes have been of intense recent interest.[59] While structure−NLO activity studies for second-order properties have met with much success, much less is known of how to design efficient third-order NLO materials. Recently, some of us found that third-order responses for 14-valence electron gold acetylide complexes were very high,[60] and significantly higher than those of analogous 18-valence electron ruthenium[61,62] or nickel complexes,[63] the opposite trend to that observed for second-order properties.[61−64] This unexpected result encouraged us to widen the scope of our NLO studies to embrace other gold complexes, and we report herein third-order NLO data for some of the gold dithiolate complexes prepared in the current study.

Some of these results have been the subject of a preliminary communication.[65]

Experimental Section

Infrared spectra were recorded in the range 4000−200 cm^{-1} on a Perkin-Elmer 16F PC FT-IR spectrophotometer with Nujol mulls between polyethylene sheets. Conductivities were measured 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. ^1H and ^{13}C NMR spectra were recorded on a Varian Unity 300 spectrometer. Chemical shifts are referred to tetramethylsilane (TMS). The ^{13}C resonances of PPN [PPN = $(Ph_3P)_2N$] appear, with little variations, at δ 127 (m, *i*-C), 130 (m, *o*-C), 132 (m, *m*-C), and 134 (s, *p*-C) in $CDCl_3$ and are not given below. Because of insufficient solubility, the NMR spectra of the thallium complexes **1** and **2** could not be measured.

X-ray Structure Determinations. Yellow prisms of **5** or **6**·$0.5Me_2CO$ were mounted on glass fibers in inert oil and transferred to the cold gas stream of the diffractometer. For **5**: Stoe STADI-4 diffractometer, ω/θ scans, cell constants from $\pm\omega$ values of 64 reflections in the range 2θ 20−23°. For **6**·$0.5Me_2CO$: Siemens P4 diffractometer, ω scans, cell constants from setting angles of 64 reflections in the range 2θ 7−25°. Structures were solved by the heavy atom method and refined anisotropically on F^2 with the program SHELXL-93 (G. M. Sheldrick, University of Göttingen, Germany). A system of restraints was applied to local ring symmetry and displacement parameters of light atoms. Hydrogen atoms were included by using a riding model or rigid methyl groups. Solvent H in **6**·$0.5Me_2CO$ were not located.

Crystallographic data for **5** and **6**·$0.5Me_2CO$ have been deposited at the Cambridge Crystallographic Data Centre under deposition numbers 182/591 and 113235, respectively. The structure of **5** has been previously communicated.[65]

Measurements of cubic hyperpolarizabilities of complexes **3**·PPN, **3**·Pr_4N, **5**, and **6** were performed at 800 nm on a system consisting of a Coherent Mira Ar-pumped Ti−sapphire laser generating a mode-locked train of approximately 100 fs pulses and a Ti−sapphire regenerative amplifier pumped with a frequency-doubled Q-switched pulsed YAG laser (Spectra Physics GCR) at 30 Hz and employing chirped pulse amplification. Dichloromethane solutions were examined in a glass cell with a 0.1 cm path length. The Z-scans were recorded at two concentrations for each compound and the real and imaginary parts of the nonlinear phase change were determined by numerical fitting. The real and imaginary parts of the hyperpolarizability of the solute were then calculated by assuming linear concentration dependencies of the nonlinear phase shifts. The nonlinearities and light intensities were calibrated by using Z-scan measurements of a 1 mm thick silica plate for which the nonlinear refractive index $n_2 = 3 \times 10^{-16}$ cm^2 W^{-1} was assumed.

PPN$[AuCl_4]$ was prepared from equimolar amounts of the commercial $Na[AuCl_4]\cdot H_2O$ (SEMPSA) and the corresponding PPNCl salt. $[Tl\{CH\{C(O)Ph\}_2\}]$, PPN$[Au\{CH\{C(O)Ph\}_2\}_2]$, and $Pr_4N[AuCl_2]$ were prepared as described for the analogous [Tl(acac)], PPN$[Au(acac)_2]$, and PPN$[AuCl_2]$ complexes, respectively.[66]

$[Tl_2\{S_2C{=}C\{C(O)Me\}_2\}]_n$ (1). [Tl(acac)] (1.50 g, 4.94 mmol) was suspended in carbon disulfide (25 mL). Immediate reaction occurred to give a yellow-orange precipitate of **1**. The suspension was stirred for 30 min and excess carbon disulfide was pumped off. The resulting solid was stirred with diethyl ether for 40 min, filtered off, and air-dried. Yield: 1.41 g, 98%. Anal. Calcd for $C_6H_6O_2S_2Tl_2$: C, 12.36; H, 1.04; S, 11.00. Found: C, 12.37; H, 0.94; S, 11.45. Mp 220 °C (dec). IR (cm^{-1}): 1650 s, 1644 s, 1562 s, 1556 s, 1376 s, 1268 s, 1194 m, 1048 m, 970 m, 856 s, 782 m, 672 m, 614 m, 578 s, 54 m, 524 m, 466 w, 400 w, 368 w, 302 w, 292 w.

$[Tl_2\{S_2C{=}C\{C(O)Ph\}_2\}]_n$ (2). $[Tl\{CH\{C(O)Ph\}_2\}]$ (400 mg, 0.93 mmol) was suspended in carbon disulfide (5 mL). A deep red solution was obtained, which was stirred for 30 min. Addition of diethyl ether (35 mL) led to the precipitation of **2** as an orange solid, which was filtered off, washed with diethyl ether (20 mL), and air-dried. Yield: 325 mg, 98%. Anal. Calcd for $C_{16}H_{10}O_2S_2Tl_2$: C, 27.18; H, 1.43; S, 9.07. Found: C, 27.09; H, 1.32; S, 9.33. Mp 110 °C. IR (cm^{-1}): 1632 m, 1592 m, 1574 m, 1300−1400 s, 1236 s, 1176 m, 1140 m, 1074 m, 1012 m, 930 m, 834 m, 800 m, 786 m, 704 m, 692 m, 664 m, 604 m, 530 m, 260 w.

$(PPN)_2[Au_2\{\mu\text{-}\kappa^2\text{-}S_2C{=}C\{C(O)Me\}_2\}_2]$ (3·PPN): Method A. Carbon disulfide (4 mL) was added to a colorless solution of PPN$[Au(acac)_2]$ (820 mg, 0.88 mmol) in acetone (50 mL). The resulting yellowish solution, which turned orange within a few minutes, was stirred for 1 h. Evaporation of the solvent to ca. 4 mL led to the precipitation of **3**·PPN as a yellow microcrystalline solid that was filtered off, washed with acetone (2 mL) and diethyl ether (8 mL), and air-dried. Yield: 746 mg, 93%.

