CS_2 insertion into a gold–carbon bond. First syntheses and characterization of 2,2-diacetylethylene-1,1-dithiolato complexes. Crystal structure of $[N(PPh_3)_2][Au\{\eta^2\text{-}S_2C{=}C(COMe)_2\}_2]$†

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The reaction of $[N(PPh_3)_2][Au(acac)_2]$ (acac = acetylacetonate) with CS_2 gives $[N(PPh_3)_2]_2[Au_2\{\mu^2:\eta^2\text{-}S_2C{=}C(COMe)_2\}_2]$, which reacts with $PhICl_2$ to give $[N(PPh_3)_2][Au\{\eta^2\text{-}S_2C{=}C(COMe)_2\}_2]$, for which the crystal structure is determined; these are the first characterized 2,2-diacetylethylene-1,1-dithiolato complexes of any element.

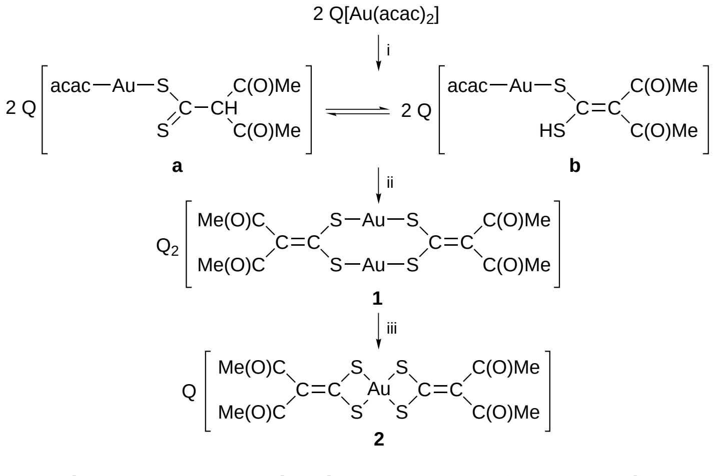
Interest in gold complexes containing S-bonded ligands stems from their potential application in the glass and ceramic industries[1] and, more importantly, in medicine (chrysotherapy).[2] Thiolatogold(I) complexes such as the commercial Myocrisin, Allochrysine, Solganol, or Auranofin, are among the most efficient antiarthritic drugs.[2] In addition, Solganol and Auranofin show *in vitro* inhibitory effects on Human Immunodeficiency Virus 1,[3] high cytotoxicity to tumor cells[4] and activity against i.p. P388 leukaemia.[5]

We have found that CS_2 reacts with $[N(PPh_3)_2][Au(acac)_2]$[6] to give $[N(PPh_3)_2]_2[Au_2\{\mu^2:\eta^2\text{-}S_2C{=}C(COMe)_2\}_2]$ **1** (Scheme 1). As far as we are aware, this is the first fully characterized 2,2-diacetylethylene-1,1-dithiolato complex of any element.

In the absence of any mechanistic data, we assume that the CS_2 inserts into one of the gold–carbon bonds to produce a dithiocarboxylato complex **a** (see Scheme 1), likely to be in tautomeric equilibrium with the ethylene-1,1-dithiolato form **b**, the remaining acac ligand being responsible for intermolecular deprotonation and subsequent dimerization to give **1** with concomitant formation of acetylacetone.

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 perthio-carbonato, or chlorodithioformiato complexes, respectively.[7] 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 $[Au\{\eta^1\text{-}C_5Me_5)(PR_3)]$ complexes to give dithiocarboxylato complexes $[Au\{\eta^1\text{-}S_2CC_5Me_5)(PR_3)_n]$ (R = Ph, n = 2; R = Pr^i, n = 3)[8] or into an Au–Cl bond of $[Au_2Cl_6]$ to give the chlorodithioformate complex $[AuCl_2(\eta^2\text{-}S_2CCl)]$.[9] We have ourselves described the insertion of CS_2 into an Au–S (or S–H) bond in $[N(PPh_3)_2][Au(SH)_2]$ to produce the first trithiocarbonatogold complex.[10] In the reaction of CS_2 with $[Au(C_6F_5)(PPh_2CHPPh_2Me)]$ the complex $[Au^{III}\{PPh_2C(PPh_2Me)CS_2\}_2][Au^{I}(C_6F_5)_2]$, resulting from a carbon–carbon coupling reaction, is obtained.[11]

