{μ-2-[1-(*N,N*-Dimethylamino)ethyl]ferrocene-1,1'-diylbis(diphenylphosphine)-κ²*P*:*P'*}bis[thiocyanatogold(I)]

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The title compound, [Au$_2$Fe(C$_{38}$H$_{37}$NP$_2$)(SCN)$_2$], is a dinuclear gold(I) complex containing an unsymmetrical bidentate ferrocenyl–phosphine ligand. Selected geometrical parameters for the compound are Au—P = 2.265 (2) and 2.260 (3) Å, Au—S = 2.327 (3) and 2.313 (3) Å, and P—Au—S = 175.61 (9) and 176.86 (9)°.

Comment

Organometallic ligands are employed conveniently as a route to the synthesis of heterometallic complexes. Transition metal complexes with phosphine ligands containing ferrocene groups are currently receiving a great deal of attention, as shown by the large number of complexes reported with 1,1'-bis(diphenylphosphino)ferrocene (dppf) as the chelating ligand with interesting properties and geometric features. Examples in the literature where it is employed as a ligand include the ruthenium-, rhodium- and palladium-catalysed hydrogenation of olefins (Butler *et al.*, 1985; Cullen *et al.*, 1985; Hayashi & Kumada, 1982), nickel- and palladium-catalysed Grignard cross-coupling reactions (Hayashi *et al.*, 1982; Brown & Cooley, 1990), and as a ligand for catalytic olefin reduction (Hillman *et al.*, 1985). Catalytic reactions with gold include the gold(I)-catalysed aldol reactions of enolates with aldehydes to give optically active β-hydroxycarbonyl compounds (Ito *et al.*, 1986). Reacting the {μ-2-[1-(*N,N*-dimethylamino)ethyl]-ferrocene-1,1'-diylbis(diphenylphosphine)-κ²*P*:*P'*}bis[chlorogold(I)] complex (Sam *et al.*, 2005) with two equivalents of KSCN yields the title compound, (I). This compound was synthesized in order to investigate substitution reaction mechanisms and to improve solubility compared with the bis[chlorogold(I)] complex.
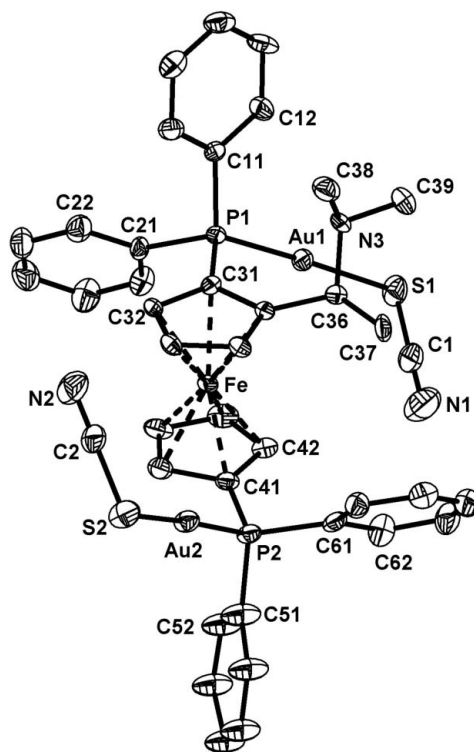