Method B. To a solution of PPN$[AuCl_2]$ (120 mg, 0.15 mmol) in acetone (25 mL) was added compound **1** (87 mg, 0.15 mmol). The resulting orange suspension was stirred for 16 h and filtered through Celite to remove the TlCl formed. Upon evaporation of the clear orange

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filtrate (3 mL), a yellow precipitate of **3**·PPN formed, which was filtered off, washed with acetone (2 × 2 mL) and diethyl ether (4 mL), and air-dried. Yield: 80 mg, 59%. Anal. Calcd for $C_{84}H_{72}Au_2N_2O_4P_4S_4$: C, 55.45; H, 3.99; N, 1.54; S, 7.05. Found: C, 55.52; H, 4.02; N, 1.57; S, 7.19. Mp 179 °C. IR (cm^{-1}): 1698 s, 1678 s, 1580 vs, 1184 s, 868 m, 626 m, 350 w. NMR ($CDCl_3$, δ): ^1H, 2.43 (s, 12 H, Me), 7.3−7.7 (m, 60 H, PPN); ^{13}C, 32.10 (Me), 140.83 (C2), 184.39 (C1), 199.91 (CO).

$(Pr_4N)_2[Au_2\{\mu\text{-}\kappa^2\text{-}S_2C{=}C\{C(O)Me\}_2\}_2]$ (3·Pr_4N). To a suspension of [Tl(acac)] (1.28 g, 4.22 mmol) in dichloromethane (25 mL) was added $Pr_4N[AuCl_2]$ (911 mg, 2.01 mmol). The resulting white suspension was stirred for 20 min and filtered through Celite to remove the precipitate of TlCl. The clear filtrate was evaporated to dryness and the remaining residue was dissolved in acetone (50 mL). Carbon disulfide (6 mL) was then added. An orange color developed immediately. The solution was stirred for 1 h and filtered through Celite to remove insoluble impurities. Partial evaporation of the solvent (4 mL) led to the precipitation of **3**·Pr_4N as a yellow solid, which was filtered off, washed with acetone (2 × 3 mL) and diethyl ether (10 mL), and air-dried. Yield: 583 mg, 52%. Anal. Calcd for $C_{36}H_{68}Au_2N_2O_4S_4$: C, 38.78; H, 6.15; N, 2.51; S, 11.50. Found: C, 38.46; H, 6.26; N, 2.45; S, 11.58. Mp 147 °C. Λ_M (acetone, 4.8×10^{-4} M) 124 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): 1692 vs, 1564 vs, 1556 vs, 1292 vs, 1182 s, 1102 m, 1052 m, 996 s, 968 s, 924 m, 860 m, 800 m, 762 m, 676 w, 628 m, 564 m, 532 w, 510 m, 432 m, 352 m, 234 w. NMR ($CDCl_3$, δ): ^1H, 1.07 (t, Pr_4N, 24 H), 1.78 (m, Pr_4N, 16 H), 2.41 (s, Me, 12 H), 3.33 (m, Pr_4N, 16 H); ^{13}C, 11.03 (Pr_4N), 15.85 (Pr_4N), 31.97 (Me), 60.50 (Pr_4N), 140.88 (C2), 181.24 (C1), 199.60 (CO).

$(PPN)_2[Au_2\{\mu\text{-}\kappa^2\text{-}S_2C{=}C\{C(O)Ph\}_2\}_2]$ (4). Method A. To a solution of $PPN[AuCl_2]$ (150 mg, 0.19 mmol) in acetone (30 mL) was added [Tl{CH{C(O)Ph}$_2$}] (163 mg, 0.38 mmol). The resulting white suspension was stirred for 20 min and filtered through Celite to remove the precipitate of TlCl. Carbon disulfide (4 mL) was added to the colorless filtrate and the resulting yellowish solution, which turned orange within a few minutes, was stirred for 2 h. Evaporation of the solvent to ca. 8 mL led to the precipitation of **4** as an orange microcrystalline solid, which was filtered off, washed with acetone (6 mL) and diethyl ether (10 mL), and dried in the oven at 60 °C for 24 h. Yield: 168 mg, 87%.

Method B. To a solution of $PPN[AuCl_2]$ (251 mg, 0.31 mmol) in acetone (50 mL) was added compound **2**. The resulting orange suspension was stirred for 40 min and filtered through Celite to remove TlCl. Partial evaporation of the clear orange filtrate (8 mL) led to the precipitation of **4** as an orange solid, which was filtered off, washed with acetone (6 mL) and diethyl ether (12 mL), and dried in the oven at 60 °C for 24 h. Yield: 272 mg, 85%. Anal. Calcd for $C_{104}H_{80}Au_2N_2O_4P_4S_4$: C, 60.41; H, 3.90; N, 1.35; S, 6.20. Found: C, 60.28; H, 3.89; N, 1.39; S, 6.03. Mp 210 °C. IR (cm^{-1}): 1632 m, 1600 m, 1592 m, 1574 m, 842 m, 654 m, 576 w. NMR (DMSO-d_6, δ): ^1H, 7.07−7.13 (m, 8 H, Ph), 7.42−7.66 (m, 68 H, PPN + Ph), 7.79−7.83 (m, 4 H, Ph); ^{13}C, 127.71 (s, Ph), 128.69 (s, Ph), 130.50 (s, Ph), 133.21 (s, *i*-C, Ph), 140.45 (s, C2), 182.67 (s, C1), 193.92 (s, CO).

$PPN[Au\{\kappa^2\text{-}S_2C{=}C\{C(O)Me\}_2\}_2]$ (5). To a solution of $PPN[AuCl_4]$ (520 mg, 0.59 mmol) in dichloromethane (40 mL) was added compound **1** (622 mg, 1.07 mmol). The resulting orange suspension was stirred for 45 min and filtered through Celite to remove TlCl. Partial evaporation of the clear red solution (10 mL) and addition of diethyl ether (30 mL) caused the precipitation of a small amount of a yellow solid (the excess of $PPN[AuCl_4]$), which was removed by filtration. Evaporation of the clear filtrate to ca. 8 mL led to the precipitation of **5** as a gold-yellow microcrystalline solid. Yield: 460 mg, 79%. Anal. Calcd for $C_{48}H_{42}AuNO_4P_2S_4$: C, 53.18; H, 3.91; N, 1.29; S, 11.83. Found: C, 53.11; H, 3.89; N, 1.31; S, 12.01. Mp 143 °C. Λ_M (acetone, 5.3×10^{-4} M) 80 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): 1666 s, 1634 s, 1348 s, 1198 s, 860 w, 618 m, 578 m, 370 w. NMR ($CDCl_3$, δ): ^1H, 2.33 (s, 12 H, Me), 7.3−7.7 (m, 30 H, PPN); ^{13}C, 31.75 (Me), 136.22 (C2), 183.90 (C1), 196.83 (CO).

