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Synthesis and crystallographic studies of 2-(diphenylphosphinothioyl)-2-(3-oxobut-1-en-yl)-ferrocene

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Keywords: crystal structure; organometallic chemistry; 2-(diphenylphosphinothioyl)-2-(3-oxobut-1-en-yl)ferrocene chemistry; aldol/elimination reaction.

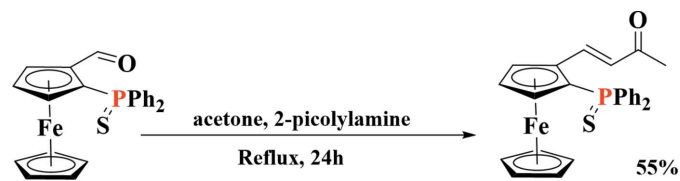
CCDC reference: 2099273

Supporting information: this article has supporting information at journals.iucr.org/e

As a follow-up to our research on the chemistry of disubstituted ferrocene derivatives, the synthesis and the structure of the title compound, 2-(diphenylphosphinothioyl)-2-(3-oxobut-1-en-yl)ferrocene, $[\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_{21}\text{H}_{18}\text{OPS})]$, are described. The molecule is built up from a ferrocene unit disubstituted by an S-protected diphenylphosphine group and by a methylvinylketone chain. The crystal structure features weak C—H···O and C—H···S interactions, which build a two-dimensional network. This structure is compared to that of the related disubstituted diphenylphosphino ferrocene.

1. Chemical context

Over the last few years, our team has developed several bidentate phosphine-containing planar chiral ferrocene ligands and tested them in various asymmetric catalytic reactions (Manoury & Poli, 2011). In particular, some P,O ligands were synthesized from 2-(diphenylphosphinothioyl)ferrocenecarboxaldehyde (Mateus *et al.*, 2006). This compound can be easily obtained as a racemic mixture or as each pure enantiomer and bears a versatile aldehyde function, which can be used to obtain more complex molecules. In this context, we were delighted to report a new and efficient aldol/elimination reaction of the aldehyde group to yield the corresponding enone under mild conditions (see Scheme) using a weak base (*pK*_a of 2-picoyl amine is 8.60; Milette *et al.*, 2010).



Similar compounds have been synthesized but using the Wittig reaction, which requires the synthesis of a specific phosphonium reagent and the use of a strong base, such as *n*-butyllithium (Ye *et al.*, 2017; Schaarschmidt *et al.*, 2014; Štěpnička *et al.* 2008) or sodium hydride (Stepnicka *et al.*, 2008). Indeed, the aldol/elimination sequence has been used to functionalize ferrocenecarboxaldehyde, which is a much less crowded analog of 2-(diphenylphosphinothioyl)ferrocenecarboxaldehyde but with a much stronger base such as NaOH, KOH or *t*BuOK (see, for instance, Achelle *et al.*, 2012; Romanov *et al.*, 2015; Li *et al.*, 2020; Wiczorek *et al.*, 2016).

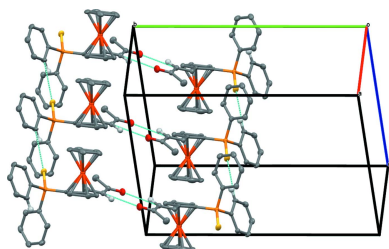


Table 1
Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C22—H22···O1 ⁱ	0.95	2.63	3.548 (4)	164
C112—H112···S1 ⁱⁱ	0.95	2.83	3.576 (3)	136
C116—H116···S1	0.95	2.89	3.374 (3)	113
C21—H21···S1	0.95	2.87	3.604 (3)	135

Symmetry codes: (i) $-x + 1, -y + 2, -z + 1$; (ii) $x - 1, y, z$.

2. Structural commentary

The molecule is built up from a ferrocene unit disubstituted by an *S*-protected diphenylphosphine group and by a methylvinylketone chain (Fig. 1). As is usually observed for thio-phenylphosphine ferrocenyl derivatives, the P atom is roughly in the plane of the Cp ring, deviating from the mean plane by -0.034 (5) Å, whereas the S atom is offset from this plane by 1.159 (6) Å. The two Cp rings have a staggered conformation with a twist angle of *ca* 37.1°. The O atom is *trans* to the ferrocene unit with respect to the C=C double bond. The torsion angle of the C2—C21—C22—C23 chain is 172.4 (4)° and the plane containing the double bond is twisted with respect to the Cp ring by 22.8 (2)°. This molecule has a planar chirality related to the occurrence of two different substituents on the Cp ring; however, as the space group is centrosymmetric, the two enantiomers *R/S* are present in equal numbers within the crystal. Two intramolecular C—H···S interactions occur (Table 1).