(I)
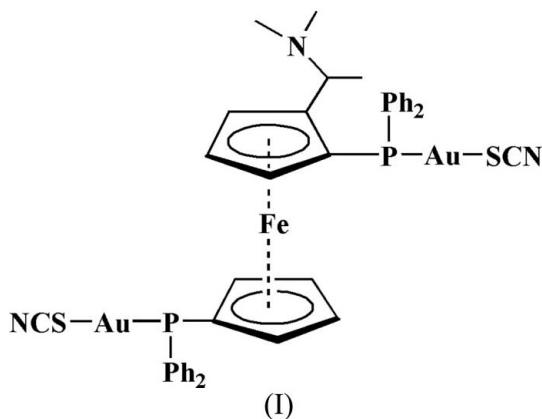
Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 30% probability level. In the numbering scheme, the first digit refers to the number of the ring and the second to the number of the atom in the ring. H atoms have been omitted for clarity.
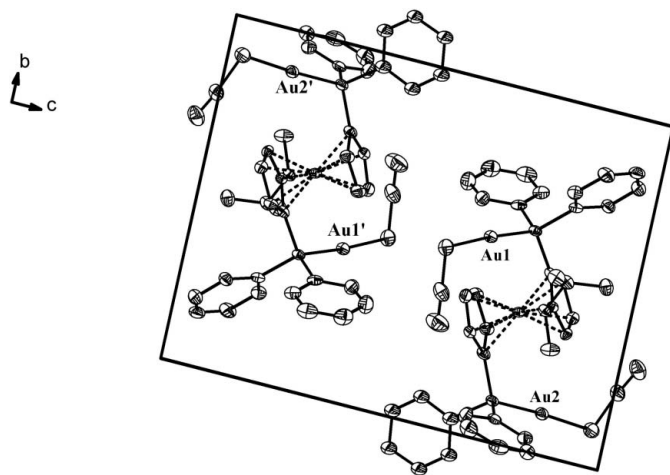

Figure 2
A partial packing diagram of (I). H atoms have been omitted for clarity.

The structure of (I) is a dinuclear gold(I) complex with the SCN⁻ ligands in a *trans* orientation (Fig. 1). The coordination around the Au atom is approximately linear, as expected in Au^I complexes. The ferrocene group acts as a P,P'-bridging ligand. The two Cp groups are approximately parallel and orientated anticlinal in a partially eclipsed manner relative to each other. The phenyl rings are approximately perpendicular to each other with an average C—P—C angle of 106.9 (5)°.

Selected geometric parameters are presented in Table 1. The average Au—P and Au—S bond distances and P—Au—S bond angle are 2.263 (3) Å, 2.320 (3) Å and 176.24 (9)°, respectively, which are within the normal range for ferrocene-type complexes. The coordination of the SCN⁻ ion displays a bent orientation, typical of soft acid/base interactions.

The title compound is compared in Table 3 with other closely related Au^I complexes from the literature, with the Au—P bond lengths comparing well with those of similar complexes. However, an increase of approximately 0.1 Å is noted in Au—X bond distances in (I) compared with the chlorogold(I) complexes. These bond distances are much longer in the [(dppf)(AuI)₂] complex (Canales *et al.*, 1997), due to differences in the *trans* influence of SCN, I and Cl. The P—Au—X bond angles of (I) are in agreement with those of the listed complexes.

The packing of the molecules in the unit cell is presented in Fig. 2. Weak intermolecular C—H···N hydrogen bonding is observed in the crystal structure of (I) (Table 2). The structure contains no π–π interactions.

Experimental

Compound (I) was prepared by a procedure similar to that previously described by Gimeno *et al.* (1993). A solution of [(dppf-CH(CH₃)N(CH₃)₂)(AuCl)₂] (Sam *et al.*, 2005) (0.05 g, 0.05 mmol) in a mixture of dichloromethane (4 ml) and acetone (3 ml) was treated with KSCN (0.01 g, 0.1 mmol) and the mixture was stirred for 1 h. The solution was filtered through Celite and the solvent evaporated to a small volume. Addition of diethyl ether gave the desired product (0.03 g, 58%), which was recrystallized from a mixture of dichloromethane and diethyl ether (1:1) to provide X-ray quality crystals.