$PPN[AuCl_2\{\kappa^2\text{-}S_2C{=}C\{C(O)Me\}_2\}]$ (6). To a solution of complex **5** (380 mg, 0.35 mmol) in dichloromethane (40 mL) was added solid $PhICl_2$ (97 mg, 0.35 mmol). An immediate color change from bright yellow to orange-yellow was observed. The solution was stirred for 1.5 h and filtered through Celite. Partial evaporation of the solvent (10 mL) and addition of diethyl ether (40 mL) led to slow precipitation of **6** as a bright yellow microcrystalline solid, which was filtered off, washed with diethyl ether (10 mL), and air-dried. Yield: 312 mg, 91%. Anal. Calcd for $C_{42}H_{36}AuCl_2NO_2P_2S_2$: C, 51.44; H, 3.70; N, 1.43; S, 6.54. Found: C, 51.31; H, 3.69; N, 1.46; S, 6.46. Mp 90 °C (dec). Λ_M (acetone, 5.1×10^{-4} M) 87 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): 1628 m, 1578 m, 616 m, 310 m, 276 m (br). NMR ($CDCl_3$, δ): ^1H, 2.38 (s, 6 H, Me), 7.3−7.7 (m, 30 H, PPN).

$PPN[AuBr_2\{\kappa^2\text{-}S_2C{=}C\{C(O)Me\}_2\}]$ (7). A solution of bromine (16 mg, 0.10 mmol) in dichloromethane (10 mL) was added to a stirred solution of complex **5** (109 mg, 0.10 mmol) in dichloromethane (15 mL). The resulting orange-red solution was stirred for 2 h, after which time the color changed to orange-yellow. Partial evaporation of the solvent (6 mL) and addition of diethyl ether (30 mL) led to the precipitation of **7** as an orange-yellow microcrystalline solid, which was filtered off, washed with diethyl ether (10 mL) and air-dried. Yield: 100 mg, 93%. Anal. Calcd for $C_{42}H_{36}AuBr_2NO_2P_2S_2$: C, 47.16; H, 3.39; N, 1.31; S, 5.99. Found: C, 47.25; H, 3.46; N, 1.21; S, 5.66. Mp 78 °C. Λ_M (acetone, 4.9×10^{-4} M) 95 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): 1628 m, 1574 m, 616 m, 210 m. NMR ($CDCl_3$, δ): ^1H, 2.37 (s, 6 H, Me), 7.3−7.7 (m, 30 H, PPN).

$PPN[AuI_2\{\kappa^2\text{-}S_2C{=}C\{C(O)Me\}_2\}]\cdot0.5Et_2O$ (8). To a solution of complex **5** (108 mg, 0.10 mmol) in dichloromethane (30 mL) was added solid iodine (27 mg, 0.10 mmol). The iodine dissolved in ca. 10 min to give a red solution that was stirred for 5 h and filtered through anhydrous $MgSO_4$ to remove insoluble impurities. The solvent was then evaporated to ca. 6 mL and diethyl ether (30 mL) was added. On storage of the resulting red solution at −20 °C for 18 h, red plates of **8** formed. Yield: 82 mg, 68%. Anal. Calcd for $C_{44}H_{41}AuI_2NO_{2.5}P_2S_2$: C, 44.02; H, 3.44; N, 1.17; S, 5.16. Found: C, 44.09; H, 3.33; N, 1.24; S, 5.11. Mp 81 °C. Λ_M (acetone, 3.1×10^{-4} M) 117 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): 1630 m, 1574 m, 614 w, 604 w, 278 w. NMR ($CDCl_3$, δ, at −50 °C): ^1H, 1.25 (t, 3 H, Me, Et_2O), 2.40 (s, 6 H, Me), 3.51 (q, 2 H, CH_2, Et_2O), 7.5−7.7 (m, 30 H, PPN).

$[Au\{\kappa^2\text{-}S_2C{=}C\{C(O)Me\}_2\}(phen)]CF_3SO_3$ (9). To a solution of complex **6** (98 mg, 0.10 mmol) in acetone (20 mL) were added 1,10-phenanthroline·H_2O (20 mg, 0.10 mmol) and $Tl(CF_3SO_3)$ (71 mg, 0.20 mmol). The resulting yellow suspension was stirred for 45 min. After decantation of the solution, the solid was treated with several portions of acetone (8 × 10 mL) and the extracts combined with the first solution were filtered through Celite to give a clear pale yellow solution. Evaporation of the solvent to ca. 4 mL led to the precipitation of **9** as a pale yellow solid that was filtered off, washed with acetone (2 × 5 mL) and diethyl ether (10 mL), and dried with a nitrogen stream. Yield: 38 mg, 54%. Anal. Calcd for $C_{19}H_{14}AuF_3N_2O_5S_3$: C, 32.58; H, 2.01; N, 4.00; S, 13.73. Found: C, 32.64; H, 1.96; N, 3.99; S, 13.72. Dec pt 177 °C. Λ_M (acetone, 4.1×10^{-4} M) 128 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): 1640 m, 1606 w, 1588 m, 1520 m, 1392 s, 1270 s, 1224 m, 1160 m, 1030 s, 878 w, 854 m, 638 s, 612 w, 572 w, 518 w, 434 w, 316 w. NMR (DMSO-d_6, δ): ^1H, 2.52 (s, 6 H, Me), 8.38 [dd, 2 H, H3 + H8 (phen)], 8.46 [s, 2 H, H5 + H6 (phen)], 9.24 [d, 2 H, H4 + H7 (phen), $^3J_{HH} = 8.4$ Hz], 9.37 [d, 2 H, H2 + H9 (phen), $^3J_{HH} = 5.1$ Hz]; ^{13}C, 31.74 (Me), 143.83 (C2), 183.18 (C1), 194.93 (CO).

