Gold(I) and Gold(III) Complexes with the 1,1′-Bis(diethyldithiocarbamate)ferrocene Ligand

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Abstract: The reaction of $FcLi_2 \cdot TMDA$ [$Fc = (\eta^5\text{-}C_5H_4)_2Fe$; TMDA = tetramethylenediamine] with $(S_2CNEt_2)_2$ affords the ferrocene derivative $Fc(S_2CNEt_2)_2$, which reacts with several gold(I) or gold(III) precursors. Thus the treatment with [AuCl(tht)] (tht = tetrahydrothiophene) or $[Au(OTf)(PPh_3)]$ (OTf = trifluoromethanesulfonate) gives the complexes $[Au_2Cl_2\{Fc(S_2CNEt_2)_2\}]$ or $[Au_2(PPh_3)_2\{Fc(S_2CNEt_2)_2\}](OTf)_2$. The gold(III) derivatives $[Au_2\{(C_6F_5)_3\}_2\{Fc(S_2CNEt_2)_2\}]$ and $[Au_2\{(C_6F_5)_2Cl\}_2\{Fc(S_2CNEt_2)_2\}]$ were obtained by reaction of $Fc(S_2CNEt_2)_2$ with $[Au(C_6F_5)_3(OEt_2)]$ or $[Au(C_6F_5)_2(\mu\text{-}Cl)]_2$, respectively. $Fc(S_2CNEt_2)_2$ and $[Au_2Cl_2\{Fc(S_2CNEt_2)_2\}]$ have been characterised by X-ray diffraction studies. A new type of η^2 interaction found between the gold complex and the cyclopentadienyl ligand was studied by the extended Hückel method; it consists of carbon-to-gold electron donation in the absence of back-donation. The interaction was also detected by density functional calculations, which showed the energy of the three independent molecules to be comparable.

Keywords: density functional calculations • extended Hückel calculations • gold • pi interactions • structure elucidation

Introduction

In the last few years the chemistry of ferrocene and the design of new compounds containing the ferrocene unit have received much attention; this is associated with their widespread utility, for example, in organic synthesis, catalysis and material chemistry.[1, 2] Numerous derivatives have been described in which the ferrocene unit is bound to a fragment containing one or more donor atoms.[1] Studies of these ligands are important because the complexes thus obtained may have interesting redox properties or unusual structures.

Although 1,1′-bis(diethyldithiocarbamate)ferrocene, $Fc(S_2CNEt_2)_2$ (**1**), was synthesised more than ten years ago,[3] its ligand properties have not been studied. As part of our investigations of ferrocene derivatives[4–8] we have synthesised a polymeric chain complex of this ligand with silver, in which the silver atom is bound to the dithiocarbamate unit and also, in a η^2 fashion, to the cyclopentadienyl ring.[9] Here we report further complexation studies of the ligand to gold(I) or gold(III) centres, together with the crystal structures of the ligand **1** and the gold(I) complex $[Au_2Cl_2\{Fc(S_2CNEt_2)_2\}]$ (**2**). The structure of the gold compound is unprecedented because the Au atoms are bound to the cyclopentadienyl rings through the π system, similar to the situation in the polymeric silver derivative.

Results and Discussion

The reaction of dilithioferrocene with tetraethylthiuram disulfide affords **1** in high yield. This compound had been reported previously,[3] but characterisation by X-ray diffraction had not been carried out. We have confirmed the structure by X-ray analysis; the molecule is shown in Figure 1, with a selection of bond lengths and angles in Table 1. The cyclopentadienyl rings are eclipsed (torsion angle C-Cp-Cp-C

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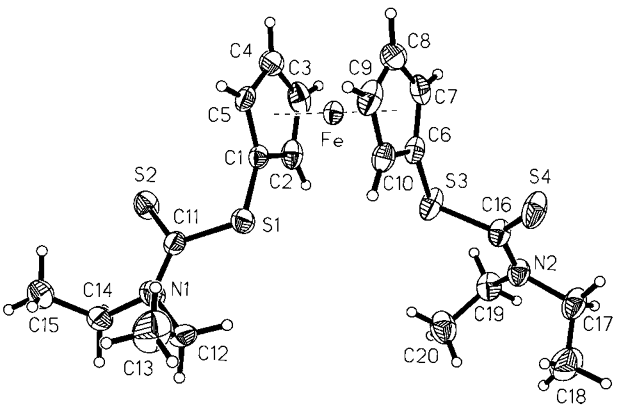


Figure 1. Atom-numbering scheme for the molecular structure of **1** in the crystal. Radii are arbitrary. Displacement parameter ellipsoids represent 50% probability surfaces. Only one component of the disordered ethyl group (see text) is shown.

