

Chien Ing Yeo and Edward R.T. Tiekink\*

# Crystal structure of $(\mu_2$ -1,1'-bis(diphenylphosphino)ferrocene-*P,P'*)-bis[(*Z*)-*O*-isopropyl *N*-(4-chlorophenyl)thiocarbamato-*S*]-di-gold(I) acetonitrile di-solvate, $C_{54}H_{50}Au_2Cl_2FeN_2O_2P_2S_2 \cdot 2(C_2H_3N)$

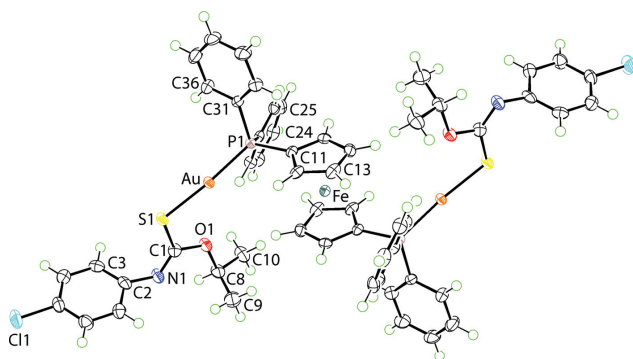


Table 1: Data collection and handling.

Crystal:	Yellow plate
Size:	0.26 × 0.17 × 0.04 mm
Wavelength:	Mo K $\alpha$ radiation (0.71073 Å)
$\mu$ :	5.73 mm <sup>-1</sup>
Diffractometer, scan mode:	SuperNova, $\omega$
$\theta_{\max}$ , completeness:	27.5°, >99%
$N(hkl)_{\text{measured}}$ , $N(hkl)_{\text{unique}}$ , $R_{\text{int}}$ :	32730, 6449, 0.059
Criterion for $I_{\text{obs}}$ , $N(hkl)_{\text{gt}}$ :	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$ , 6051
$N(\text{param})_{\text{refined}}$ :	334
Programs:	CrysAlis <sup>PRO</sup> [1], SHELX [2, 3], WinGX/ORTEP [4]

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## Abstract

$C_{58}H_{56}Au_2Cl_2FeN_4O_2P_2S_2$ , triclinic,  $P\bar{1}$  (no. 2),  $a = 8.5422(3)$  Å,  $b = 13.2143(4)$  Å,  $c = 14.0226(4)$  Å,  $\alpha = 65.764(3)^\circ$ ,  $\beta = 78.311(2)^\circ$ ,  $\gamma = 80.090(3)^\circ$ ,  $V = 1406.39(8)$  Å<sup>3</sup>,  $Z = 1$ ,  $R_{\text{gt}}(F) = 0.0213$ ,  $wR_{\text{ref}}(F^2) = 0.0477$ ,  $T = 100$  K.

CCDC no.: 2015449

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 (dppf)(AuCl)<sub>2</sub> (0.255 g, 0.25 mmol) in acetonitrile (20 mL), followed by addition of iPrOC(=S)N(H)C<sub>6</sub>H<sub>4</sub>Cl-4 (0.115 g, 0.50 mmol) in dichloromethane (20 mL). After stirring for 3 h, the solution was left for slow evaporation at room temperature, yielding yellow crystals after 3 weeks. Yield: 0.278 g (79%).

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**M. pt:** (Biobase automatic melting point apparatus MP450): 473–474 K.

