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Crystal structure of $(\mu_2\text{-}1,1'\text{-bis(diphenylphosphino)ferrocene-}\kappa^2P,P')\text{-bis}[(Z)N\text{-(3-fluorophenyl)-}O\text{-methylthiocarbamato-}S]\text{digold(I) chloroform solvate, } C_{50}H_{42}Au_2F_2FeN_2O_2P_2S_2, CHCl_3$

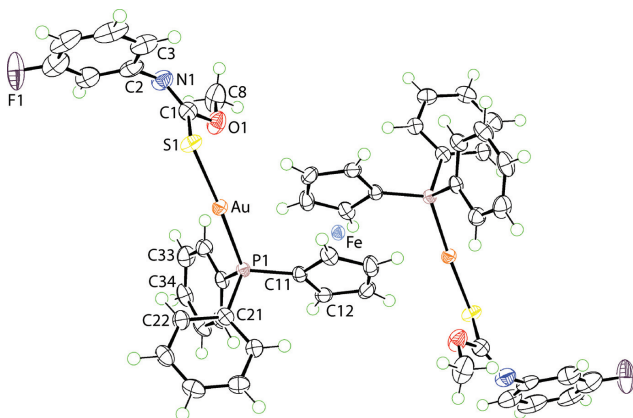


Table 1: Data collection and handling.

Crystal:	Yellow prism
Size:	0.17 × 0.05 × 0.04 mm
Wavelength:	Cu K α radiation (1.54184 Å)
μ :	16.4 mm ⁻¹
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{\max} , completeness:	75.3°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	123988, 5168, 0.032
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 5144
$N(\text{param})_{\text{refined}}$:	333
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

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Abstract

$C_{51}H_{43}Au_2Cl_3F_2FeN_2O_2P_2S_2$, triclinic, $P\bar{1}$ (no. 2), $a = 8.3276(1)$ Å, $b = 13.1116(1)$ Å, $c = 13.5547(1)$ Å, $\alpha = 110.309(1)^\circ$, $\beta = 103.132(1)^\circ$, $\gamma = 105.601(1)^\circ$, $V = 1249.86(2)$ Å³, $Z = 1$, $R_{\text{gt}}(F) = 0.0153$, $wR_{\text{ref}}(F^2) = 0.0387$, $T = 100(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

NaOH (Merck; 0.020 g, 0.50 mmol) in water (5 mL) was added to a suspension of (1,1'-bis(diphenylphosphino)ferrocene)(AuCl)₂ (0.255 g, 0.25 mmol) in acetonitrile (20 mL), followed by the addition of MeOC(=S)N(H)C₆H₄F-3

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Au	0.45643(2)	0.34168(2)	0.77818(2)	0.01626(3)
Fe	1.000000	0.500000	1.000000	0.01450(9)
S1	0.31541(8)	0.37156(5)	0.62939(4)	0.02324(11)
P1	0.57851(7)	0.30475(4)	0.92180(4)	0.01350(9)
O1	0.5854(2)	0.33053(16)	0.58040(14)	0.0294(4)
N1	0.3507(3)	0.28430(19)	0.42603(17)	0.0278(4)
C1	0.4183(3)	0.3229(2)	0.53228(19)	0.0233(4)
F1 ^a	−0.2568(3)	0.0653(2)	0.2115(3)	0.0487(10)
C2 ^a	0.1761(3)	0.2779(2)	0.37891(19)	0.0272(5)
C3 ^a	0.1425(4)	0.3784(3)	0.3867(2)	0.0348(6)
H3 ^a	0.236784	0.453628	0.425506	0.042*
C4 ^a	−0.0305(4)	0.3671(3)	0.3372(2)	0.0420(7)
H4 ^a	−0.053256	0.436184	0.344892	0.050*
C5 ^a	−0.1700(4)	0.2598(3)	0.2775(2)	0.0397(7)
H5 ^a	−0.287719	0.253455	0.243817	0.048*
C6 ^a	−0.1319(4)	0.1622(3)	0.2688(2)	0.0388(6)
C7 ^a	0.0372(3)	0.1682(2)	0.3175(2)	0.0303(5)
H7 ^a	0.058289	0.098518	0.309305	0.036*
F1 ^b	−0.0843(5)	0.4492(3)	0.3442(3)	0.0363(12)
C2 ^b	0.1761(3)	0.2779(2)	0.37891(19)	0.0272(5)
C3 ^b	0.1425(4)	0.3784(3)	0.3867(2)	0.0348(6)
H3 ^b	0.236784	0.453628	0.425506	0.042*
C4 ^b	−0.0305(4)	0.3671(3)	0.3372(2)	0.0420(7)
C5 ^b	−0.1700(4)	0.2598(3)	0.2775(2)	0.0397(7)
H5 ^b	−0.287719	0.253455	0.243817	0.048*
C6 ^b	−0.1319(4)	0.1622(3)	0.2688(2)	0.0388(6)
H6 ^b	−0.226204	0.087084	0.227218	0.047*
C7 ^b	0.0372(3)	0.1682(2)	0.3175(2)	0.0303(5)
H7 ^b	0.058289	0.098518	0.309305	0.036*
C8	0.6778(4)	0.2941(3)	0.5045(2)	0.0387(6)
H8A	0.614528	0.210000	0.454137	0.058*

Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
H8B	0.799639	0.308510	0.548048	0.058*
H8C	0.681881	0.339014	0.459848	0.058*
C11	0.7782(3)	0.42193(17)	1.02663(17)	0.0153(4)
C12	0.9308(3)	0.4161(2)	1.09540(18)	0.0196(4)
H12	0.946794	0.346465	1.093458	0.024*
C13	1.0537(3)	0.5332(2)	1.16701(18)	0.0256(5)
H13	1.166715	0.555670	1.221521	0.031*
C14	0.9786(3)	0.6112(2)	1.14312(19)	0.0263(5)
H14	1.033045	0.694599	1.179118	0.032*
C15	0.8096(3)	0.54384(18)	1.05696(18)	0.0201(4)
H15	0.730718	0.573791	1.024820	0.024*
C21	0.4276(3)	0.27759(17)	0.99589(17)	0.0159(4)
C22	0.2548(3)	0.19333(19)	0.93185(19)	0.0201(4)
H22	0.220999	0.151187	0.852737	0.024*
C23	0.1329(3)	0.1714(2)	0.9838(2)	0.0235(4)
H23	0.015681	0.113932	0.940316	0.028*
C24	0.1816(3)	0.2331(2)	1.0993(2)	0.0235(4)
H24	0.097664	0.217616	1.134673	0.028*
C25	0.3520(3)	0.3173(2)	1.16331(19)	0.0225(4)
H25	0.384615	0.359716	1.242283	0.027*
C26	0.4757(3)	0.33958(18)	1.11171(18)	0.0183(4)
H26	0.592789	0.397064	1.155553	0.022*
C31	0.6231(3)	0.17129(17)	0.87648(17)	0.0166(4)
C32	0.6276(3)	0.12053(19)	0.76878(19)	0.0220(4)
H32	0.617237	0.159307	0.721449	0.026*
C33	0.6473(3)	0.0129(2)	0.7303(2)	0.0263(5)
H33	0.651058	−0.021340	0.656980	0.032*
C34	0.6613(3)	−0.04423(19)	0.7986(2)	0.0251(5)
H34	0.672344	−0.118317	0.771493	0.030*
C35	0.6594(3)	0.00602(19)	0.9064(2)	0.0229(4)
H35	0.670834	−0.033015	0.953438	0.028*
C36	0.6408(3)	0.11374(18)	0.94581(19)	0.0191(4)
H36	0.640025	0.148349	1.019900	0.023*
C41 ^c	0.0333(7)	0.0640(5)	0.5186(4)	0.0343(12)
H41 ^c	0.069902	0.128863	0.495681	0.041*
Cl1 ^c	−0.0393(2)	0.11231(13)	0.63193(12)	0.0438(3)
Cl2 ^c	0.2189(2)	0.02762(16)	0.56068(19)	0.0580(4)
Cl3 ^c	−0.1383(3)	−0.05837(18)	0.40422(15)	0.0766(7)

^aOccupancy: 0.592(5), ^bOccupancy: 0.408(5), ^cOccupancy: 0.5.

[5] (0.093 g, 0.50 mmol) in acetonitrile (20 mL) and stirred for 3 h. The resulting mixture was left for slow evaporation at room temperature, yielding crystals after 4 weeks. Yield: 0.240 g (73%). **M. pt.** (Biobase automatic melting point apparatus MP450): 451–452 K. **Elemental Analysis** for C₅₀H₄₂Au₂F₂FeN₂O₂P₂S₂ (Leco TruSpec Micro CHN Elemental Analyser): C, 45.61; H, 3.22; N, 2.13%. Found: C, 45.21; H, 4.23 N, 2.41%. **IR** (Bruker Vertex 70v FTIR Spectrophotometer; cm^{−1}): 1435 (s) ν(C=N), 1140 (s) ν(C=O), 1091 (s) ν(C–S). **¹H NMR** (Bruker Ascend 400 MHz NMR spectrometer with chemical shifts relative to Me₄Si in CDCl₃ solution at 298 K, ppm): δ 7.49–7.43 (m, br, 20H, Ph₂P), 7.07 (dt, 2H, aryl-H5, ⁴J_{HF} = 7.11 Hz, ³J_{HH} = 7.31 Hz), 6.67–6.61 (m, br, 4H,