3. Supramolecular features

The packing of the structure is stabilized by weak C—H···O and C—H···S interactions (Table 1). The C—H···O interaction results in the formation of a pseudo-dimer through an $R_2^2(8)$ graph-set motif (Etter *et al.*, 1990; Bernstein *et al.*, 1995) (Fig. 2). The C—H···S interactions build up a chain parallel to the *b* axis and these chains are further associated by the C—

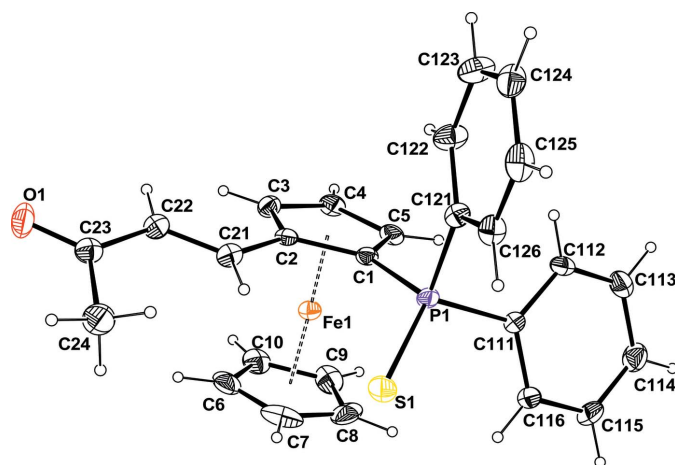


Figure 1
Molecular structure of the title compound with the atom-labeling scheme. Ellipsoids are drawn at the 50% probability level and the H atoms are represented as small circle of arbitrary radii.

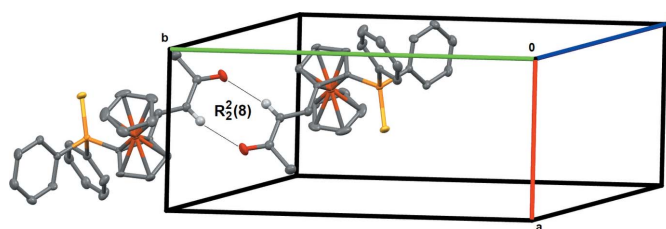


Figure 2
Partial packing view showing the formation of the $R_2^2(8)$ pseudo-ring arranged around the $(1/2, 1, 1/2)$ inversion center.

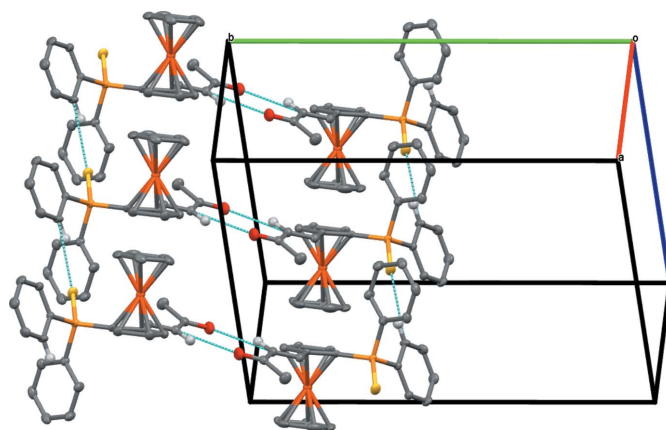


Figure 3
Partial packing view showing the formation of the ribbon parallel to the $(0\bar{1}1)$ plane.

H···O interactions of the pseudo-dimer, building a ribbon parallel to the $(0\bar{1}1)$ plane (Fig. 3).

4. Database survey

A search of the Cambridge Structural Database (CSD version 5.42, update 2020.3; Groom *et al.*, 2016) does not reveal any structures with ferrocenyl disubstituted by a thiodiphenylphosphine and a vinyl; however, a search using a fragment containing a ferrocenyl disubstituted by an unprotected phosphine and a vinyl substituent (Fig. 4) reveals 15 hits of which seven can be compared with the title compound, having only different substituents R^1 and R^2 (Fig. 4). A comparison of C—C and C—P distances and dihedral angles between the Cp ring

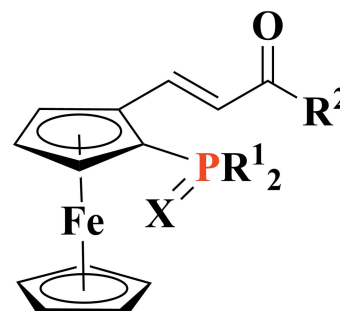


Figure 4
The model used for the CCDC search.