Results and Discussion

Synthesis of Thallium(I) Complexes. β-Diketonates [Tl{CH{C(O)R}$_2$}] react with an excess of carbon disulfide to give $[Tl_2\{S_2C{=}C\{C(O)R\}_2\}]_n$ [R = Me (**1**) or Ph (**2**)] that can be isolated in nearly quantitative yields (Scheme 1). The formation of complexes **1** and **2** probably involves nucleophilic attack on the CS_2 molecule by a β-diketonato ligand and subsequent deprotonation of the resulting intermediate dithiocarboxylato complex by a second β-diketonato ligand. Alkaline 1,1-ethylenedithiolates are prepared from methylene active compounds, carbon disulfide, and a base.[67] As far as we are aware, **1** and **2** are the first 1,1-dithiolato complexes of thallium. The

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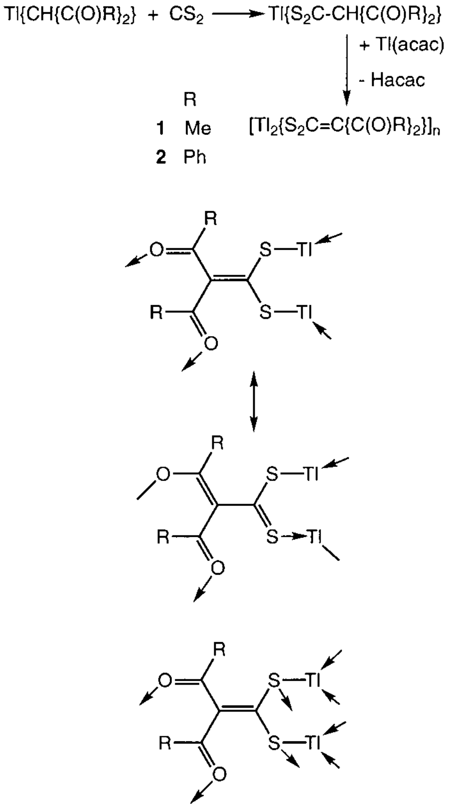
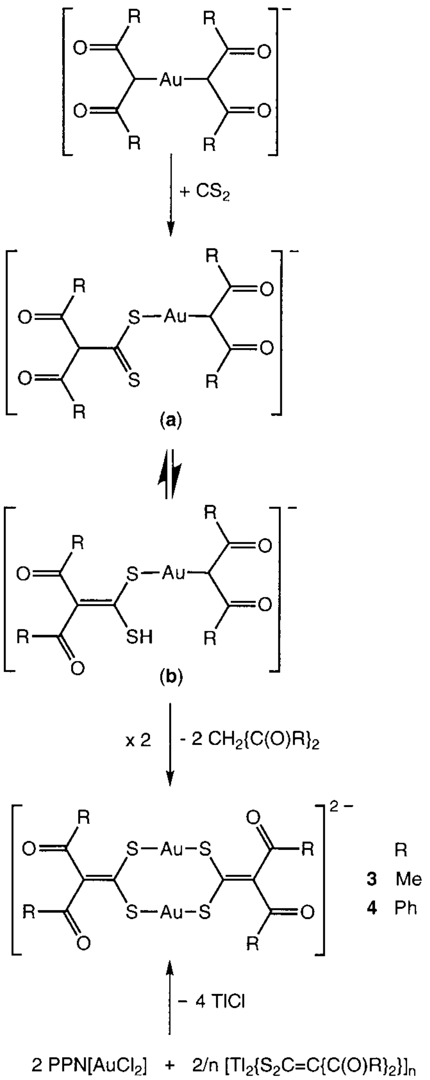
Scheme 1



coordination sphere of the thallium could be completed through κ^4-S-bridging of the ligand and/or by using the oxygen lone pairs leading to a polymeric compound (Scheme 1).

Synthesis of Gold(I) Complexes. Acetylacetonato gold(I) complexes have been extensively used as intermediates in the synthesis of gold(I) complexes by reacting them with phosphonium,[68−76] sulfoxonium,[77] and ammonium[78,79] salts, alkynes,[76,80,81] thiols,[82] H_2S,[83] and, in general, with protic acids.[84−93] Now we report that the β-diketonato complexes PPN-$[Au\{CH\{C(O)R\}_2\}_2]$ (R = Me or Ph) can also react with an excess of carbon disulfide in acetone, at room temperature, to give orange solutions in ca. 1 h. Upon partial evaporation of the solvent, the complexes $(PPN)_2[Au_2\{\mu\text{-}\kappa^2\text{-}S_2C{=}C\{C(O)R\}_2\}_2]$ precipitate as yellow (R = Me, **3**·PPN) or orange (R = Ph, **4**·PPN) solids that can be isolated in ca. 90% yield (Scheme 2). The complex **3**·Pr_4N can be obtained in 52% yield following

Scheme 2



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a similar procedure. In the absence of mechanistic data, we assume that CS_2 inserts into one of the Au−C bonds of $[Au\{CH\{C(O)R\}_2\}_2]^-$ to produce a dithiocarboxylato complex **a** (Scheme 2), which is probably in tautomeric equilibrium with the thioenol form **b**. The remaining β-diketonato ligand would be responsible for intermolecular deprotonation, likely to occur on the SH group, and subsequent dimerization to give complexes **3** or **4**, with concomitant formation of acetylacetone or dibenzoylmethane, respectively.