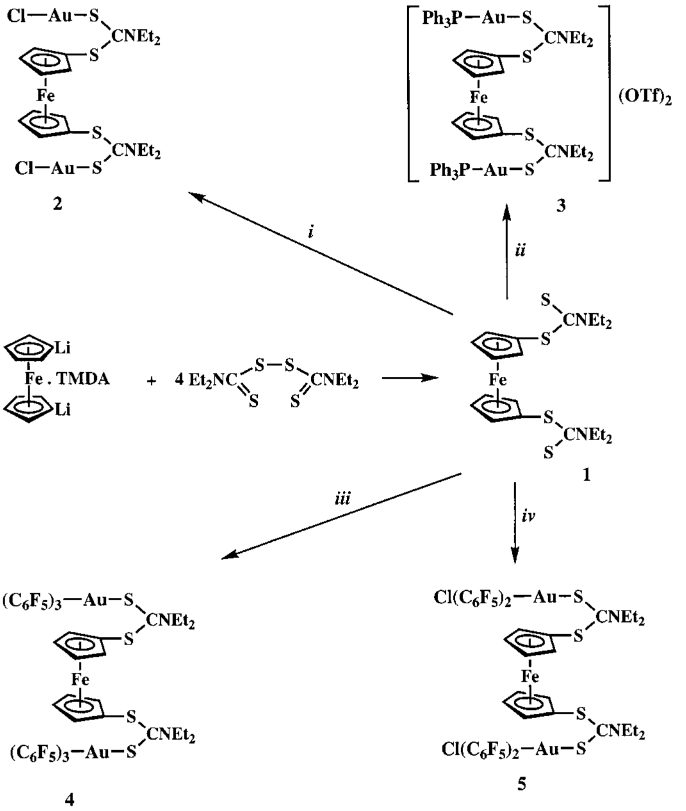
Table 1. Selected bond lengths [Å] and angles [°] for **1**.

S1–C1	1.751(2)	S1–C11	1.790(2)
S2–C11	1.656(2)	S3–C6	1.749(2)
S3–C16	1.790(2)	S4–C16	1.658(2)
C11–N1	1.326(3)	N1–C12	1.465(4)
N1–C14	1.473(3)	C16–N2	1.339(3)
N2–C17	1.476(3)	N2–C19	1.478(3)
C1-S1-C11	102.80(10)	C6-S3-C16	102.94(10)
C2-C1-S1	125.6(2)	C5-C1-S1	125.5(2)
C7-C6-S3	124.9(2)	C10-C6-S3	126.2(2)
N1-C11-S2	124.2(2)	N1-C11-S1	114.5(2)
S2-C11-S1	121.27(12)	C11-N1-C12	124.0(2)
C11-N1-C14	120.7(2)	C12-N1-C14	114.5(2)
N1-C12-C13	107.4(3)	N1-C14-C15	113.1(2)
N2-C16-S4	125.8(2)	N2-C16-S3	112.4(2)
S4-C16-S3	121.72(12)	C16-N2-C17	120.5(2)
C16-N2-C19	123.5(2)	C17-N2-C19	116.0(2)
N2-C17-C18	113.0(2)	N2-C19-C20	115.6(2)

Abstract in Spanish: *Por tratamiento de $FcLi_2 \cdot TMDA$ [$Fc = (\eta^5\text{-}C_5H_4)_2Fe$; TMDA = tetrametilenodiamina] con $(S_2CNEt_2)_2$ se obtiene el derivado de ferroceno, $Fc(S_2CNEt_2)_2$. Este reacciona con diversos compuestos de oro(I) y oro(III) como [AuCl(tht)] (tht = tetrahidrotiofeno) o [Au(OTf)(PPh$_3$)] (OTf = trifluorometilsulfonato) para dar los complejos $[Au_2Cl_2\{Fc(S_2CNEt_2)_2\}]$ o $[Au_2(PPh_3)_2\{Fc(S_2CNEt_2)_2\}](OTf)_2$. Los derivados de oro(III) $[Au_2\{(C_6F_5)_3\}_2\{Fc(S_2CNEt_2)_2\}]$ y $[Au_2\{(C_6F_5)_2Cl\}_2\{Fc(S_2CNEt_2)_2\}]$ se preparan por reacción de $Fc(S_2CNEt_2)_2$ con $[Au(C_6F_5)_3(OEt_2)]$ o $[Au(C_6F_5)_2(\mu\text{-}Cl)]_2$, respectivamente. Los compuestos $Fc(S_2CNEt_2)_2$ y $[Au_2Cl_2\{Fc(S_2CNEt_2)_2\}]$ se han caracterizado por difracción de rayos X. El complejo de oro revela una interacción η^2 de los dos átomos de oro con los anillos ciclopentadienilo del ligando. La naturaleza de este nuevo tipo de interacción se ha estudiado por el método Hückel extendido y consiste en donación electronica de los átomos de carbono al oro; no existiendo retrodonación. Cálculos de DFT detectan igualmente este tipo de interacción y muestran, además, que la energía de las tres moléculas independientes es comparable.*

4°, where Cp indicates the respective ring centroid), but the diethyldithiocarbamate groups are not (S-Cp-Cp-S 76°), thus presenting a synclinal eclipsed conformation that is not common in this type of ferrocene derivative. The distance from the iron atom to the mean plane of each Cp ring is 1.647(1) Å and the sulfur atoms are located 0.196(3) and 0.204(3) Å out of the same plane, displaced towards the iron centre. As expected, S2–C11 (1.656(2) Å) and S4–C16 (1.658(2) Å) correspond to S=C double bonds, whereas S1–C11 (1.790(2) Å) and S3–C6 (1.749(2) Å) are single bonds. These bond lengths are similar to those found in related dithiocarbamate ligands, such as $CH_2[S_2CN(CH_2Ph)_2]_2$,[10] or in metal complexes with monodentate dithiocarbamate, such as $[Au(S_2CNEt_2)(PPh_3)]$.[11]