Ref	X	C2-C21	C21-C22	C22-C23	C1-P1	Cp1/C2>C23	R ¹	R ²
Title compound	S	1.459 (4)	1.340 (4)	1.470 (4)	1.795 (3)	22.8 (2)	Ph	Me
BETBOU	Lone pair	1.454	1.334	1.465	1.819	6.7		Ph
CIVHAR	Lone pair	1.448	1.330	1.467	1.818	9.7	Ph	C(O)Me
KOBXUW	Lone pair	1.460	1.326	1.472	1.819	8.5		Ph
KOBYAD	Lone pair	1.456	1.321	1.469	1.827	17.7		Ph
KOBYEH	Lone pair	1.466	1.336	1.469	1.805	6.4		Ph
KOCLEV	Lone pair	1.455	1.334	1.460	1.811	12.3	Ph	
KOCLIZ	Lone pair	1.458	1.331	1.468	1.812	13.9	Ph	
WIXYAD	Lone pair	1.469	1.323	1.462	1.804	13.1	Ph	

Figure 5

Comparison of bond distances (Å) and dihedral angles between the substituted Cp ring (Cp1) and the vinyl mean plane (°) for closely related compounds (CIVHAR: Stepnicka *et al.*, 2008; BETBOU: Kehr *et al.*, 2017; KOB***: Schaarschmidt *et al.*, 2014; WIXYAD: Iftime *et al.*, 2000).

and vinyl mean plane are shown in Fig. 5. Clearly the substituent on the phosphine has some influence on the C–P bond lengths, which range from 1.795 (3) Å for the title compound to 1.827 Å for the [η^5 -1-dicyclohexylphosphino-2-(2-phenylethenyl)cyclopentadienyl](η^5 -cyclopentadienyl)-iron compound (Schaarschmidt *et al.*, 2014) in which the phosphine bears two cyclohexyl substituents that are rather bulky. The occurrence of the S atom attached to the phosphine in the title compound may explain why the shortest value observed for the title compound. There is no significant difference in the C–C bonds within the vinyl moiety, showing that these values are not affected by the substituent, whereas the discrepancy observed for the dihedral angles between the vinyl unit and the Cp rings (6.4 to 22.8°) is related to the nature of the R¹ and R² substituents on the vinyl unit. The largest value of 22.8°, observed for the title compound, is related to the weak C21–H21...S1 interaction.

5. Synthesis and crystallization

To a solution of 2-(diphenylphosphinothioyl)ferrocene-carboxaldehyde (220 mg, 0.51 mmol) in acetone (40 mL) was added 2-picolyamine (0.2 mL, 1.53 mmol). The reaction mixture was refluxed for 24–36h with TLC monitoring of the consumption of aldehyde. After complete consumption, the reaction mixture was evaporated *in vacuo* and extracted with dichloromethane and washed with three portions of water. The combined organic layers were dried over Na₂SO₄, filtered and evaporated to dryness. The crude material was purified by silica gel column chromatography with a hexane–ether mixture (1/1, v/v) to obtain the product as a red solid (0.13 g, 55%). Monocrystals suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a dichloromethane solution of 4-(2-thiodiphenylphosphinoferrocenyl)-but-3-ene-one.

¹H NMR (ppm, CD₂Cl₂): δ 8.46 (1H, *d*, *J* = 16.3Hz, vinyl); 7.90–7.80 (*m*, 1H, Ph); 7.65–7.15 (9H, *m*, Ph); 6.28 (1H, *d*, *J* =

Table 2

Experimental details.