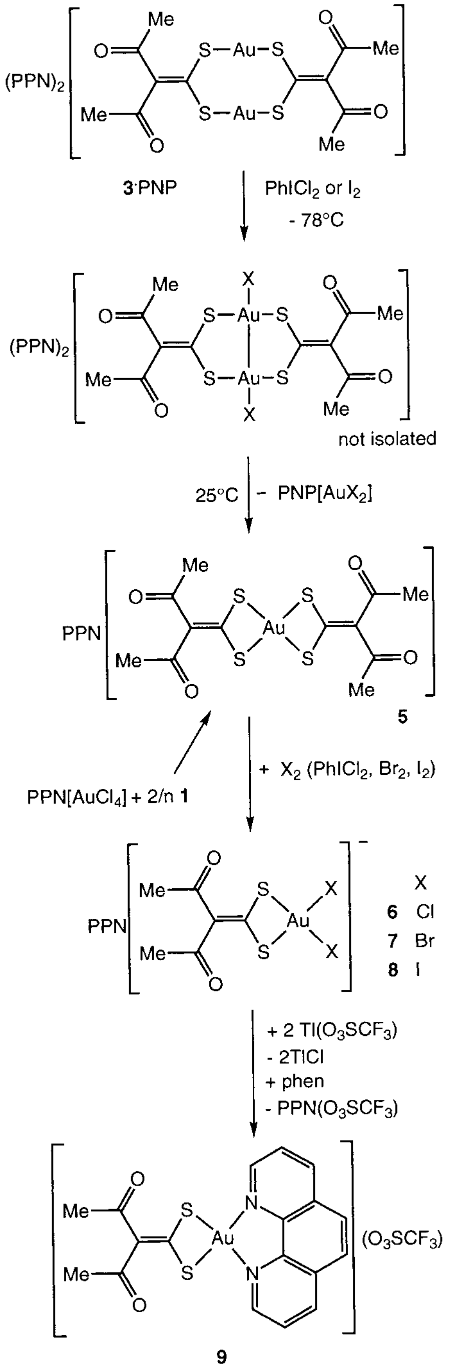
Insertion reactions of CS_2 into transition metal−H, −C, −N, −P, −S, or −Cl bonds are known to produce dithioformiato, dithiocarboxylato, dithiocarbamato, phosphinodithiocarboxylato, trithio- or perthiocarbonato, or chlorodithioformato complexes, respectively.[94,95] However, in the case of gold these reactions have scarcely been studied and thus only two other CS_2 insertion reactions have been described so far, namely, those into the Au−C bond in $[Au(\eta^1\text{-}C_5Me_5)(PR_3)]$ to give dithiocarboxylato complexes $[Au(\kappa^1\text{-}S_2CC_5Me_5)(PR_3)_n]$ ($R = Ph$, $n = 2$; or $R = Pr^i$, $n = 1$)[96] or into an Au−Cl bond of $[Au_2Cl_6]$ to give the chlorodithioformiato complex $[AuCl_2(\kappa^2\text{-}S_2CCl)]$.[97] We have described the insertion of CS_2 into a Au−S (or S−H) bond in $PPN[Au(SH)_2]$ to produce the first trithiocarbonato gold complex, $[Au_2(\mu\text{-}\kappa^2\text{-}CS_3)_2]^{2-}$.[98,99]

Alternatively, complexes **3** or **4** can be prepared by direct reaction of the thallium derivative **1** or **2**, respectively, with $PPN[AuCl_2]$ in 1:1 molar ratio (Scheme 2). However, the attempts to prepare neutral complexes of formulas $[\{Au(PPh_3)\}_2\{\mu\text{-}\kappa^2\text{-}S_2C{=}C\{C(O)R\}_2\}]$ or $[Au_2(\mu\text{-dppm})\{\mu\text{-}\kappa^2\text{-}S_2C{=}C\{C(O)R\}_2\}]$ by reacting **1** or **2** with $[AuCl(PPh_3)]$ or $[(AuCl)_2(\mu\text{-dppm})]$ or $[Au(acac)(PPh_3)]$ with CS_2 have been unsuccessful, as these reactions give mixtures of several products that we could not separate.

Reactions of $(PPN)_2[Au_2\{\mu\text{-}\kappa^2\text{-}S_2C{=}C\{C(O)Me\}_2\}_2]$ (3·PPN) with $PhICl_2$ and I_2. Many binuclear gold(I) complexes, in which bidentate ligands such as dithiocarbamates, dithiophosphates, phosphorus diylides, etc., hold two gold(I) centers at a short distance, undergo oxidative addition of halogens, pseudohalogens, or alkyl halides to give gold(II) complexes containing a metal−metal bond.[100] Complexes **3** and **4** are expected to have dimeric structures with a very short Au···Au distance, as do the related 1,1-dithiolato complexes $[Au_2\{\mu\text{-}\kappa^2\text{-}S_2C{=}C(CN)_2\}_2]^{2-}$,[54] $[Au_2(\mu\text{-}\kappa^2\text{-}CS_3)_2]^{2-}$,[98] and $[Au_2\{\mu\text{-}\kappa^2\text{-}S_2C{=}NCN\}_2]^{2-}$.[101] We carried out the reactions of **3**·PPN with $PhICl_2$ and I_2 to explore the possibility of obtaining gold(II) complexes.

The reaction of **3**·PPN with 1 equiv of $PhICl_2$ in dichloromethane at −78 °C gives a dark green solution that presumably contains the desired gold(II) complex $(PPN)_2[Au_2Cl_2\{\mu\text{-}\kappa^2\text{-}S_2C{=}C\{C(O)Me\}_2\}_2]$. However, it is unstable above −20 °C and disproportionates to the gold(III) complex $PPN[Au\{\kappa^2\text{-}S_2C{=}C\{C(O)Me\}_2\}_2]$ (**5**) and $PPN[AuCl_2]$ (Scheme 3). Small amounts of the heteroleptic complex $PPN[AuCl_2\{\kappa^2\text{-}S_2C{=}C\{C(O)Me\}_2\}]$ (**6**) are also produced in this reaction, probably because of the oxidation of **5** by unreacted $PhICl_2$ (see below). Addition of diethyl ether to the reaction mixture in CH_2Cl_2 causes the selective precipitation of $PPN[AuCl_2]$, which can thus be separated by filtration. Complexes **5** and **6** crystallize on evaporation of the filtrate and cannot be easily separated. The preparations of pure samples of **5** and **6** are described below. Under the same reaction conditions, complex **3**·PPN reacts with 1 equiv of I_2 in dichloromethane, eventually giving **5** and $PPN[AuI_2]$. These two complexes coprecipitate on addition of diethyl ether, giving an analytically equimolar mixture.

Scheme 3



This result parallels the reported reactions of $(Bu_4N)_2[Au_2\{\mu\text{-}\kappa^2\text{-}S_2C{=}C(CN)_2\}_2]$ with $PhICl_2$ and Br_2 at low temperature to give the corresponding dinuclear gold(II) complexes $(Bu_4N)_2[Au_2X_2\{\mu\text{-}\kappa^2\text{-}S_2C{=}C(CN)_2\}_2]$, which, in turn, disproportionate to $Bu_4N[Au\{\kappa^2\text{-}S_2C{=}C(CN)_2\}_2]$ and $Bu_4N[AuX_2]$ at room temperature, although in this case the gold(II) complexes are stable enough to be isolated.[54] We have recently described the reactions of the dinuclear trithiocarbonato complex $(PPN)_2[Au_2$-

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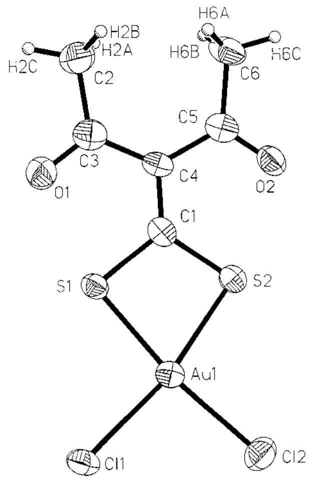