The reactivity of the ligand **1** towards several gold compounds has been studied (Scheme 1). Treatment of **1** with 2 equiv. of [AuCl(tht)] (tht = tetrahydrothiophene) leads to the dinuclear gold species **2**, which is an orange air- and moisture-stable solid. In the IR spectrum a band at 1512(m) cm^{-1} is assigned to the $\tilde{\nu}$(C=N) vibration; $\tilde{\nu}$(Au–Cl) appears at 335(m) cm^{-1}. The ^{1}H NMR spectrum includes two multiplets arising from the α and β protons of the cyclopentadienyl groups; the two ethyl groups of the dithiocarbamate units are nonequivalent and therefore produce two triplets and two quartets. This behaviour of the ethyl protons is attributable to the restricted rotation around the carbamate C–N bond; the rotation barrier about this bond has been estimated.[3]



Scheme 1. Synthetic routes to the gold complexes: i) 2[AuCl(tht)]; ii) 2[Au(OTf)(PPh$_3$)]; iii) 2[Au(C$_6$F$_5$)$_3$(OEt$_2$)]; iv) [Au(C$_6$F$_5$)$_2$(μ-Cl)]$_2$.

The positive liquid secondary-ion mass spectrum (LSIMS) of **2** shows the peak arising by loss of one chloride ligand at $m/z = 909$ (10%) and also the fragment $[\mathrm{Au}\{\mathrm{Fc}(\mathrm{S_2CNEt_2})_2\}]^+$ at $m/z = 677$ (100%).

The structure of **2** has been established by X-ray diffraction; selected bond lengths and angles are given in Table 2. The complex crystallises with three independent molecules in the asymmetric unit. There are no short gold–gold interactions in any of the molecules, although such contacts are common in dinuclear complexes. The Au−S and Au−Cl distances are 2.240–2.251 (average 2.245) Å and 2.263–2.284 (average 2.270) Å, respectively. The Au−S distances are shorter than those found in other bis(dithiocarbamate) digold(I) complexes (2.293(6) Å[12–14]) or in $[\mathrm{Au_2}\{\mu\text{-}(\mathrm{CH_2})_2\mathrm{PPh_2}\}(\mu\text{-}\mathrm{S_2CNEt_2})]$ (2.326(6) Å),[15] but are consistent with other S donors coordinated *trans* to Cl, such as $[\mathrm{AuCl(SPPh_3)}]$ (2.246(1) Å)[16] or $[\mathrm{AuCl(C_5H_{10}N_2S)}]$ (2.25(1) Å).[17]

Table 2. Selected bond lengths [Å] and angles [°] for **2**.

Au1−S1	2.245(4)	Au1−Cl1	2.282(4)
Au2−S3	2.240(5)	Au2−Cl2	2.284(4)
S1−C11	1.70(2)	S2−C1	1.74(2)
S2−C11	1.78(2)	S3−C16	1.70(2)
S4−C6	1.75(2)	S4−C16	1.78(2)
N1−C11	1.33(2)	N1−C12	1.45(2)
N1−C14	1.51(2)	N2−C16	1.29(2)
N2−C19	1.50(2)	N2−C17	1.53(3)
Au1′−S1′	2.243(4)	Au1′−Cl1′	2.268(4)
Au2′−S3′	2.239(5)	Au2′−Cl2′	2.272(4)
S1′−C11′	1.72(2)	S2′−C1′	1.75(2)
S2′−C11′	1.76(2)	S3′−C16′	1.73(2)
S4′−C6′	1.74(2)	S4′−C16′	1.76(2)
N1′−C11′	1.31(2)	N1′−C12′	1.48(2)
N1′−C14′	1.49(2)	N2′−C16′	1.33(2)
N2′−C19′	1.48(2)	N2′−C17′	1.48(2)
Au1″−S1″	2.252(5)	Au1″−Cl1″	2.264(5)
Au2″−S3″	2.251(5)	Au2″−Cl2″	2.263(5)
S1″−C11″	1.72(2)	S2″−C1″	1.77(2)
S2″−C11″	1.79(2)	S3″−C16″	1.73(2)
S4″−C6″	1.75(2)	S4″−C16″	1.78(2)
N1″−C11″	1.31(2)	N1″−C12″	1.46(2)
N1″−C14″	1.48(2)	N2″−C16″	1.28(2)
N2″−C17″	1.49(2)	N2″−C19″	1.50(2)
S1-Au1-Cl1	172.8(2)	S3-Au2-Cl2	172.3(2)
C11-S1-Au1	115.3(6)	C1-S2-C11	107.6(8)
C16-S3-Au2	116.0(6)	C6-S4-C16	108.3(8)
C11-N1-C12	122.9(13)	C11-N1-C14	122.4(14)
C12-N1-C14	114.7(12)	C16-N2-C19	123(2)
C16-N2-C17	124(2)	C19-N2-C17	112(2)
N1-C11-S1	118.1(13)	N1-C11-S2	114.0(12)
S1-C11-S2	127.7(10)	N1-C12-C13	113.1(13)
N1-C14-C15	112.8(12)	N2-C16-S3	118.4(14)
N2-C16-S4	114.5(13)	S3-C16-S4	127.0(10)
C18-C17-N2	99(2)	N2-C19-C20	115.5(14)
S1′-Au1′-Cl1′	174.1(2)	S3′-Au2′-Cl2′	171.0(2)
C11′-S1′-Au1′	113.2(6)	C1′-S2′-C11′	106.2(8)
C16′-S3′-Au2′	115.5(6)	C6′-S4′-C16′	109.3(8)
C11′-N1′-C12′	121.4(14)	C11′-N1′-C14′	122.5(14)
C12′-N1′-C14′	115.6(13)	C16′-N2′-C19′	121.0(14)
C16′-N2′-C17′	121.7(13)	C19′-N2′-C17′	117.3(13)
N1′-C11′-S1′	118.3(13)	N1′-C11′-S2′	115.2(12)
S1′-C11′-S2′	126.5(10)	N1′-C12′-C13′	115.6(14)
N1′-C14′-C15′	111.8(13)	N2′-C16′-S3′	117.4(12)
N2′-C16′-S4′	114.8(11)	S3′-C16′-S4′	127.5(9)
N2′-C17′-C18′	111.4(13)	N2′-C19′-C20′	114.5(13)
S1″-Au1″-Cl1″	176.9(2)	S3″-Au2″-Cl2″	178.7(2)
C11″-S1″-Au1″	105.6(6)	C1″-S2″-C11″	110.6(8)
C16″-S3″-Au2″	106.6(6)	C6″-S4″-C16″	100.7(8)
C11″-N1″-C12″	121.0(14)	C11″-N1″-C14″	125(2)
C12″-N1″-C14″	113.6(13)	C16″-N2″-C17″	121.9(13)
C16″-N2″-C19″	123.7(14)	C17″-N2″-C19″	113.9(12)
N1″-C11″-S1″	121.9(13)	N1″-C11″-S2″	125.7(13)
S1″-C11″-S2″	112.2(9)	N1″-C12″-C13″	113.4(14)
N1″-C14″-C15″	114.0(14)	N2″-C16″-S3″	120.7(12)
N2″-C16″-S4″	122.3(12)	S3″-C16″-S4″	117.1(8)
N2″-C17″-C18″	112.6(13)	N2″-C19″-C20″	109.9(13)