Crystal data	[Fe(C ₅ H ₅)(C ₂₁ H ₁₈ OPS)]
Chemical formula	470.32
<i>M_r</i>	Monoclinic, <i>P</i> ₂ /c
Crystal system, space group	Temperature (K)
Temperature (K)	110
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.3643 (9), 17.909 (2), 16.710 (2)
β (°)	95.230 (4)
<i>V</i> (Å ³)	2194.8 (5)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.87
Crystal size (mm)	0.1 × 0.07 × 0.01
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (SADABS; Krause <i>et al.</i> , 2015)
<i>T</i> _{min} , <i>T</i> _{max}	0.673, 0.730
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	43009, 5657, 3907
<i>R</i> _{int}	0.113
(sin θ/λ) _{max} (Å ⁻¹)	0.688
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.053, 0.144, 1.03
No. of reflections	5657
No. of parameters	272
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	1.43, -0.50

Computer programs: APEX2 and SAINT (Bruker, 2015), SHELXT (Sheldrick, 2015a), SHELXL2018 (Sheldrick, 2015b), ORTEP3 (Burnett & Johnson, 1996); ORTEP-3 for Windows (Farrugia, 2012) and Mercury (Macrae *et al.*, 2020).

16.3Hz, vinyl); 5.01 (1H, *m*, subst. Cp); 4.65 (1H, *m*, subst. Cp); 4.39 (5H, *s*, subst. Cp); 4.07 (1H, *m*, subst. Cp); 3.87 (3H, *s*, CH₃).

¹³C NMR (ppm, CD₂Cl₂): δ 198.16 (*s*, C=O); 143.46 (*s*, vinyl); 134.93 (δ , *J*_{CP} = 87.4Hz, quat Ph); 133.01 (δ , *J*_{CP} = 86.6Hz, quat Ph); 132.03 (δ , *J*_{CP} = 11.0Hz, CH Ph); 131.69 (δ , *J*_{CP} = 10.7Hz, CH Ph); 131.54 (δ , *J*_{CP} = 3.0Hz, CH Ph *para*); 131.39 (δ , *J*_{CP} = 3.0Hz, CH Ph *para*); 128.40 (δ , *J*_{CP} = 12.5Hz, CH Ph); 128.19 (δ , *J*_{CP} = 12.4Hz, CH Ph); 126.89 (*s*, vinyl); 83.06 (δ , *J*_{CP} = 10.7Hz, quat Cp); 77.44 (δ , *J*_{CP} = 11.9Hz, subst Cp); 77.00 (δ , *J*_{CP} = 93.2Hz, quat Cp); 71.87 (*s*, Cp); 71.85 (δ , *J*_{CP} = 10.3Hz, subst Cp); 69.90 (δ , *J*_{CP} = 8.4Hz, subst Cp); 25.87 (*s*, CH₃).

³¹P NMR (δ , ppm, CD₂Cl₂): δ 41.01.

HRMS (DCI, CH₄): 471.0638 (100%, calculated for C₂₆H₂₄FeOPS [*M*] 471.0635).

M.p.: 441 K (dec).

IR (ATR mode, diamond crystal): ν_{\max} (solid)/cm⁻¹: 1630 (*s*), 1607 (*s*), 1677 (*w*), 1364 (*m*), 1335 (*m*), 1264 (*s*), 1226 (*m*), 1165 (*s*), 1099 (*s*), 1055 (*m*), 987 (*s*), 863 (*w*), 832 (*m*), 822 (*s*), 760 (*s*), 7478 (*m*), 712 (*s*), 698 (*s*), 690 (*s*), 660 (*s*), 640 (*s*), 614 (*sm*), 583 (*m*), 534 (*s*).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms attached to C atoms were fixed geometrically and treated as riding with C–H =

0.95 Å (aromatic) or 0.98 Å (methyl) with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{CH aromatic})$ or $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{CH}_3)$. In the final difference-Fourier map, there is a large residual density, 1.43 e Å⁻³ in the vicinity (1.20 Å) of the H24A atom of the terminal methyl group; it is roughly located in the (100) plane; no chemically logical explanation could be found to explain this residual density.

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Uchchhal Bandyopadhyay, Basker Sundararaju, Rinaldo Poli, Eric Manoury and Jean-Claude Daran

Computing details

Data collection: *APEX2* (Bruker, 2015); cell refinement: *SAINT* (Bruker, 2015); data reduction: *SAINT* (Bruker, 2015); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *ORTEP-III* (Burnett & Johnson, 1996); *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *SHELXL2018* (Sheldrick, 2015b).