Figure 1. Ellipsoid representation of **6**·0.5Me$_2$CO with 50% probability ellipsoids and the labeling scheme. Selected bond lengths (in angstroms): Au(1)−Cl(1) 2.3662(13), 2.3491(13); Au(1)−Cl(2) 2.3626(14), 2.3542(14); Au(1)−S(1) 2.2961(13), 2.2864(12); Au(1)−S(2) 2.2969(12), 2.2951(12); C1−S1 1.736(5), 1.725(4); C1−S2 1.732(5), 1.740(4); C1−C4 1.374(6), 1.375(6). Selected bond angles (in degrees): S(1)−Au(1)−S(2), 74.10(4), 74.14(4); S(1)−Au(1)−Cl(1) 93.65(5), 95.06(5); Cl(1)−Au(1)−Cl(2) 95.64(5), 94.44(5); Cl(2)−Au(1)−S(2) 96.64(5), 96.32(5); C(4)−C(1)−S(1) 126.04(4), 127.7(3); C(4)−C(1)−S(2) 128.1(4), 126.5(3).

(μ-κ^2-CS$_3$)$_2$] with PhICl$_2$ or I$_2$ to give PPN[Au(κ^2-CS$_3$)$_2$] and PPN[AuX$_2$] (X = Cl or I).[99]

Synthesis of Gold(III) Complexes. Complex **5** is best prepared by reacting PPN[AuCl$_4$] with [Tl$_2${S$_2$C═C{C(O)-Me}$_2$}] (**1**) in a 1:2 molar ratio in dichloromethane (Scheme 3). However, it is convenient to use a slight excess of PPN-[AuCl$_4$], which prevents the formation of a brown oil when diethyl ether is added to precipitate complex **5**. Attempts to prepare the analogous PPN[Au{κ^2-S$_2$C═C{C(O)Ph}$_2$}$_2$] by reacting PPN[AuCl$_4$] with [Tl$_2${S$_2$C═C{C(O)Ph}$_2$}]$_n$ (**2**) were unsuccessful; following the same procedure as for the preparation of **5**, this reaction produces a brown viscous oil.

By reacting **5** with 1 equiv of PhICl$_2$, Br$_2$, or I$_2$ in dichloromethane, the complexes PPN[AuX$_2${κ^2-S$_2$C═C{C(O)-Me}$_2$}] [X = Cl (**6**), Br (**7**), or I (**8**)] are obtained in quantitative (**6**, **7**) or moderate (**8**) yields. The halogens oxidize one of the 2,2-diacetyl-1,1-ethylenedithiolato ligands in **5**, probably to dimeric or oligomeric species containing S−S bonds; we were not able to identify these species. The created vacancies are then occupied by the halide ligands. We have previously reported the halogen oxidation of one of the trithiocarbonato ligands in [Au(κ^2-CS$_3$)$_2$]$^-$ to give [AuX$_2$(κ^2-CS$_3$)]$^-$.[99] Complexes **6**−**8** are stable in the solid state but decompose in solution in a few hours. The cationic complex [Au{κ^2-S$_2$C═C{C(O)Me}$_2$}-(phen)]CF$_3$SO$_3$ (**9**) can be obtained by reacting **6** with TlCF$_3$SO$_3$ and 1,10-phenanthroline in a 1:2:1 molar ratio in acetone.

Structure of Complexes: Crystal structures of PPN[Au-{κ^2-S$_2$C═C{C(O)Me}$_2$}$_2$] (5) and PPN[AuCl$_2${κ^2-S$_2$C═C-{C(O)Me}$_2$}]·0.5Me$_2$CO (6·0.5Me$_2$CO). The crystals suitable for a X-ray analysis were obtained by slow diffusion of diethyl ether into acetone solutions of **5** or **6**, respectively. The structure of **5** has been reported preliminarily.[65] Here we will compare it with that of **6** (Figure 1 and Table 1). The asymmetric unit of **5** contains one cation and two half-anions, whereas that of **6** contains two entire anions and cations and one molecule of acetone.

In complex **5** both anions show almost identical centrosymmetric [Au{κ^2-S$_2$C═C{C(O)Me}$_2$}$_2$] *E,Z*-conformation, whereas in **6**·0.5Me$_2$CO, the anions display very similar features with the 2,2-diacetyl-1,1-ethylenedithiolato ligands in the *Z,Z* conformation. In both complexes the gold atoms are in square-planar environments distorted by the small bite of the 2,2-diacetyl-1,1-ethylenedithiolato ligand, the angles S−Au−S being only 74.16(4)° or 74.46(4)° in **5** and 74.10(4)° or 74.14(4)° in **6**·0.5Me$_2$CO. Therefore, the S(2)−Au(1)−S(1A) angles in **5** [105.84(4)°, 105.54(4)°] or the Cl(1)−Au(1)−Cl(2), Cl(1)−Au-(1)-S(1), and Cl(2)−Au(1)−S(2) angles in **6**·0.5Me$_2$CO [95.64-(5)°, 94.44(5)°; 93.65(5)°, 95.06(5)°; and 96.64(5)°, 96.32(5)°, respectively] are wider than the ideal value of 90°.

In complex **5** the Au(1), S(1), S(2), C(1), and C(2) atoms are coplanar (mean deviation 0.054 and 0.044 Å) with both acetyl groups twisted out of this plane, one of them considerably (torsion angle 55.0°, 48.1°), the other one only slightly (torsion angle 8.7°, 12.9°). In complex **6**·0.5Me$_2$CO the Cl, Au, and S atoms are essentially coplanar (mean deviation 0.027, 0.010 Å) as previously found in PPN[AuCl$_2$(κ^2-CS$_3$)][99] and [AuCl$_2$(κ^2-S$_2$CCl)].[97] The whole 2,2-diacetyl-1,1-ethylenedithiolato ligand is also practically planar (mean deviation 0.050, 0.055 Å), its plane deviating only very slightly from that of the AuCl$_2$S$_2$ moiety (interplanar angle 8.5, 2.9°).

The C(1)−C(4) bond distance in **6**·0.5Me$_2$CO [1.374(6), 1.375(6) Å] is close to the higher limit of the range found for C(sp^2)═C(sp^2) double bonds (1.294−1.392 Å)[102] and slightly longer than those found in complex **5** [1.353(6) or 1.365(4) Å],[65] the 1,1-ethylenedithiolato complexes K[Cu(ded)$_2$] [where ded = (EtO$_2$C)$_2$C═CS$_2$$^{2-}$] and (BzPh$_3$P)$_2$[Ni(ded)$_2$] [1.32(2) and 1.367(6) Å, respectively],[34] or the ketene dithioacetal (MeS)$_2$C═C{C(O)Me}$_2$ [1.351(5) Å].[103] Conjugation of the carbonyl groups with the C═C double bond, favored by the planarity of the ligand, may account for the longer C(1)−C(4) bond distances found in **6**·0.5Me$_2$CO.

