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Solvent-free [μ-ferrocene-1,1′-diylbis(diphenylphosphine-*P*)]bis[chlorogold(**I**)]

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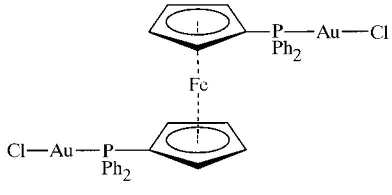
The title compound, $[Au_2Cl_2\{Fe(C_{17}H_{14}P)_2\}]$, (I), contains the expected linear gold centres. The ferrocene moiety acts as a *P*,*P*′-bridging ligand, wherein the Fe atom lies on an inversion centre. The P—Au—Cl angle is 177.56 (8)° and bond distances Au—P and Au—Cl are 2.2261 (18) and 2.2781 (18) Å, respectively. The structure is almost identical to that of the metal complex in $(I)\cdot 2CH_2Cl_2$ [Canales, Gimeno, Jones, Laguna & Sarroca (1997). *Inorg. Chem.* **36**, 5206–5211], but differs considerably from that in $3(I)\cdot 2CHCl_3$ [Hill, Girard, McCabe, Johnson, Stupik, Zhang, Reiff & Eggleston (1989). *Inorg. Chem.* **28**, 3529–3533], in that in the latter, the two independent molecules are linked by a short Au···Au contact.

Comment

Much attention has been focused on the diphoshine 1,1′-bis(diphenylphosphino)ferrocene (dppf). Although it was synthesized about 30 years ago (Sollot *et al.*, 1965; Bishop *et al.*, 1971; Marr & Hunt, 1969), its reactivity is still being widely studied due to its catalytic potential, industrial importance and chemical uniqueness. Various complexes of Co, Ni (Rudie *et al.*, 1978), Hg (Mann *et al.*, 1974), Mo, W (Baker *et al.*, 1986) Pd (Hayaski *et al.*, 1979), Pt (Clemente *et al.*, 1986), or Rh (Cullen *et al.*, 1985) have been described. As part of our work on the chemistry of the dppf ligand, we have recently reported some silver and gold derivatives (Gimeno *et al.*, 1993, 1995; Canales *et al.*, 1996, 1997). Among the latter, the title compound, $[Au_2Cl_2(\mu\text{-dppf})]$, (I), is interesting because of the antitumour activity found in some bis(diphenylphosphine)gold(I) derivatives. Two structures of (I) have already been published; the first (Hill *et al.*, 1989) was a chloroform solvate [ratio (I):$CHCl_3$ of 3:2] with two independent molecules of (I), one with inversion symmetry, whereas the second (Canales *et al.*, 1997) was a dichloromethane disolvate in which the molecule of (I) also displayed inversion symmetry. Here, we present the structure of a solvent-free form.



(I)

Compound (I) (Fig. 1) crystallizes with the Fe atom on an inversion centre. The dppf ligand coordinates both gold centres. The P—Au—Cl angle is approximately linear at 177.56 (8)°. The Au—P and Au—Cl bond distances are 2.2261 (18) and 2.2781 (18) Å, respectively, which compare well with those found in the two previously reported determinations [Au—P 2.2262 (13) and 2.222–2.239 Å; Au—Cl 2.2815 (13) and 2.273–2.300 Å; values from Canales *et al.* (1997) are given first]. The Fe atom lies 1.652 (3) Å out of each cyclopentadienyl (Cp) ring. The P—Au—Cl axis is rotated by 30.7 (5)° out of the Cp plane, as defined by the torsion angle C2—C1—P—Au. For the phenyl rings, the corresponding angles are C12—C11—P—Au = 54.5 (5)° and C22—C21—P—Au = −0.1 (6)°. The Au···Fe distance within the molecule is 4.1458 (7) Å. The shortest Au···Au^i contact is 6.3212 (13) Å [symmetry code: (i) $-x, 1-y, 1-z$]. Because of the imposed symmetry, the Cp rings are exactly parallel and ideally stag-