The reaction of methylene active compounds with CS_2 and $LiNR_2$, NaH,[12] or K_2CO_3,[13] led to the synthesis of the corresponding 2,2-disubstituted ethylene-1,1-dithiolate salts, which were treated *in situ* with MeI to give ketene dithioacetals. In this context acetylacetone has been used to prepare the 2-acetyl-2-oxopropylidene-*S*,*S*-acetal $[(MeS)_2C{=}C\text{-}\{C(O)Me\}_2]$.[13–15] Our synthetic method is, therefore, unprecedented. Ketene dithioacetals are of current interest because the double carbon–carbon bond they present is amenable to both nucleophilic and electrophilic attack.[14] Indeed, they are very versatile starting materials for the synthesis of a wide variety of fused heterocycles,[13,16] polysubstituted pyridines,[17] pyrazoles,[18] *etc.* On the other hand, the interest in ketene dithioacetals with electron-withdrawing substituents stems from some of their physical properties as push–pull polarized ethylenes. Thus, the effect of chiral substituents or hydrogen bonding on second-order non-linearity,[19] the free energy of activation for rotation around the carbon–carbon double



Scheme 1 Q = $[N(PPh_3)_2]$, acac = acetylacetonate. *Reagents and conditions*: i, CS_2 (excess) in acetone, 1 h, room temp; ii, −2 Hacac; iii, + Cl_2IPh − PhI − $Q[AuCl_2]$, CH_2Cl_2, 45 min, room temp.

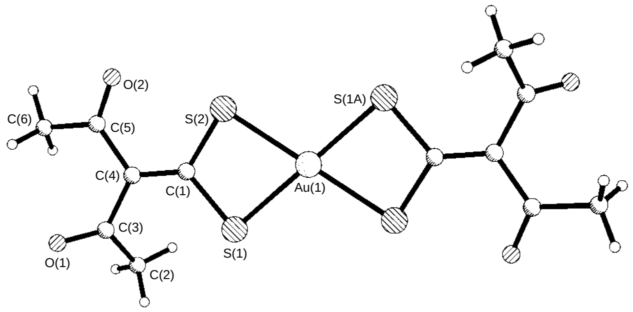


Fig. 1 Structure of one of the two independent anions of **2**. Selected bond lengths (Å) and angles (°): Au(1)–S(1) 2.3234(13), 2.3375(13), Au(1)–S(2) 2.3479(12), 2.3217(12), C(1)–S(1) 1.758(4), 1.748(4), C(1)–S(2) 1.744(4), 1.755(4), C(1)–C(4) 1.353(6), 1.365(6); S(1)–Au(1)–S(2) 74.16(4), 74.46(4), S(2)–Au(1)–S(1A) 105.84(4), 105.54(4), S(1)–C(1)–S(2) 107.0(2), 107.2(2), S(1)–C(1)–C(4) 125.8(3), 126.1(3), S(2)–C(1)–C(4) 127.2(3), 126.8(4).

bond,[15,20] or the influence of the double bond twisting on the position of the IR $\nu_{C=C}$ stretching band[21] or on the photoionization energy[22] have been studied. Our synthesis opens a new access for such studies. The only 2,2-diacetylethylene-1,1-dithiolato complexes (of Mn^{II}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}) mentioned in the literature were prepared from the corresponding sodium salt of the ligand and their composition was only established by elemental analysis, while amperometric and potentiometric titrations were unsuccessful.[23]

Many dinuclear gold(I) complexes are known to undergo oxidative addition reactions with halogens, pseudohalogens or alkyl halides to give gold(II) complexes containing a gold–gold bond.[24] However, when complex **1** is treated with an equimolar amount of Cl_2IPh in dichloromethane a disproportionation reaction takes place, giving $[N(PPh_3)_2][AuCl_2]$ along with the gold(III) complex $[N(PPh_3)_2][Au\{\eta^2\text{-}S_2C{=}C(COMe)_2\}_2]$ **2**. The same behaviour has previously been observed for other dithiolato,[25] dialkyldithiocarbamato,[26] or trithiocarbonato[27] gold(I) complexes.