The Au−S(1) and Au−S(2) bond distances in **5** [2.3234-(13), 2.3375(13); 2.3479(12), 2.3217(12) Å], are longer than the homologous values in **6**·0.5Me$_2$CO [2.2961(13), 2.2864-(12); 2.2969(12), 2.2951(12) Å]. The higher electronegativity of the AuCl$_2$ moiety compared to AuS$_2$ could enhance the polarizing ability of the gold center, thus strengthening the Au−S bond.

IR Spectra. The solid-state IR spectra of the gold complexes containing the 2,2-diacetyl-1,1-ethylenedithiolato ligand show several bands in the region 1700−1400 cm^{-1} arising from vibration modes that involve C═O and C═C bonds. In some cases, their assignation to ν(C═O) or ν(C═C) may not be accurate since these modes are likely to be coupled, as in several carbonyl-containing *push*−*pull* ethylenes for which vibrational studies have been carried out.[104] However, to simplify the present discussion, we shall use ν(C═O) and ν(C═C) to refer to the bands that appear in the 1700−1400 cm^{-1} region. Additionally, it is reasonable that the bands that appear at higher frequencies largely reflect the strength of the C═O bond, thus providing an indication of the extent of the conjugation within the ligand, which, in turn, could be related to the disposition (coplanar or twisted) of the acetyl groups with respect to the planar S$_2$C═C moiety.

The IR spectrum of **3** shows two (PPN salt) or only one (Pr$_4$N salt) strong ν(C═O) bands at 1698 and 1678 cm^{-1} or at 1692 cm^{-1}, respectively. A strong ν(C═C) band is observed at 1580 (PPN salt) or 1564 cm^{-1} (Pr$_4$N salt). The position of these bands

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Table 1. Crystal Data for Compound 6·0.5 Me_2CO

compd	**6**·0.5 Me_2CO
mol formula	$C_{43.5}H_{39}AuCl_2NO_{2.5}P_2S_2$
mol wt	1009.68
wavelength (Å)	0.710 73
temp (K)	173(2)
cryst size (mm)	0.45 × 0.25 × 0.15
cryst syst	triclinic
space group	$P\bar{1}$
a (Å)	9.8414(14)
b (Å)	17.337(2)
c (Å)	26.086(3)
α (deg)	101.078(10)
β (deg)	98.179(10)
γ (deg)	102.857(10)
volume (Å^3), Z	4178.0(9), 4
ρ(calc) (M g^{-3})	1.605
F(000)	2008
μ (mm^{-1})	3.865
θ range for data collection (deg)	3.04−25.00
limiting indices	$-11 \leq h \leq 11, -19 \leq k \leq 19, -30 \leq l \geq 30$
reflns collected	14 761
indep reflns	14 587 ($R_{int} = 0.0250$)
abs. correction	ψ scans
max and min transm	1.000 and 0.606
refinement method	full matrix least squares on F^2
data/restrs/params	14 587/815/957
goodness-of-fit on F^2	0.898
R1[a]	0.0311
wR2[b]	0.0646
largest diff, peak and hole (eÅ^3)	1.127 and −0.881

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

suggests that conjugation is absent and that probably all acetyl groups are twisted out of the main plane of the molecule.

The IR spectrum of complex **5** shows a pattern very similar to that found for the isostructural complexes $BzPh_3P[M(ded)_2]$ [where ded = $(EtO_2C)_2C{=}CS_2{}^{2-}$] [M = Au(III) or Cu(III)] and $(BzPh_3P)_2[Ni(ded)_2]$. According to the assignment proposed by Coucouvanis,[33,105] the bands at 1666 and 1634 cm^{-1} in the spectrum of **5** correspond to ν(C=O) while that at 1438 cm^{-1} corresponds to ν(C=C). The presence of two ν(C=O) bands in the IR spectra of these complexes has been attributed to the different disposition of the ethoxycarbonyl groups. In fact, the crystal structures of $K[Cu(ded)_2]$ and $(BzPh_3P)_2[Ni(ded)_2]$ show, in common with that of complex **5** (see above), one of the C(O)R groups of each ethylenedithiolato ligand to be twisted out of the plane of the ligand, while the other remains coplanar, thus allowing conjugation.[34]

The IR spectra of complexes **6**−**8** show two medium-intensity bands around 1630 and 1574 cm^{-1} assignable to ν(C=O) modes. For the cationic complex **9** a similar pattern is observed, with two bands at 1640 and 1588 cm^{-1}. Extensive conjugation may account for these low values, and indeed, the crystal structure of **6** (see above) shows totally planar 2,2-diacetyl-1,1-ethylenedithiolato ligands. On the basis of IR data, the 2,2-diacetyl-1,1-ethylenedithiolato ligands in complexes **7**−**9** probably adopt the same conformation. The frequency of the ν(C=C) band is expected to decrease for complexes **6**−**9** and cannot be unequivocally assigned.

Bands corresponding to ν(Au−S) could not be unequivocally assigned, except for complex **5**, for which the IR spectrum shows a weak band at 370 cm^{-1}. This value compares well to that found for the related gold(III) complexes PPN[Au(κ^2-CS_3)$_2$][99] and [Au(κ^2-S_2CNBu_2)$_2$]$^+$[106] (380 cm^{-1} in both cases). The spectrum of the chlorocomplex **6** shows two bands at 310 and 276 cm^{-1} corresponding to the two IR-active ν(Au−Cl) modes. For the analogous bromocomplex **7**, only one of the ν(Au−Br) bands can be observed at 210 cm^{-1}.

NMR Spectra. The 2,2-diacetyl-1,1-ethylenedithiolato complexes (**3**, **5**−**9**) show one singlet resonance for the methyl groups, thus proving their equivalence in solution. In the ^{1}H NMR spectra this resonance is in the narrow range from 2.33 (**5**) to 2.52 (**9**), showing the minimal electronic influence of the remaining ligands or the oxidation state of gold on the distant C(O)Me group. The higher δ value corresponds to the cationic gold(III) complex **9**.