2-(Diphenylphosphinothioyl)-2-(3-oxobut-1-en-yl)ferrocene

Crystal data

[Fe(C₅H₅)(C₂₁H₁₈OPS)]

$M_r = 470.32$

Monoclinic, $P2_1/c$

$a = 7.3643$ (9) Å

$b = 17.909$ (2) Å

$c = 16.710$ (2) Å

$\beta = 95.230$ (4)°

$V = 2194.8$ (5) Å³

$Z = 4$

$F(000) = 976$

$D_x = 1.425$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 4518 reflections

$\theta = 2.7\text{--}24.2^\circ$

$\mu = 0.87$ mm⁻¹

$T = 110$ K

Platelet, orange yellow

$0.1 \times 0.07 \times 0.01$ mm

Data collection

Bruker APEXII CCD
diffractometer

Radiation source: micro-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan
(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.673$, $T_{\max} = 0.730$

43009 measured reflections

5657 independent reflections

3907 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.113$

$\theta_{\max} = 29.3^\circ$, $\theta_{\min} = 3.7^\circ$

$h = -10 \rightarrow 10$

$k = -24 \rightarrow 24$

$l = -22 \rightarrow 20$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.053$

$wR(F^2) = 0.144$

$S = 1.03$

5657 reflections

272 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0664P)^2 + 1.8414P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$

$$\Delta\rho_{\max} = 1.43 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.50 \text{ e } \text{\AA}^{-3}$$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Fe1	0.39674 (5)	0.81999 (2)	0.74273 (2)	0.01578 (14)
S1	0.61309 (10)	0.63480 (5)	0.64301 (5)	0.0248 (2)
P1	0.35129 (10)	0.65181 (4)	0.64545 (5)	0.01527 (18)
O1	0.7131 (3)	0.95064 (13)	0.44772 (14)	0.0292 (5)
C1	0.2847 (4)	0.74695 (16)	0.65962 (17)	0.0147 (6)
C2	0.3485 (4)	0.81389 (16)	0.62101 (17)	0.0151 (6)
C3	0.2527 (4)	0.87556 (17)	0.65055 (18)	0.0183 (6)
H3	0.267892	0.926260	0.635831	0.022*
C4	0.1317 (4)	0.84957 (18)	0.70518 (19)	0.0196 (6)
H4	0.051683	0.879705	0.732889	0.024*
C5	0.1495 (4)	0.77100 (17)	0.71171 (18)	0.0181 (6)
H5	0.084008	0.739506	0.744651	0.022*
C6	0.6382 (4)	0.8733 (2)	0.7754 (2)	0.0296 (8)
H6	0.699427	0.906469	0.742541	0.036*
C7	0.6625 (5)	0.7957 (2)	0.7792 (2)	0.0344 (9)
H7	0.742647	0.767350	0.749659	0.041*
C8	0.5462 (5)	0.7670 (2)	0.8349 (2)	0.0336 (9)
H8	0.534168	0.716032	0.849153	0.040*
C9	0.4507 (5)	0.8281 (2)	0.86554 (19)	0.0287 (8)
H9	0.363864	0.825418	0.904144	0.034*
C10	0.5090 (4)	0.89381 (19)	0.8279 (2)	0.0259 (7)
H10	0.467609	0.943108	0.836689	0.031*
C21	0.4977 (4)	0.81952 (17)	0.56951 (17)	0.0182 (6)
H21	0.573671	0.777207	0.564631	0.022*
C22	0.5325 (4)	0.88155 (17)	0.52879 (17)	0.0192 (6)
H22	0.446573	0.921101	0.528844	0.023*
C23	0.6929 (4)	0.89337 (17)	0.48403 (18)	0.0202 (6)
C24	0.8396 (5)	0.8344 (2)	0.4856 (2)	0.0289 (8)
H24A	0.918833	0.844327	0.442775	0.043*
H24B	0.783093	0.785139	0.477308	0.043*
H24C	0.912153	0.835465	0.537758	0.043*
C111	0.2541 (4)	0.60087 (16)	0.72528 (17)	0.0157 (6)
C112	0.0667 (4)	0.58941 (18)	0.72292 (18)	0.0207 (7)
H112	-0.010291	0.605709	0.677569	0.025*
C113	-0.0085 (4)	0.55449 (18)	0.78603 (19)	0.0246 (7)
H113	-0.136781	0.547765	0.784222	0.029*