The isolated complexes **1** and **2** have been fully characterized by C, H, N, S analyses, IR spectroscopy and ^1H and ^{13}C NMR. The X-ray crystal structure of complex **2** (Fig. 1),‖ shows it to crystallize with two independent half-anions and one $[N(PPh_3)_2]$ cation in the asymmetric unit. Both anions show almost identical inversion-symmetric $[Au\{\eta^2\text{-}S_2C{=}C(COMe)_2\}_2]$ *E*,*Z*-conformations. The gold atoms are in distorted square-planar environments, the angles around gold differing from the ideal value of 90° because of the small bite of the dithiolate ligand [S(1)–Au(1)–S(2) 74.16(4), 74.46(4)°; S(1)–Au(1)–S(2′) 105.84(4), 105.54(4)°, respectively]. The Au(1), S(1), S(2), C(1) and C(2) atoms are coplanar (mean deviation 0.054, 0.044 Å), with both acetyl groups twisted out of this plane, one of them considerably (torsion angle 55, 48°), the other one slightly (torsion angle 9, 13°, respectively). The C(1)–C(4) bond distances [1.353(6), 1.365(4) Å] lie in the range expected for $C(sp^2){=}C(sp^2)$ double bonds (1.294–1.392)[28] and are similar to that found in the closely related ketene *S*,*S*-dithioacetal $(MeS)_2C{=}C\{C(O)Me\}_2$ (1.351 Å) which shows a twisted (torsion angle 14°) *E*,*E*-conformation.[29]

Apart from bands due to the cation, the solid-state IR spectrum of **1** shows two strong ν(C=O) bands at 1698 and 1678 cm^{-1} and a strong ν(C=C) band at 1580 cm^{-1}, while the ν(AuS) band(s) cannot be assigned unequivocally because of the presence of bands from the $[N(PPh_3)_2]$ cation in the 400–300 cm^{-1} region. The position of the ν(C=O) band suggest that conjugation plays at best a marginal role.[29] The IR spectrum of **2** shows two strong ν(C=O) bands at 1664 and 1636 cm^{-1} and a medium ν(AuS) band at 370 cm^{-1}. The frequency of the ν(C=C) band is expected to decrease because of conjugation with one of the acetyl groups and cannot be unequivocally assigned.

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Footnotes and References

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‖ *Crystal data* for complex **2**: $C_{48}H_{42}AuNO_4P_2S_4$, triclinic, space group $P\bar{1}$, T = 143 K, a = 10.729(3), b = 11.853(3), c = 18.076(4) Å, α = 83.13(2), β = 81.62(2), γ = 79.75(2)°, U = 2227.6(10) Å^3, Z = 2, λ(Mo-Kα) = 0.710 73 Å, μ = 3.61 mm^{-1}, D_c = 1.616 Mg m^{-3}. Data collection: Yellow prism 0.55 × 0.40 × 0.30 mm, Stoe STADI-4 diffractometer, 9522 intensities of which 7867 independent, $2\theta_{max}$ 50°, absorption corrections based on ψ-scans with transmissions 0.776–0.933. *Structure solution and refinement*: heavy-atom method, refined anisotropically on F^2 (program SHELXL-93, G.M. Sheldrick, University of Göttingen). H atoms with riding model or as rigid methyl groups. In the C(=O)Me groups of the second anion, the slightly short C–C and long C=O bonds and the difficulty in locating methyl H may indicate some disorder. Final $wR(F^2)$ 0.0742, $R(F)$ 0.0296, 547 parameters, 464 restraints, S = 1.09, max $\Delta\rho$ 1.4 e Å^{-3}. CCDC 182/591.

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