The three independent molecules display distinct conformations. In molecule 1 (Figure 2) the Cp rings are staggered (C1-Cp-Cp-C8 −33°), whereas in the other two molecules they are eclipsed (C1′-Cp-Cp-C9′ 9°, C1′-Cp-Cp-C8′ 6°). This is also reflected in the S-Cp-Cp-S angles, which are −177°, 152°, 153°; the dithiocarbamate groups are thus pseudo-antiperiplanar across the ferrocene ring system, in contrast with the pseudo-*gauche* arrangement in the free ligand (see above). More importantly, the S−Au−Cl side chains adopt quite different positions; in molecules 1 and 2 the Au atoms lie above the *ipso*-C atoms of the Cp rings in a manner reminiscent of the above-mentioned silver polymer[9] (Au1 ⋯ C1 2.98 Å, Au2 ⋯ C6 3.06 Å, Au1′ ⋯ C1′ 3.08 Å, Au2′ ⋯ C6′ 3.08 Å), whereas in molecule 3 (Figure 3) the side chain is rotated so that the Au atoms lie between the Cp rings, displaced sideways (Au1″ ⋯ Fe″ 5.49 Å, Au2″ ⋯ Fe″ 4.83 Å). The torsion angles mainly responsible for this are C1-S2-C11-S1 and C6-S4-C16-S3, which are −5°, 1°; 24°, 7°; 152°, −118° in molecules 1–3 respectively.

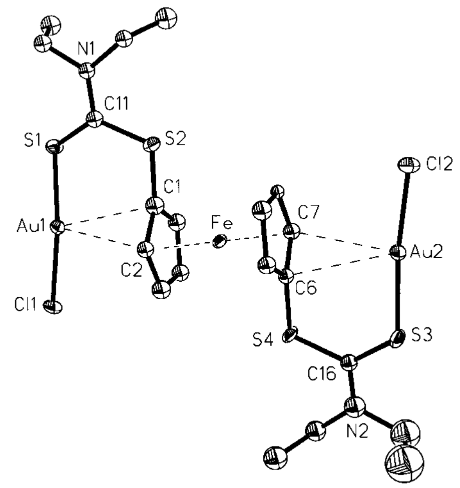


Figure 2. Atom-numbering scheme for the molecular structure of molecule 1 of complex **2** in the crystal. Radii are arbitrary. Displacement parameter ellipsoids represent 50% probability surfaces. Hydrogen atoms are omitted for clarity.

The different conformations of the three molecules are also evident in the geometry of the Au atoms; in molecules 1 and 2 the Cl-Au-S angles are distorted from linearity and range from 171.0(2)° to 174.1(2)°, whereas in molecule 3 they are almost linear (176.9(2)° and 178.7(2)°). The distortion of the Cl-Au-S angles in molecules 1 and 2 is a consequence of the weak interactions of the Au atoms with the cyclopentadienyl C−C bond. Interactions of Au atoms with π systems are not common; only the complex $[\mathrm{Au(C_5H_5)(PPh_3)}]$[18] shows a slip distortion towards a η^3-mode of coordination. In addition to

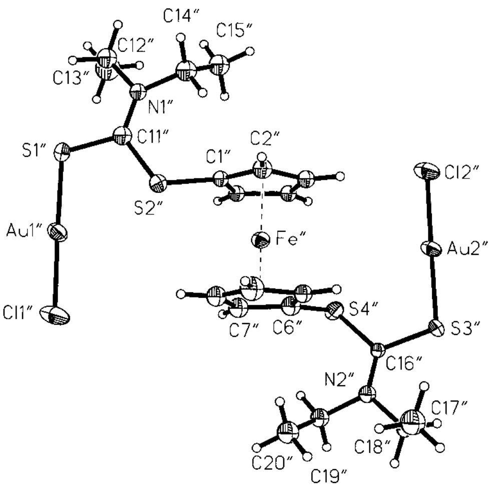


Figure 3. Atom-numbering scheme for the molecular structure of molecule 3 of complex **2** in the crystal. Displacement parameter ellipsoids represent 50% probability surfaces.

the Au–C σ bond (2.175(9) Å), two Au $\cdots$ C contacts (2.791(9) and 2.688(9) Å) with the Cp C atoms adjacent to the *ipso* position are observed. The η^5 coordination of the cyclopentadienyl ring to the iron atom may be responsible for the longer interatomic distances.