Crystal data

[Au₂Fe(C₃₈H₃₇NP₂)(NCS)₂]	$V = 1929.5$ (14) Å³
$M_r = 1135.57$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.955$ Mg m⁻³
$a = 9.021$ (5) Å	Mo $K\alpha$ radiation
$b = 13.397$ (5) Å	$\mu = 8.18$ mm⁻¹
$c = 16.684$ (5) Å	$T = 293$ (2) K
$\alpha = 89.956$ (5)°	Needle, orange
$\beta = 82.946$ (5)°	$0.37 \times 0.14 \times 0.08$ mm
$\gamma = 74.740$ (5)°	

Data collection

Bruker SMART 1K CCD diffractometer	10576 measured reflections
ω scans	6743 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)	5497 reflections with $I > 2\sigma(I)$
$T_{min} = 0.260$, $T_{max} = 0.519$	$R_{int} = 0.103$
	$\theta_{max} = 25.0°$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.058$	$w = 1/[\sigma^2(F_o^2) + (0.1108P)^2]$
$wR(F^2) = 0.158$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} = 0.001$
6743 reflections	$\Delta\rho_{max} = 3.11$ e Å⁻³
421 parameters	$\Delta\rho_{min} = -3.23$ e Å⁻³

Table 1
Selected geometric parameters (Å, °).

Au1—P1	2.265 (2)	P2—C41	1.769 (10)
Au1—S1	2.327 (3)	S1—C1	1.678 (15)
Au2—P2	2.260 (3)	S2—C2	1.673 (12)
Au2—S2	2.313 (3)	N1—C1	1.158 (18)
P1—C31	1.799 (9)	N2—C2	1.133 (16)
P1—Au1—S1	175.61 (9)	C1—S1—Au1	95.9 (4)
P2—Au2—S2	176.86 (9)	C2—S2—Au2	103.1 (4)
C11—P1—C21	107.1 (4)	N1—C1—S1	178.7 (13)
C61—P2—C51	106.7 (6)	N2—C2—S2	174.5 (12)

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C54—H54$\cdots$N1^i	0.93	2.61	3.501 (18)	160

Symmetry code: (i) $-x, -y + 2, -z + 1$.

Table 3
Comparative geometric parameters (Å, °) for selected gold(I) ferrocenyl complexes (X = Cl, SCN, I).

Complex	Au—P	Au—X	P—Au—X
[(dppf)(AuCl)$_2$]^a	2.226 (1)	2.278 (1)	177.56 (8)
[(dppf-R)(AuCl)$_2$]^b	2.237 (2)	2.271 (3)	175.4 (1)
	2.224 (2)	2.278 (2)	174.0 (1)
[(dppf-R)(AuSCN)$_2$]^c	2.265 (2)	2.327 (3)	175.61 (9)
	2.260 (3)	2.313 (3)	176.86 (9)
[(dppf)(AuI)$_2$]^d	2.248 (9)	2.545 (3)	177.7 (2)
	2.240 (8)	2.561 (2)	176.3 (2)
[(dppf-L)$_2$(AuCl)$_3$]^e	2.31 (2)	2.52 (3)	113 (2)
	2.28 (2)	2.20 (2)	177 (2)

Notes: (a) Crespo et al. (2000); (b) Sam et al. (2005), R = –CH(CH$_3$)N(CH$_3$)$_2$, dppf is 1,1'-bis(diphenylphosphino)ferrocene; (c) this work, R = –CH(CH$_3$)N(CH$_3$)$_2$; (d) Canales et al. (1997), isolated as the CH$_2$Cl$_2$ solvate. (e) Togni et al. (1990), L = –CH(CH$_3$)N(CH$_3$)CH$_2$CH$_2$N(CH$_3$)$_2$, isolated as the Et$_2$O solvate.

Methyl H atoms were placed in calculated positions with C—H = 0.96 Å and torsion angles were refined to fit the electron density; U_{iso}(H) = 1.5U_{eq}(C). Other H atoms were placed in calculated positions with C—H = 0.93 (aromatic) or 0.98 Å (methine) and refined in riding mode; U_{iso}(H) = 1.2U_{eq}(C). The deepest hole and highest peak of residual electron density are located within 1.0 Å of atom Au1.

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Berndt, 2005); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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