Elemental Analysis for  $C_{54}H_{50}Au_2Cl_2FeN_2O_2P_2S_2$  (Leco TruSpec Micro CHN Elemental Analyser): C, 46.14; H, 3.58; N, 1.99%. Found: C, 46.03; H, 3.28; N, 1.86%. **IR** (Bruker Vertex 70v FTIR Spectrophotometer; cm<sup>-1</sup>): 1435 (s)  $\nu$ (C=N), 1140 (s)  $\nu$ (C–O), 1091 (s)  $\nu$ (C–S). **<sup>1</sup>H NMR** (Bruker Ascend 400 MHz NMR spectrometer with chemical shifts relative to tetramethylsilane in CDCl<sub>3</sub> solution at 298 K, ppm):  $\delta$  7.50–7.40 (m, br, 20H, Ph<sub>2</sub>P), 7.07 (d, 4H, m-aryl-H,  $J_{\text{HH}} = 8.52$  Hz), 6.79 (d, 4H, o-aryl-H,  $J_{\text{HH}} = 8.48$  Hz), 5.29 (sept, 2H, OCH,  $J_{\text{HH}} = 6.17$  Hz), 4.64 (s, br, 4H,  $\beta$ -PC<sub>5</sub>H<sub>4</sub>), 4.21 (s, br, 4H,  $\gamma$ -PC<sub>5</sub>H<sub>4</sub>), 1.33 (d, 12H, CH<sub>3</sub>,  $J_{\text{HH}} = 6.20$  Hz). **<sup>13</sup>C{<sup>1</sup>H} NMR** (as for <sup>1</sup>H NMR):  $\delta$  163.6 (Cq), 149.8 (aryl,  $C_{\text{ipso}}$ ), 133.6 (d, m-PC<sub>6</sub>H<sub>5</sub>,  $^3J_{\text{CP}} = 14.02$  Hz), 131.7 (d, p-PC<sub>6</sub>H<sub>5</sub>,  $^4J_{\text{CP}} = 2.25$  Hz), 130.8 (d, i-PC<sub>6</sub>H<sub>5</sub>,  $^1J_{\text{CP}} = 58.57$  Hz), 129.0 (d, o-PC<sub>6</sub>H<sub>5</sub>,  $^2J_{\text{CP}} = 11.52$  Hz), 128.7 (aryl,  $C_{\text{meta}}$ ), 127.4 (aryl,  $C_{\text{para}}$ ), 123.3 (aryl,  $C_{\text{ortho}}$ ), 75.0 (d,  $\beta$ -PC<sub>5</sub>H<sub>4</sub>,  $^2J_{\text{CP}} = 8.46$  Hz), 74.8 (d,  $\gamma$ -PC<sub>5</sub>H<sub>4</sub>,  $^3J_{\text{CP}} = 13.15$  Hz), 71.8 (d,  $\alpha$ -PC<sub>5</sub>H<sub>4</sub>,  $^1J_{\text{CP}} = 65.48$  Hz), 70.6 (OCH), 22.2 (CH<sub>3</sub>). **<sup>31</sup>P{<sup>1</sup>H} NMR** (as for <sup>1</sup>H NMR but with chemical shift referenced to 85% aqueous H<sub>3</sub>PO<sub>4</sub> as the external reference):  $\delta$  32.6.

Crystals of (I) for the X-ray structure determination were grown from the slow evaporation of an acetonitrile 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  $U_{\text{iso}}(\text{H}) = 1.2$ –1.5  $U_{\text{eq}}(\text{C})$ . The maximum and minimum residual electron