The reaction of $Fc(S_2CNEt_2)_2$ with 2 equiv. $[Au(OTf)(PPh_3)]$ (OTf = trifluoromethanesulfonate) gives the cationic gold derivative $[Au_2(PPh_3)_2\{Fc(S_2CNEt_2)_2\}](OTf)_2$ (**3**), which is a moisture- and air-stable yellow solid that behaves as a 1:2 electrolyte in acetone. In the IR spectrum the bands from the PPh_3 group and the ionic triflate[19] are at 1264 (vs, br) $[\tilde{\nu}_{as}(SO_3)]$, 1224 (s) $[\tilde{\nu}_s(CF_3)]$, 1155 (s) $[\tilde{\nu}_{as}(CF_3)]$ and 1023 (s) $[\tilde{\nu}_s(SO_3)]$ cm^{-1}. The $\tilde{\nu}$(C=N) vibration appears at 1518(m) cm^{-1}. The pattern of the ^{1}H NMR spectrum is the same as for complex **2** and the $^{31}P\{^1H\}$ NMR spectrum shows a singlet as a result of the equivalence of the two phosphorus atoms.

Gold(III) derivatives have been prepared by reaction of $Fc(S_2CNEt_2)_2$ with $[Au(C_6F_5)_3(OEt_2)]$ or $[Au(C_6F_5)_2(\mu\text{-}Cl)]_2$ to give the neutral complexes $[Au_2\{(C_6F_5)_3\}_2\{Fc(S_2CNEt_2)_2\}]$ (**4**) or $[Au_2\{(C_6F_5)_2Cl\}_2\{Fc(S_2CNEt_2)_2\}]$ (**5**). Both are yellow solids, air and moisture stable, and nonconducting in acetone solutions. In their IR spectra the bands from the pentafluorophenyl groups are at 1507 (s), 969 (s), 807 (m) and 793 (m) cm^{-1} for **4** and 1510 (s), 970 (s), 810 (m) and 800 (m) cm^{-1} for **5**. The vibrations $\tilde{\nu}$(C=N) appear at 1612 (w) and 1638 (w) (**4**) and 1617 (w) (**5**). In complex **5** the vibration $\tilde{\nu}$(Au–Cl) is at 334 (m) cm^{-1}.

In the ^{1}H NMR spectrum of **4** the cyclopentadienyl protons are inequivalent and thus eight multiplets appear; the ethyl protons of the dithiocarbamate groups are also inequivalent and four triplets and four quartets are present. Usually, complexes with disubstituted ferrocene ligands show two multiplets in the ^{1}H NMR spectra for the α and β protons of the cyclopentadienyl rings, even though in the solid state (because of the different ring conformations) the eight protons are inequivalent. This is, however, seldom observed; sometimes when the temperature is lowered four proton signals, or in a few cases eight, are resolved. This fluxional behaviour is very common in ferrocene derivatives and has been studied for systems such as the 1,1′-bis(diphenylphosphino)ferrocene ligand.[1] In complex **4** the presence of three rigid pentafluorophenyl groups on each Au atom probably prevents the torsional twist of the Cp rings even at room temperature. In the ^{19}F NMR spectrum the inequivalence of the $Au(C_6F_5)_3$ units can be observed; six signals appear for each unit (three signals for the *ortho*, *meta* and *para* fluorine of each C_6F_5 group) because of the equivalence of the mutually *trans* pentafluorophenyl groups. This also proves the nonexistence of fluxionality between the two Cp rings.

In the ^{1}H NMR spectrum of **5** the α and β protons of the Cp rings are equivalent and therefore only two multiplets appear. In the ^{19}F NMR spectrum there are six signals for the two different pentafluorophenyl groups.

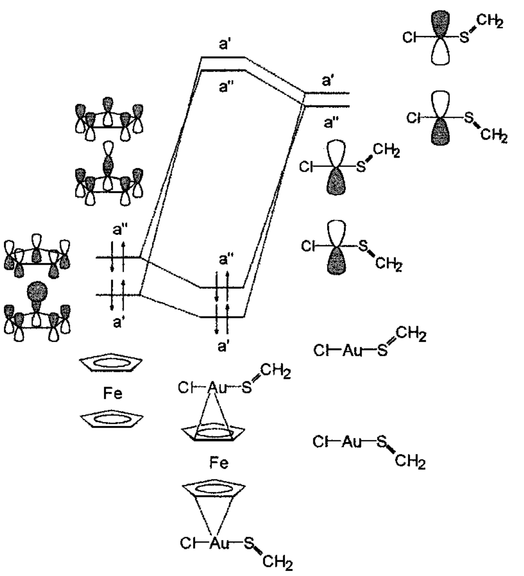
In the positive LSIMS the molecular peaks appear at m/z = 1876 (**4**, 2%) and 1619 (**5**, 3%). The fragments arising by the loss of one $Au(C_6F_5)_3$ or $Au(C_6F_5)_2Cl$ unit are also present at m/z = 1179 (16%) and 1047 (7%), respectively.