C114	0.1032 (5)	0.52926 (19)	0.8520 (2)	0.0265 (7)
H114	0.051826	0.505580	0.895551	0.032*
C115	0.2907 (5)	0.53900 (19)	0.8537 (2)	0.0267 (7)
H115	0.367996	0.520842	0.898038	0.032*
C116	0.3662 (4)	0.57508 (17)	0.79095 (18)	0.0202 (6)
H116	0.494365	0.582127	0.792935	0.024*
C121	0.2198 (4)	0.62196 (17)	0.55413 (17)	0.0172 (6)
C122	0.0639 (5)	0.65958 (19)	0.5239 (2)	0.0258 (7)
H122	0.025180	0.702742	0.550738	0.031*
C123	-0.0366 (5)	0.63428 (19)	0.4543 (2)	0.0294 (8)
H123	-0.143308	0.660150	0.433628	0.035*
C124	0.0204 (5)	0.57107 (19)	0.41551 (19)	0.0257 (7)
H124	-0.046804	0.553753	0.367907	0.031*
C125	0.1738 (5)	0.53371 (18)	0.4459 (2)	0.0253 (7)
H125	0.211159	0.490163	0.419431	0.030*
C126	0.2746 (4)	0.55824 (17)	0.51434 (19)	0.0211 (7)
H126	0.381137	0.531932	0.534462	0.025*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe1	0.0149 (2)	0.0185 (2)	0.0138 (2)	0.00177 (17)	0.00064 (16)	-0.00037 (17)
S1	0.0137 (4)	0.0228 (4)	0.0384 (5)	0.0056 (3)	0.0057 (3)	0.0026 (3)
P1	0.0126 (4)	0.0148 (4)	0.0185 (4)	0.0030 (3)	0.0017 (3)	0.0020 (3)
O1	0.0346 (13)	0.0265 (13)	0.0273 (13)	-0.0097 (11)	0.0069 (10)	0.0070 (10)
C1	0.0107 (13)	0.0166 (15)	0.0165 (14)	0.0022 (11)	0.0000 (11)	0.0008 (11)
C2	0.0122 (13)	0.0180 (15)	0.0145 (14)	0.0019 (11)	-0.0022 (11)	0.0008 (11)
C3	0.0205 (15)	0.0158 (15)	0.0179 (15)	0.0014 (12)	-0.0017 (12)	0.0000 (12)
C4	0.0136 (14)	0.0210 (16)	0.0243 (16)	0.0060 (12)	0.0023 (12)	-0.0021 (13)
C5	0.0092 (13)	0.0238 (17)	0.0217 (15)	0.0022 (12)	0.0033 (11)	0.0012 (12)
C6	0.0207 (17)	0.043 (2)	0.0235 (17)	-0.0084 (15)	-0.0076 (13)	0.0031 (15)
C7	0.0179 (16)	0.055 (3)	0.0286 (19)	0.0117 (16)	-0.0066 (14)	-0.0145 (17)
C8	0.043 (2)	0.0265 (19)	0.0271 (18)	-0.0002 (16)	-0.0214 (16)	0.0042 (15)
C9	0.0310 (18)	0.040 (2)	0.0150 (16)	-0.0072 (16)	0.0017 (13)	-0.0031 (14)
C10	0.0279 (17)	0.0236 (18)	0.0247 (17)	-0.0024 (14)	-0.0059 (13)	-0.0083 (14)
C21	0.0204 (15)	0.0175 (15)	0.0164 (15)	0.0020 (12)	0.0003 (12)	-0.0009 (12)
C22	0.0209 (15)	0.0192 (16)	0.0174 (15)	0.0015 (12)	0.0014 (12)	-0.0006 (12)
C23	0.0218 (16)	0.0196 (16)	0.0188 (15)	0.0001 (13)	-0.0008 (12)	-0.0028 (12)
C24	0.0243 (17)	0.030 (2)	0.0331 (19)	0.0044 (14)	0.0069 (14)	0.0034 (15)
C111	0.0158 (14)	0.0145 (14)	0.0168 (14)	0.0003 (11)	0.0008 (11)	0.0007 (11)
C112	0.0160 (14)	0.0256 (17)	0.0196 (15)	-0.0015 (13)	-0.0038 (12)	0.0041 (13)
C113	0.0203 (16)	0.0262 (18)	0.0273 (18)	-0.0057 (13)	0.0024 (13)	0.0008 (14)
C114	0.0316 (18)	0.0254 (18)	0.0229 (17)	-0.0034 (14)	0.0046 (14)	0.0056 (14)
C115	0.0310 (18)	0.0242 (18)	0.0237 (17)	0.0003 (14)	-0.0049 (14)	0.0095 (14)
C116	0.0187 (15)	0.0168 (16)	0.0241 (16)	0.0009 (12)	-0.0030 (12)	0.0018 (12)
C121	0.0188 (14)	0.0190 (15)	0.0143 (14)	0.0019 (12)	0.0037 (11)	0.0008 (12)
C122	0.0301 (18)	0.0209 (17)	0.0254 (17)	0.0101 (14)	-0.0032 (14)	-0.0046 (13)
C123	0.036 (2)	0.0261 (18)	0.0241 (17)	0.0089 (15)	-0.0073 (14)	-0.0014 (14)