Cubic Hyperpolarizabilities. The third-order NLO responses of a range of inorganic complexes and organic compounds have been investigated recently,[59] but these responses can incorporate both resonant and nonresonant contributions. A major goal of current research is to correlate variations in molecular composition with nonresonant third-order NLO merit, but many studies report data with resonant NLO contributions. For example, the third-order optical nonlinearities of metal 1,2-dithiolenes have been of recent interest,[107] with γ values by third harmonic generation in the range 10^{-33}−10^{-32} esu at both 1064 and 1907 nm. However, metal 1,2-dithiolene complexes are reported to have strong π−π* transitions in the region 700−1400 nm, suggesting that the observed nonlinearities are resonantly enhanced, rendering discussion of structure−property trends somewhat speculative. No third-order NLO data for 1,1-dithiolene complexes are extant, so a study of the current series of complexes is of interest. Importantly, the optical absorption spectra of the 1,1-ethylenedithiolato complexes **3**·PPN, **3**·Pr_4N, **5**, and **6** all show maxima at shorter wavelength than 400 nm,

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Table 2. Linear Optical and Cubic Nonlinear Optical Response Parameters for Complexes **3**·PPN, **3**·Pr_4N, **5**, and **6**[a]

complex	λ (nm) [ϵ (10^4 M^{-1} cm^{-1})]	γ_{800} (10^{-36} esu) real	γ_{800} (10^{-36} esu) imaginary
3·PPN	393 (3.02)	215 ± 20	37 ± 10
3·Pr_4N	390 (3.95)	96 ± 15	44 ± 10
5	356 (6.76)	88 ± 15	6 ± 3
6	313 (2.65)	45 ± 20	3 ± 2

[a] All measurements were made in CH_2Cl_2 solvent. All complexes are optically transparent at 800 nm.

in contrast to the previously reported 1,2-dithiolene complexes, which should minimize resonant contributions and facilitate structure−NLO activity correlations.

Third-order nonlinearities of **3**·PPN, **3**·Pr_4N, **5**, and **6** were evaluated by the Z-scan technique;[108] the results of these measurements are given in Table 2. Relatively high concentrations of these complexes were utilized for the Z-scan measurements. Some errors are introduced in assuming a constant density equal to that of the solvent and a local field factor obtained from the solvent refractive index; these are, however, lower in magnitude than the errors quoted in the tabulated data. The real components of the nonlinearities are positive, and the imaginary components are small, consistent with little contribution from two-photon absorption. It is likely then that the dispersion effect of two-photon states is not contributing significantly to the measured nonlinearities, permitting cautious comment on the effect of structural variation on nonlinear optical merit [it should be emphasized, though, that the presence of imaginary components in the γ values for **3**·PPN, **3**·Pr_4N, **5**, and **6** (associated with nonlinear absorption) suggests that electronic resonance enhancement still exists].

Replacing counterion PPN with Pr_4N in proceeding from **3**·PPN to **3**·Pr_4N leads to a 50% decrease in the real part of γ. It is not likely that **3**·PPN exists as an ion pair in dichloromethane, so the contributions of the cation and anion to the nonlinearity should be additive. As the nonlinearity of Pr_4N is likely to be below the level of detection, this suggests that the cation and anion of **3**·PPN are contributing equally ($\approx 100 \times 10^{-36}$ esu) to the measured γ and that PPN^+ is responsible for approximately 50×10^{-36} esu. Utilizing this benchmark for the contribution of PPN to the measured nonlinearities of **5** and **6** suggests that the contributions of the anions to these nonlinearities is very small (essentially zero for the anion in **6** and approximately 40×10^{-36} esu for the anion in **5**).

Variations in measurement wavelength, laser pulse duration, solvent, and other factors make it very difficult to compare results (in an absolute sense) with those from other laboratories. Data from the present series of complexes are, on average, lower than those we observed previously for donor−acceptor gold acetylide complexes.[60] Of more utility and significance are comparisons within the systematically varied series of complexes in the current study. It is not surprising that extension of the π-system in progressing from **6** to **5** results in an increase in nonlinearity. The structurally unique feature in **3**·PPN and **3**·Pr_4N compared to **5** is the dimetallacycle containing two gold and four sulfur atoms, and it may be this unit with its polarizable electrons that is responsible for the further increase in cubic nonlinearities observed (as mentioned above, the anions in **3** are contributing approximately 100×10^{-36} esu to the nonlinearity). It is significant that no gold···gold interaction is observed in the structures of **5** and **6**·$0.5Me_2CO$, but a short Au···Au interaction is expected in **3**·PPN and **3**·Pr_4N by analogy with the structures of related complexes, e.g., $[Au_2(\mu\text{-}CS_3)_2]^{2-}$.[98,99] To the best of our knowledge, this is the first report of a short Au···Au interaction enhancing γ. Our Z-scan measurements have been carried out on solution samples. There are comparatively few well-characterized examples of Au···Au interactions persisting in solution, a necessary prerequisite from which to make observations similar to our own. However, Au···Au bonding in the solid state is a common motif. The present results suggest that attention should be focused on solid-state gold-containing materials, in which a significant Au···Au interaction has been demonstrated, for third-order nonlinear optics, particularly those with infinite linear chain Au···Au···Au··· interactions.

Conclusions

We have described the first fully characterized 2,2-acetyl- and 2,2-benzoyl-1,1-ethylenedithiolato complexes. As far as we are aware, those of thallium(I) are the first 1,1-ethylenedithiolato complexes of this element. The gold(I) and thallium(I) derivatives **1**−**4** have been obtained in high yields by reacting the corresponding β-diketonates with CS_2. Alternatively, gold(I) complexes **3** and **4** can be obtained by reacting $[AuCl_2]^-$ with the corresponding thallium salt. These represent new syntheses of 1,1-ethylenedithiolato complexes. Gold(III) complexes have also been obtained through different methods. Thus, the homoleptic complex **5** can be obtained by halogen oxidation of the gold(I) complex **3**·PPN or by reacting $[AuCl_4]^-$ with the thallium complex **1**. One of the dithiolato ligands in **5** can be substituted by two halide ligands (Cl, Br, or I) by reacting it with the corresponding halogen. When allowance is made for the contribution of the counterions, the anions in complexes **3** have significantly greater cubic optical nonlinearities, as measured by Z-scan at 800 nm, than do the anions in complexes **5** and **6**, a result we ascribe to the presence in the former complex of a dimetallacycle, which contains two gold and four sulfur atoms and possesses a significant Au···Au interaction.

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Supporting Information Available: One X-ray crystallographic file, in CIF format, for complex **6**·$0.5Me_2CO$, and five tables showing crystal data, atomic coordinates, bond lengths and angles, anisotropic and isotropic displacement parameters, and hydrogen coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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