Molecular Orbital Calculations

Extended Hückel calculations[20] were undertaken to gain an understanding of the novel interactions involving gold described above. With experimental coordinates taken from the X-ray structure, a first set of calculations showed interactions either between Au and two C atoms in molecules 1 and 2 or between Au and S in molecule 3, overlap populations ranging respectively from 0.001 to 0.012 (Au–C) and 0.003 to 0.021 (Au–S). These values indicate weak interactions, which are not surprising with the linear coordination exhibited by Au^I and the long distances involved ($d_{Au-C} > 2.98$ Å, $d_{Au-S} > 3.05$ Å), but they are reminiscent of other weak interactions involving Au atoms.[21] A model was constructed that allowed a fragment analysis, but avoided consideration of the scission of the S–C bond (C1–S2 in molecule 1, for instance). The interaction between Au and the two C atoms of the cyclopentadienyl ligand is depicted in Scheme 2. As there are two Au atoms in the molecule, each of them interacting with one of the Cp rings, we can see both the symmetric and the antisymmetric combinations of the two Au p orbitals that act as acceptors.

The Cp rings donate electrons from two ferrocene molecular orbitals (MOs) derived from the symmetric and antisymmetric combinations of the Cp totally symmetric a_1 orbital. The C atoms contribute strongly to these ferrocene MOs and are the only ones involved in the interaction. As Scheme 2 shows, the fragment orbitals are slightly stabilised when the interaction occurs. There is no back-donation to the empty ferrocene levels, as these are high-energy Fe–Cp antibonding levels, located mainly in the metal and not in the C atoms.

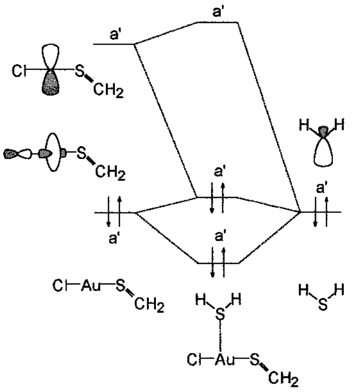
Another interesting aspect of this arrangement is the η^2-Cp coordination to Au. We studied the haptotropic migration by methods similar to those used previously for other fragments;[22] we found that when the gold fragment moves from the centre of the ring towards the edge, the edge position has the lowest energy, allowing for minimal repulsion between all



Scheme 2. Interaction between Au and two C atoms of a Cp ring in a model of molecules 1 and 2 of complex **2**.

the occupied levels and leading to the weak interaction described.

In the isomeric molecule 3, the contact between the Au atom and the second S atom of the thiocarbamate ligand is short. The S–Au interaction is similar to the weak Au–Au interactions described previously (Scheme 3).



Scheme 3. Interaction between Au and S in a model of molecule 3 of complex **2**.

There is a four-electron destabilising interaction between the S sp lone pair and the Au sz^2 orbital, which is relieved by mixing-in of the Au p orbital. The main stabilisation is achieved by electron donation from sulfur to empty gold p orbitals.

Density functional calculations (DFT single-point) were performed with the experimentally observed isomeric structures of the three molecules of **2**. The energies obtained were -320.42, -321.40 and -321.47 eV for molecules 1, 2 and 3, respectively. Molecules 1 and 2 have the same arrangement, with Au close to two C atoms of the Cp ring, whereas 3 exhibits the short Au$\cdots$S contact. Interestingly, the largest energy difference is between 1 and 2, and 3 is the most stable. All of these energy differences are small, however, and may not be very significant as they are of the same order of magnitude as crystal packing effects and other interactions taking place in the solids. In molecules 1 and 2 we could detect, in the DFT calculations, a small positive overlap population (ranging from 0.0052 to 0.0120) between Au and C.

These new compounds thus demonstrate how the coordination sphere of Au can be extended if the atoms become involved in weak interactions, not only with other Au atoms, but also with C atoms from a cyclopentadienyl ring or S.

Experimental Section

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer 883 spectrophotometer with Nujol mulls between polyethylene sheets. Conductivities were measured in about 5×10^{-4} M solutions with a Philips 9509 conductimeter. C and H analyses were carried out with a Perkin-Elmer 2400 microanalyser. Mass spectra were recorded on a VG Autospec by the LSIMS technique, with nitrobenzyl alcohol as matrix. NMR spectra were recorded on a Varian Unity 300 spectrometer and a Bruker ARX 300 spectrometer in CDCl$_3$. Chemical shifts are cited relative to SiMe$_4$ (^{1}H, external) and 85% H$_3$PO$_4$ (^{31}P, external). The starting materials [AuCl(tht)],[23] [Au(C$_6$F$_5$)$_3$(OEt$_2$)][24] and [Au(C$_6$F$_5$)$_2$(μ-Cl)][25] were prepared by published procedures. [Au(OTf)(PPh$_3$)] was prepared by reaction of [AuCl(PPh$_3$)] with Ag(OTf) in dichloromethane.