**Table 2:** Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub> <sup>*</sup> / <i>U</i> <sub>eq</sub>
Au	0.63437(2)	0.01557(2)	0.79829(2)	0.01259(4)
Fe	1.000000	0.000000	1.000000	0.01140(11)
Cl1	0.30531(9)	−0.41350(7)	0.51971(6)	0.03149(18)
S1	0.56705(7)	−0.09673(6)	0.72579(5)	0.01631(14)
P1	0.69419(7)	0.14215(5)	0.85151(5)	0.01115(13)
O1	0.8815(2)	−0.09928(16)	0.67806(14)	0.0185(4)
N1	0.7767(3)	−0.2071(2)	0.62072(18)	0.0196(5)
C1	0.7534(3)	−0.1410(2)	0.6678(2)	0.0167(6)
C2	0.6508(3)	−0.2509(2)	0.6030(2)	0.0175(6)
C3	0.5600(3)	−0.1887(2)	0.5226(2)	0.0193(6)
H3	0.571185	−0.111362	0.484707	0.023*
C4	0.4526(3)	−0.2381(2)	0.4966(2)	0.0193(6)
H4	0.390654	−0.195181	0.441463	0.023*
C5	0.4377(3)	−0.3500(2)	0.5520(2)	0.0200(6)
C6	0.5270(3)	−0.4141(2)	0.6328(2)	0.0225(6)
H6	0.515209	−0.491324	0.670599	0.027*
C7	0.6335(3)	−0.3638(2)	0.6577(2)	0.0203(6)
H7	0.695383	−0.407050	0.712781	0.024*
C8	1.0411(3)	−0.1426(2)	0.6401(2)	0.0208(6)
H8	1.036905	−0.151679	0.573342	0.025*
C9	1.0896(4)	−0.2542(3)	0.7226(3)	0.0301(7)
H9A	1.010962	−0.306160	0.736061	0.045*
H9B	1.093678	−0.245513	0.788192	0.045*
H9C	1.195837	−0.283438	0.697280	0.045*
C10	1.1511(3)	−0.0545(3)	0.6167(2)	0.0241(6)
H3A	1.111529	0.015982	0.563525	0.036*
H3B	1.259812	−0.078303	0.589654	0.036*
H3C	1.153145	−0.043980	0.681625	0.036*
C11	0.7855(3)	0.0922(2)	0.96937(19)	0.0123(5)
C12	0.7605(3)	−0.0127(2)	1.0558(2)	0.0156(5)
H12	0.696711	−0.070811	1.058430	0.019*
C13	0.8422(3)	−0.0193(2)	1.1371(2)	0.0189(6)
H13	0.847480	−0.083630	1.206642	0.023*
C14	0.9189(3)	0.0796(2)	1.1017(2)	0.0185(6)
H14	0.986627	0.097186	1.142312	0.022*
C15	0.8839(3)	0.1491(2)	0.9984(2)	0.0165(5)
H15	0.921614	0.224289	0.953905	0.020*
C21	0.8292(3)	0.2338(2)	0.74741(19)	0.0127(5)
C22	0.9218(3)	0.1946(2)	0.6736(2)	0.0160(5)
H22	0.907810	0.123750	0.676131	0.019*
C23	1.0347(3)	0.2587(2)	0.5961(2)	0.0194(6)
H23	1.098916	0.231416	0.546289	0.023*
C24	1.0531(3)	0.3626(2)	0.5918(2)	0.0211(6)
H24	1.131216	0.406174	0.539390	0.025*
C25	0.9581(3)	0.4036(2)	0.6634(2)	0.0195(6)
H25	0.970266	0.475519	0.659216	0.023*
C26	0.8451(3)	0.3396(2)	0.7415(2)	0.0156(5)
H26	0.779454	0.367751	0.790232	0.019*
C31	0.5156(3)	0.2303(2)	0.8757(2)	0.0127(5)
C32	0.4632(3)	0.2343(2)	0.9748(2)	0.0181(6)
H32	0.526413	0.195654	1.030079	0.022*
C33	0.3183(3)	0.2950(2)	0.9932(2)	0.0227(6)
H33	0.282174	0.296676	1.061239	0.027*
C34	0.2270(3)	0.3527(2)	0.9127(2)	0.0252(7)
H34	0.128475	0.394374	0.925154	0.030*

**Table 2 (continued)**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub> <sup>*</sup> / <i>U</i> <sub>eq</sub>
C35	0.2801(3)	0.3494(3)	0.8139(2)	0.0262(7)
H35	0.217724	0.389728	0.758392	0.031*
C36	0.4225(3)	0.2882(2)	0.7947(2)	0.0196(6)
H36	0.456788	0.285674	0.726794	0.024*
N41	0.8023(4)	0.4581(3)	−0.0728(3)	0.0438(8)
C41	0.7217(4)	0.4258(3)	0.0054(3)	0.0322(7)
C42	0.6152(4)	0.3863(3)	0.1074(3)	0.0447(9)
H42A	0.626695	0.304563	0.138649	0.067*
H42B	0.503501	0.413410	0.096107	0.067*
H42C	0.644434	0.414601	0.155314	0.067*

density peaks of 1.15 and 1.02 eÅ<sup>−3</sup>, respectively, were located 0.99 Å and 0.66 Å, respectively, from the Au atom.

### Comment

The original interest in binuclear phosphane gold(I) thioamide molecules of the formula dppf{Au[SC(OR)=NC<sub>6</sub>H<sub>4</sub>Y-4]}<sub>2</sub> related to an investigation of the solid-state photoluminescent properties of the R=Me and Y=NO<sub>2</sub> derivative, isolated as a di-chloroform solvate [5]; dppf is 1,1'-bis(diphenylphosphino)ferrocene. Subsequently, crystal structure determinations for the R=Et and Y=H, as a dichloromethane solvate [6], and R=iPr with Y=Me [7] and Y=NO<sub>2</sub>, isolated as a di-chloroform solvate [8], species have been described. In this contribution, the crystal and molecular structures of the R=iPr and Y=Cl compound isolated as an acetonitrile di-solvate, (I), is described.