C124	0.0356 (19)	0.0241 (17)	0.0172 (16)	-0.0054 (15)	0.0020 (13)	-0.0005 (13)
C125	0.0314 (18)	0.0191 (16)	0.0271 (18)	-0.0006 (14)	0.0112 (14)	-0.0053 (13)
C126	0.0215 (15)	0.0183 (16)	0.0245 (16)	0.0023 (13)	0.0072 (12)	-0.0015 (13)

Geometric parameters (Å, °)

Fe1—C1	2.028 (3)	C9—H9	0.9500
Fe1—C2	2.035 (3)	C10—H10	0.9500
Fe1—C7	2.043 (3)	C21—C22	1.340 (4)
Fe1—C8	2.043 (3)	C21—H21	0.9500
Fe1—C5	2.045 (3)	C22—C23	1.470 (4)
Fe1—C3	2.047 (3)	C22—H22	0.9500
Fe1—C6	2.048 (3)	C23—C24	1.509 (4)
Fe1—C10	2.059 (3)	C24—H24A	0.9800
Fe1—C9	2.060 (3)	C24—H24B	0.9800
Fe1—C4	2.064 (3)	C24—H24C	0.9800
S1—P1	1.9560 (11)	C111—C116	1.391 (4)
P1—C1	1.795 (3)	C111—C112	1.392 (4)
P1—C121	1.812 (3)	C112—C113	1.384 (4)
P1—C111	1.816 (3)	C112—H112	0.9500
O1—C23	1.208 (4)	C113—C114	1.390 (5)
C1—C5	1.446 (4)	C113—H113	0.9500
C1—C2	1.459 (4)	C114—C115	1.390 (5)
C2—C3	1.423 (4)	C114—H114	0.9500
C2—C21	1.459 (4)	C115—C116	1.389 (4)
C3—C4	1.412 (4)	C115—H115	0.9500
C3—H3	0.9500	C116—H116	0.9500
C4—C5	1.417 (4)	C121—C122	1.386 (4)
C4—H4	0.9500	C121—C126	1.399 (4)
C5—H5	0.9500	C122—C123	1.396 (4)
C6—C10	1.401 (5)	C122—H122	0.9500
C6—C7	1.401 (5)	C123—C124	1.389 (5)
C6—H6	0.9500	C123—H123	0.9500
C7—C8	1.417 (6)	C124—C125	1.370 (5)
C7—H7	0.9500	C124—H124	0.9500
C8—C9	1.421 (5)	C125—C126	1.377 (5)
C8—H8	0.9500	C125—H125	0.9500
C9—C10	1.420 (5)	C126—H126	0.9500
C1—Fe1—C2	42.10 (11)	C10—C6—C7	108.8 (3)
C1—Fe1—C7	112.69 (13)	C10—C6—Fe1	70.49 (19)
C2—Fe1—C7	111.19 (13)	C7—C6—Fe1	69.8 (2)
C1—Fe1—C8	111.98 (13)	C10—C6—H6	125.6
C2—Fe1—C8	139.56 (14)	C7—C6—H6	125.6
C7—Fe1—C8	40.60 (16)	Fe1—C6—H6	125.7
C1—Fe1—C5	41.60 (11)	C6—C7—C8	107.9 (3)
C2—Fe1—C5	69.73 (12)	C6—C7—Fe1	70.16 (19)
C7—Fe1—C5	142.26 (15)	C8—C7—Fe1	69.70 (19)