aryl-H2,6), 6.54–6.50 (m, br, 2H, aryl-H4), 4.69 (s, 4H, PC₅H₄), 4.26 (s, 4H, PC₅H₄), 3.89 (s, 6H, OCH₃). **¹³C{¹H} NMR** (as for ¹H NMR): δ 165.2 (C_q), 163.1 (d, aryl-C3, ¹J_{CF} = 244.29 Hz), 152.5 (d, aryl-C1, ³J_{CF} = 10.23 Hz), 133.6 (d, m-PC₅H₅, ³J_{CP} = 14.10 Hz), 131.7 (d, p-PC₅H₅, ⁴J_{CP} = 2.44 Hz), 130.6 (d, i-PC₅H₅, ¹J_{CP} = 58.83 Hz), 129.7 (d, aryl-C5, ³J_{CF} = 9.56 Hz), 129.0 (d, o-PC₅H₅, ²J_{CP} = 11.51 Hz), 117.8 (d, aryl-C6, ⁴J_{CF} = 2.60 Hz), 109.3 (d, aryl-C2, ²J_{CF} = 21.13 Hz), 109.2 (d, aryl-C4, ²J_{CF} = 22.02 Hz), 75.1 (d, β-PC₅H₄, ²J_{CP} = 8.32 Hz), 74.8 (d, γ-PC₅H₄, ³J_{CP} = 13.29 Hz), 71.8 (d, α-PC₅H₄, ¹J_{CP} = 65.83 Hz), 55.4 (OCH₃). **³¹P{¹H} NMR** (as for ¹H NMR but with chemical shift referenced to 85% aqueous H₃PO₄ as the external reference): δ 33.1. Crystals of (I) for the X-ray structure determination were grown from the slow evaporation of chloroform solution of (I) and analysed directly.

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–1.00 Å) and refined as riding with $U_{iso}(H) = 1.2–1.5U_{eq}(C)$. The 3-fluorophenyl ring was disordered over two co-planar orientations so the C atoms were exactly coincident but, two positions were apparent for the F atoms; the latter were refined independently. At the conclusion of the refinement, the major component of the ring had a site occupancy factor of 0.592(5). The solvent chloroform molecule was statistically disordered about a centre of inversion.

Comment

A recent report [6] describing the crystallographic characterisation of dppf[Au[SC(O-iPr)=NC₆H₄Cl-4]]₂ highlighted the structural diversity in these molecules; dppf is 1,1'-bis(diphenylphosphino)ferrocene. This diversity relates to the global conformations of the molecules with the important consequence being the formation or otherwise of intramolecular Au···Au (aurophilic) bonds. Thus, for the formulation dppf[Au[SC(OR)=NC₆H₄Y]]₂, when R = Me and Y = NO₂ [7] and R = iPr and Y = NO₂ [8], the molecule has an A-frame conformation which allows for the formation of an intramolecular Au···Au interaction. This is facilitated by the molecules having crystallographic 2-fold symmetry. By contrast, the other known structures adopt a motif where the Fe atom is located on a centre of inversion indicating the molecule has an open or extended conformation which precludes the formation of intramolecular Au···Au interactions. The structures adopting this second motif have R = iPr and Y = 4-Cl [6], R = Et and Y = H [9] and R = iPr and Y = 4-Me [10]. Herein, a new member of the dppf[Au[SC(OR)=NC₆H₄Y]]₂ series is described, namely that with R = Me and Y = 3-F, isolated as a chloroform solvate.

The molecular structure of the binuclear species in (I) is shown in the figure (70% displacement ellipsoids; unlabelled atoms are related by the symmetry operation $(i) 2-x, 1-y, 2-z$; minor disorder component and solvent molecule are omitted). The Fe atom is situated on a centre of inversion so the crystallographic asymmetric unit comprises half a binuclear molecule. There is also a solvent chloroform molecule in the asymmetric unit, which is statistically disordered about a centre of inversion, so the overall formulation of (I) is $dppf[Au\{SC(OMe)=NC_6H_4F-3\}]_2 \cdot CHCl_3$. The gold(I) atom exists in a linear geometry with the P1–Au–S1 angle being $176.615(19)^\circ$ as this atom is coordinated by phosphane-P [Au–P1 = $2.2533(5)$ Å] and thiolate-S [Au–S1 = $2.3065(5)$ Å] atoms. A common feature of all the reported $dppf[Au\{SC(OR)=NC_6H_4Y-4\}]_2$ structures is the formation of an intramolecular $Au \cdots O$ interaction as the thiolate ligand is orientated to place the O atom in close proximity to the Au atom. In (I), the $Au \cdots O$ separation amounts to $3.0794(18)$ Å].

Owing to the disorder in the fluorophenyl residue, a complete description of the molecular packing for (I) is precluded. Indeed, according to an analysis of the packing employing PLATON [11], there are no directional interactions between the constituents of (I). Globally, the binuclear molecules stack into columns parallel to the a -axis and define channels in which reside the chloroform molecules.

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