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*, −*y*, 2−*z*). The crystallographic asymmetric unit comprises half a binuclear molecule, as the Fe atom is situated on a centre of inversion, and a solvent acetonitrile molecule. The independent gold(I) atom adopts the expected linear geometry [P1—Au—S1 = 173.31(2)°], being coordinated by phosphane-P [Au—P1 = 2.2560(7) Å] and thiolate-S [Au—S1 = 2.3099(7) Å] atoms. The crystal structure of the uncoordinated ligand in its protonated form, i.e. iPrOC(=S)N(H)C<sub>6</sub>H<sub>4</sub>Cl-4, is available in the literature [9]. The C1—S1 [1.755(3) Å] and C1—N1 [1.265(3) Å] bond lengths in (I) are significantly elongated and contracted compared with the equivalent bonds, i.e. 1.6708(15) and 1.3388(18) Å, respectively, in the acid. As is uniformly found in dppf{Au[SC(OR)=NC<sub>6</sub>H<sub>4</sub>Y-4]}<sub>2</sub> structures, an intramolecular Au⋯O interaction is observed. In (I), the Au⋯O separation is 3.026(2) Å.

The molecular packing for (I) features P-phenyl-C—H⋯N(imino) [C23—H23⋯N1<sup>ii</sup>: H23⋯N1<sup>ii</sup> = 2.49 Å, C23⋯N1<sup>ii</sup> = 3.412(4) Å with angle at H23 = 163° for (ii)

$2-x, -y, 1-z]$  interactions that lead to the formation of supramolecular chains with a linear topology along the  $c$ -axis. The other directional interactions are of the type cyclopentadienyl- $C-H \cdots \pi$ (P-phenyl) [C12–H12 $\cdots$ Cg(C31–C36)<sup>iii</sup>: H12 $\cdots$ Cg(C31–C36)<sup>iii</sup> = 2.85 Å with angle at H12 = 156° for (iii)  $1-x, -y, 2-z]$  and chlorophenyl- $C-Cl \cdots \pi$ (P-phenyl) interactions are noted [C5–Cl1 $\cdots$ Cg(C21–C26)<sup>iv</sup>: Cl1 $\cdots$ Cg(C21–C26)<sup>iv</sup> = 3.4004(13) Å with angle at Cl1 = 129.10(10)° for (iv)  $1-x, -y, 1-z]$  which link chains into a supramolecular layer in the  $ac$ -plane. The layers stack along the  $b$ -axis without directional interactions between them. The closest contact between the binuclear and solvent acetonitrile molecules is a weak P-phenyl- $C-H \cdots N$ (acetonitrile) interaction [C26–H26 $\cdots$ N41<sup>v</sup>: H26 $\cdots$ N41<sup>v</sup> = 2.70 Å, C26 $\cdots$ N41<sup>v</sup> = 3.483(6) Å with angle at H26 = 141° for (v)  $x, y, 1+z]$ .

In order to assess the molecular packing further, the Hirshfeld surfaces were calculated along with the full and delineated two-dimensional fingerprint plots employing Crystal Explorer 17 [10] and literature procedures [11]. The most dominant contribution to the calculated surface is from  $H \cdots H$  contacts at 45.9% with the next most significant contribution coming from  $H \cdots C/C \cdots H$  contacts, at 23.1%. The percentage contribution from  $H \cdots N/N \cdots H$  contacts is 6.3% with characteristic spikes due to the  $C-H \cdots N$  interactions being apparent. Other significant contributions are made by  $H \cdots S/S \cdots H$  contacts [7.4%], at distances greater than van der Waals separation as well as contacts involving the chloride atom, i.e.  $H \cdots Cl/Cl \cdots H$  [7.6%] and  $C \cdots Cl/C \cdots Cl$  [3.1%]. The structure of the  $R = iPr$  with  $Y = Me$  derivative [7], (II), also features P-phenyl- $C-H \cdots N$ (imino) interactions leading to supramolecular chains as described for (I). Reflecting the absence of the chloride substituent present in (I), the  $H \cdots H$  surface contacts in (II) increases to 60.0% followed by  $H \cdots C/C \cdots H$  contacts at 25.0%.

Finally, it is noted that there are no  $Au \cdots Au$  (aurophilic) interactions in (I), nor are they observed in (II) [7] and in the  $R = Et$  and  $Y = H$  compound [6]. These three structures have the common feature of having the iron atom located on a centre of inversion. By contrast, the two structures with  $R = Me$  and  $Y = NO_2$  [5] and  $R = iPr$  and  $Y = NO_2$  [8]

are 2-fold symmetric and feature intramolecular  $Au \cdots Au$  interactions.

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