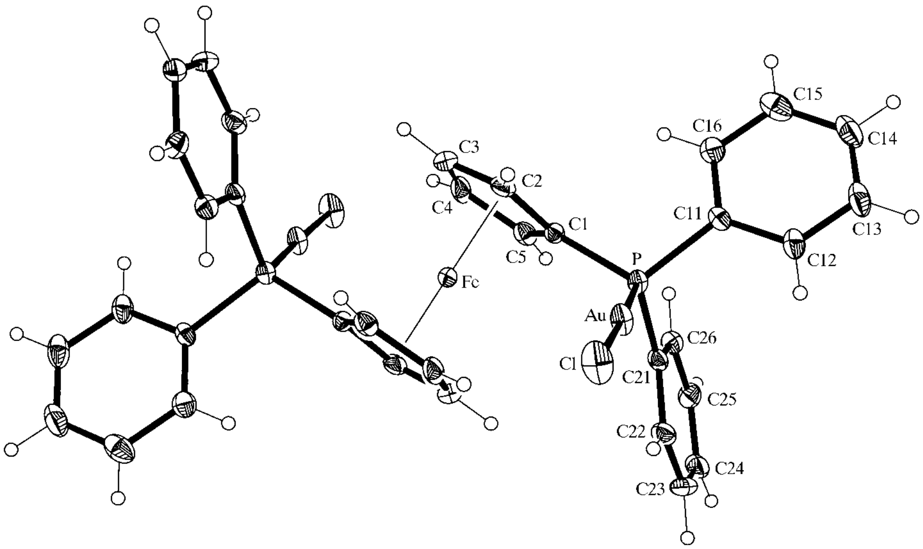


Figure 1
The molecular structure of the title compound. Ellipsoids are drawn at the 50% probability level and H atom radii are arbitrary. Only the asymmetric unit is numbered.

gered, and the torsion angle P$\cdots$*Cent*$\cdots$*Cent*$\cdots$P (*Cent* is the centre of the Cp ring) is exactly 180°.

The structure previously reported by Canales *et al.* (1997) shows little difference to that of (I). The corresponding C—C—P—Au torsion angle from the Cp ring is 30.9 (5)°; the other rings display some differences from (I), with torsion angles of 51.8 (4) and 18.9 (5)°. In the absence of any unusually short intermolecular contacts (Table 2 shows some borderline non-classical interactions, but these are unlikely to have a great influence), one must conclude that the energy balance between the two forms, which both crystallize from dichloromethane/hydrocarbon mixtures, is very delicate.

In contrast, the structure of Hill *et al.* (1989) displays some marked differences to that of (I), especially in the molecule without imposed symmetry. The Cp rings are slightly non-parallel (interplanar angle 3°) and non-ideally staggered (*e.g.* torsion angle C35$\cdots$*Cent*$\cdots$*Cent*$\cdots$C32 of 20.4°), and the angle P2$\cdots$*Cent*$\cdots$*Cent*$\cdots$P3 narrows to −125°. Additionally, there are short Au$\cdots$Au contacts of 3.083 (1) Å between the gold centres of the two molecules. More minor differences are also shown in the ring torsion angles (*e.g.* C_{Cp}—C_{Cp}—P—Au −21.1° for the symmetric molecule, and 38.1 and 31.7° for the non-symmetric molecule). The total of these differences can well account for, or at least be consistent with, the formation of a different crystalline form of (I).

Experimental

Crystals were obtained by slow diffusion of *n*-heptane into a dichloromethane solution of (I).

Crystal data

$[Au_2Cl_2\{Fe(C_{17}H_{14}P)_2\}]$
M_r = 1019.18
Monoclinic, $P2_1/n$
a = 9.038 (2) Å
b = 19.130 (4) Å
c = 9.930 (2) Å
β = 108.79 (2)°
V = 1625.4 (6) Å^3
Z = 2

D_x = 2.082 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 65 reflections
θ = 10–25°
μ = 9.730 mm^{-1}
T = 173 (2) K
Tablet, brown
0.20 × 0.15 × 0.10 mm

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: ψ scan (*XPREP*; Siemens, 1994)
T_{min} = 0.212, T_{max} = 0.378
3539 measured reflections
2859 independent reflections
2037 reflections with $I > 2\sigma(I)$

R_{int} = 0.034
θ_{max} = 25°
h = −10 → 2
k = 0 → 22
l = −11 → 11
3 standard reflections every 247 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.071
S = 0.899
2859 reflections
187 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0362P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.05 e Å^{-3}
$\Delta\rho_{min}$ = −1.01 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Au—P	2.2261 (18)	Au—Cl	2.2781 (18)
P—Au—Cl	177.56 (8)	C11—P—Au	114.1 (2)
C1—P—Au	111.0 (2)	C21—P—Au	114.2 (2)

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

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
C4—H4$\cdots$Au^{i}	0.95	2.94	3.627 (8)	130
C26—H26$\cdots$Cl^{ii}	0.95	2.93	3.550 (8)	124
C14—H14$\cdots$Cl^{iii}	0.95	2.85	3.770 (8)	163
C15—H15$\cdots$Cl^{iv}	0.95	2.96	3.681 (10)	134
C24—H24$\cdots$Au^{v}	0.95	3.11	3.859 (8)	137

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $x, y, z-1$; (iii) $x-1, y, z-1$; (iv) $-x, 1-y, 1-z$; (v) $\frac{1}{2}+x, \frac{3}{2}-y, z-\frac{1}{2}$.

A total of 56 restraints were applied, involving local phenyl-ring symmetry (*FLAT*/*SAME* in *SHELXL*97; Sheldrick, 1997). H atoms were included using a riding model, starting from idealized positions. The largest feature of residual electron density (1.06 e Å^{-3}) lies 0.98 Å from the Au atom.

Data collection: *XSCANS* (Fait, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97; molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1433). Services for accessing these data are described at the back of the journal.

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