Syntheses:

[Au$_2$Cl$_2${Fc(S$_2$CNEt$_2$)$_2$}] (2): Fc(S$_2$CNEt$_2$)$_2$ (0.048 g, 0.1 mmol) was added to a solution of [AuCl(tht)] (0.064 g, 0.2 mmol) in dichloromethane (20 mL), and the mixture was stirred for 1 h. Concentration of the solution to about 5 mL and addition of diethyl ether (10 mL) gave **2** as a yellow solid. Yield 77%; ^{1}H NMR: $\delta = 4.64$ (m, 8H; C$_5$H$_4$), 4.14 (q, 2H; CH_2CH$_3$), 3.96 (q, 2H; CH_2CH$_3$), 1.40 (t, 3H; CH$_2$$CH_3$); $C_{20}H_{28}Au_2Cl_2FeN_2S_4$: calcd C 25.40, H 2.98, N 2.96, S 13.56; found C 25.66, H 3.55, N 2.93, S 13.53.

[Au$_2$(PPh$_3$)$_2${Fc(S$_2$CNEt$_2$)$_2$}](OTf)$_2$ (3): Fc(S$_2$CNEt$_2$)$_2$ (0.048 g, 0.1 mmol) was added to a solution of [Au(OTf)(PPh$_3$)] (0.121 g, 0.2 mmol) in dichloromethane (20 mL), and the mixture was stirred for 1 h. Concentration of the solution to about 5 mL and addition of diethyl ether (10 mL) gave **3** as a yellow solid. Yield 90%; Λ_M (acetone) = 196 Ω^{-1}cm^2 mol^{-1}; ^{1}H NMR: $\delta = 4.64$ (m, 8H; C$_5$H$_4$), 4.14 (q, 2H; CH_2CH$_3$), 3.96 (q, 2H; CH_2CH$_3$), 1.40 (t, 3H; CH$_2$$CH_3$); ^{31}P{^{1}H} NMR: $\delta = 36.7$ (s). $C_{58}H_{58}Au_2F_6FeN_2O_6P_2S_6$: calcd C 41.04, H 3.44, N 1.65, S 11.33; found: C 41.42, H 3.40, N 1.43, S 10.75.

[Au$_2${Au(C$_6$F$_5$)$_3$}$_2${Fc(S$_2$CNEt$_2$)$_2$}] (4): Fc(S$_2$CNEt$_2$)$_2$ (0.048 g, 0.1 mmol) was added to a solution of [Au(C$_6$F$_5$)$_3$(OEt$_2$)] (0.154 g, 0.2 mmol) in dichloromethane (20 mL), and the mixture was stirred for 30 min. Concentration of the solution to about 1 mL and addition of hexane (10 mL) gave **4** as a yellow solid. Yield 60%; Λ_M (acetone) = 12 Ω^{-1}cm^2 mol^{-1}; ^{1}H NMR: $\delta = 4.67$ (m, 1H; C$_5$H$_4$), 4.64 (m, 1H; C$_5$H$_4$), 4.63 (m, 1H; C$_5$H$_4$), 4.56 (m, 1H; C$_5$H$_4$), 4.51 (m, 1H; C$_5$H$_4$), 4.49 (m, 1H; C$_5$H$_4$), 4.42 (m, 1H; C$_5$H$_4$), 4.39 (m, 1H; C$_5$H$_4$), 4.29 (q, 2H; CH_2CH$_3$), 3.98 (q, 2H; CH_2CH$_3$), 3.86 (q, 2H; CH_2CH$_3$), 3.84 (q, 2H; CH_2CH$_3$), 1.38 (t, 3H; CH$_2$$CH_3$), 1.33 (t, 3H; CH$_2$$CH_3$), 1.23 (t, 3H; CH$_2$$CH_3$), 1.10 (t, 3H; CH$_2$$CH_3$); ^{19}F NMR: $\delta = -120.0$ (m, 4F; *o*-F), -122.1 (m, 2F; *o*-F), -157.4 (t, ^3J(F,F) = 19.3 Hz, 2F; *p*-F), -157.5 (t, ^3J(F,F) = 19.3 Hz, 1F; *p*-F), -161.7 (m, 4F; *m*-F), -161.8 (m, 2F; *m*-F). $C_{56}H_{28}Au_2F_{30}FeN_2S_4$: calcd C 35.79, H 1.50, N 1.49, S 6.82; found C 36.10, H 1.85, N 1.95, S 7.8.

[Au$_2${Au(C$_6$F$_5$)$_2$Cl}$_2${Fc(S$_2$CNEt$_2$)$_2$}] (5): Fc(S$_2$CNEt$_2$)$_2$ (0.048 g, 0.1 mmol) was added to a solution of [Au(C$_6$F$_5$)$_2$(μ-Cl)]$_2$ (0.132 g, 0.1 mmol) in dichloromethane (20 mL) was added and the mixture was stirred for 1 h Concentration of the solution to about 5 mL and addition of hexane (10 mL) gave **5** as a yellow solid. Yield 55%; Λ_M (acetone) = 35 Ω^{-1}cm^2 mol^{-1}; ^{1}H NMR: $\delta = 4.74$ (m, 4H; C$_5$H$_4$), 4.71 (m, 4H; C$_5$H$_4$), 4.27 (q, 4H; CH_2CH$_3$), 4.06 (q, 4H; CH_2CH$_3$), 1.60 (t, 6H; CH$_2$$CH_3$), 1.26 (t, 6H; CH$_2$$CH_3$); ^{19}F NMR: $\delta = -121.2$ (m, 2F; *o*-F), -122.9 (m, 2F; *o*-F), -156.3 (t, ^3J(F,F) = 19.3 Hz, 1F; *p*-F), -157.1 (t, ^3J(F,F) = 19.3 Hz, 1F; *p*-F), -161.2 (m, 2F; *m*-F), -161.7 (m, 2F; *m*-F); $C_{44}H_{28}Au_2Cl_2F_{20}FeN_2S_4$: calcd C 32.73, H 1.73, N 1.73, S 7.93; found C 32.25, H 1.46, N 1.54, S 6.96.

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Crystallography: The crystals were mounted in inert oil on glass fibres and transferred to the cold gas stream of a Stoe STADI-4 (**1**) or Siemens P4 (**2**) diffractometer equipped with an LT-2 low-temperature attachment. Data were collected with monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The scan mode was ω/Θ (**1**) or ω (**2**). Absorption corrections were applied on the basis of Ψ-scans. The structures were solved by direct methods and refined on F^2 with the SHELXL-93 program.[26] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included as rigid methyl groups or a riding model. A system of restraints to light-atom displacement-factor components and local ring symmetry was used. In complex **1** the ethyl group C12/C13 is disordered over two sites. Further details of the data collection and structure refinement are given in Table 3. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101458. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Molecular orbital calculations: The extended Hückel method[20] with modified H_{ij} values was used for all calculations.[27] The basis set for the metal atoms consisted of ns, np and $(n-1)$d orbitals. The s and p orbitals were described by single Slater-type wave functions, and the d orbitals were taken as contracted linear combinations of two Slater-type wave functions. Only s and p orbitals were considered for S and Cl. Parameters (H_{ii} (eV), ζ): for Au: 6s −10.92, 2.602; 6p −5.55, 2.584; 5d −15.07, 6.163, 2.794 (ζ_2), 0.6442 (C_1), 0.5356 (C_2); for Fe: 4s −9.17, 1.900; 4p −5.37, 1.900; 3d −12.70, 5.350, 1.800 (ζ_2), 0.5366 (C_1), 0.6678 (C_2). Standard parameters were used for other atoms.

Calculations were performed on the three independent molecules of the real structure, and on model complexes with idealised geometries and C_s symmetry based on the crystal structures. The models were used for the orbital rationalisation of the Au−C(Cp) and Au−S long-range interactions; the results were tested with calculations on the real structures. The diethyldithiocarbamate ligand was modelled by $CH_2{=}S$ in order to allow fragment separation without the scission of a C−S bond. The bond lengths (Å) were as follows: Fe−Cp(ring centroid) 1.65, Au−Cl 2.27, Au−S 2.25, Au−C(Cp) 3.00, Au−S(SH_2) 3.00, S−C 1.70, C−C 1.40, C−H 1.08, S−H 1.30.

Table 3. Details of data collection and structure refinement for the complexes **1** and **2**.

	1	**2**
formula	$C_{20}H_{28}FeN_2S_4$	$C_{20}H_{28}Au_2Cl_2FeN_2S_4$
crystal habit	yellow tablet	yellow prism
crystal size [mm]	0.8 × 0.6 × 0.4	0.4 × 0.4 × 0.2
crystal system	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a [Å]	12.840(3)	10.912(2)
b [Å]	13.316(3)	18.365(3)
c [Å]	13.575(3)	20.543(3)
α [°]	90	79.270(10)
β [°]	107.55(2)	76.002(10)
γ [°]	90	82.690(12)
U [Å^3]	2213.0(9)	3910.1(10)
Z	4	6
ρ_{calcd} [Mg m^{-3}]	1.442	2.409
M	480.53	945.37
$F(000)$	1008	2664
T [°C]	−130	−100
$2\theta_{max}$ [°]	55	50
$\mu(Mo_{K\alpha})$ [mm^{-1}]	1.067	12.316
transmission	0.760–0.879	0.565–0.848
reflections measured	6228	13836
unique reflections	5099	13556
R_{int}	0.019	0.103
R[a] [F, $F > 4\sigma(F)$]	0.034	0.050
wR [b] (F^2, all data)	0.086	0.116
parameters	256	508
restraints	201	96
S [c]	1.037	0.815
max. $\Delta\rho$ [e Å^{-3}]	0.377	1.84

[a] $R(F) = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$. [b] $wR(F^2) = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and a and b are constants adjusted by the program. [c] $S = [\Sigma\{w(F_o^2 - F_c^2)^2\}/(n-p)]^{0.5}$, where n is the number of data and p the number of parameters.

DFT calculations[28] were carried out with the Amsterdam density functional (ADF) program[29] developed by Baerends and co-workers[30] with nonlocal exchange and correlation corrections.[31] The coordinates of molecules 1, 2 and 3 of $[Au_2Cl_2\{Fc(S_2CNEt_2)_2\}]$ (**2**) were used for single-point calculations. The relativistic effects were treated by a quasi-relativistic method in which Darwin and mass–velocity terms are incorporated.[32] In all the calculations, a triple-ζ Slater-type orbital (STO) basis set was used for Au 6s and 6p; a triple-ζ STO augmented with a 3d single-ζ polarisation function was used for S 3s and 3p, and for C 2s and 2p; a double-ζ STO was used for H 1s, Fe 4s and 4p, Cl 3s and 3p, N 2s and 2p. A frozen-core approximation was used to treat the core electrons of Fe, Cl, S, C, N and Au.

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