C8—Fe1—C5	113.44 (14)	C6—C7—H7	126.1
C1—Fe1—C3	69.37 (12)	C8—C7—H7	126.1
C2—Fe1—C3	40.80 (11)	Fe1—C7—H7	125.7
C7—Fe1—C3	138.11 (14)	C7—C8—C9	107.9 (3)
C8—Fe1—C3	178.29 (14)	C7—C8—Fe1	69.70 (19)
C5—Fe1—C3	68.27 (12)	C9—C8—Fe1	70.38 (19)
C1—Fe1—C6	140.55 (13)	C7—C8—H8	126.1
C2—Fe1—C6	111.05 (13)	C9—C8—H8	126.1
C7—Fe1—C6	40.06 (15)	Fe1—C8—H8	125.4
C8—Fe1—C6	67.70 (15)	C10—C9—C8	107.4 (3)
C5—Fe1—C6	177.42 (14)	C10—C9—Fe1	69.82 (18)
C3—Fe1—C6	110.59 (14)	C8—C9—Fe1	69.10 (18)
C1—Fe1—C10	179.48 (13)	C10—C9—H9	126.3
C2—Fe1—C10	138.35 (13)	C8—C9—H9	126.3
C7—Fe1—C10	67.51 (14)	Fe1—C9—H9	126.3
C8—Fe1—C10	67.83 (14)	C6—C10—C9	108.1 (3)
C5—Fe1—C10	137.97 (13)	C6—C10—Fe1	69.62 (19)
C3—Fe1—C10	110.83 (13)	C9—C10—Fe1	69.85 (18)
C6—Fe1—C10	39.90 (14)	C6—C10—H10	126.0
C1—Fe1—C9	139.22 (13)	C9—C10—H10	126.0
C2—Fe1—C9	178.56 (13)	Fe1—C10—H10	126.1
C7—Fe1—C9	68.00 (14)	C22—C21—C2	123.1 (3)
C8—Fe1—C9	40.52 (15)	C22—C21—H21	118.4
C5—Fe1—C9	111.67 (13)	C2—C21—H21	118.4
C3—Fe1—C9	139.05 (13)	C21—C22—C23	125.3 (3)
C6—Fe1—C9	67.54 (14)	C21—C22—H22	117.3
C10—Fe1—C9	40.33 (14)	C23—C22—H22	117.3
C1—Fe1—C4	69.08 (12)	O1—C23—C22	121.3 (3)
C2—Fe1—C4	68.66 (12)	O1—C23—C24	118.8 (3)
C7—Fe1—C4	177.37 (15)	C22—C23—C24	119.8 (3)
C8—Fe1—C4	141.06 (15)	C23—C24—H24A	109.5
C5—Fe1—C4	40.33 (12)	C23—C24—H24B	109.5
C3—Fe1—C4	40.17 (12)	H24A—C24—H24B	109.5
C6—Fe1—C4	137.36 (14)	C23—C24—H24C	109.5
C10—Fe1—C4	110.75 (13)	H24A—C24—H24C	109.5
C9—Fe1—C4	112.09 (13)	H24B—C24—H24C	109.5
C1—P1—C121	105.06 (14)	C116—C111—C112	119.3 (3)
C1—P1—C111	104.43 (13)	C116—C111—P1	120.1 (2)
C121—P1—C111	104.73 (14)	C112—C111—P1	120.6 (2)
C1—P1—S1	115.62 (10)	C113—C112—C111	120.6 (3)
C121—P1—S1	112.86 (10)	C113—C112—H112	119.7
C111—P1—S1	113.10 (10)	C111—C112—H112	119.7
C5—C1—C2	106.8 (2)	C112—C113—C114	120.2 (3)
C5—C1—P1	125.0 (2)	C112—C113—H113	119.9
C2—C1—P1	128.2 (2)	C114—C113—H113	119.9
C5—C1—Fe1	69.82 (17)	C113—C114—C115	119.4 (3)
C2—C1—Fe1	69.23 (16)	C113—C114—H114	120.3
P1—C1—Fe1	127.14 (15)	C115—C114—H114	120.3

C3—C2—C21	125.1 (3)	C116—C115—C114	120.6 (3)
C3—C2—C1	107.1 (2)	C116—C115—H115	119.7
C21—C2—C1	127.4 (3)	C114—C115—H115	119.7
C3—C2—Fe1	70.03 (16)	C115—C116—C111	120.0 (3)
C21—C2—Fe1	120.9 (2)	C115—C116—H116	120.0
C1—C2—Fe1	68.67 (16)	C111—C116—H116	120.0
C4—C3—C2	109.3 (3)	C122—C121—C126	119.3 (3)
C4—C3—Fe1	70.58 (17)	C122—C121—P1	121.6 (2)
C2—C3—Fe1	69.17 (16)	C126—C121—P1	119.1 (2)
C4—C3—H3	125.3	C121—C122—C123	120.3 (3)
C2—C3—H3	125.3	C121—C122—H122	119.9
Fe1—C3—H3	126.5	C123—C122—H122	119.9
C3—C4—C5	108.5 (3)	C124—C123—C122	119.6 (3)
C3—C4—Fe1	69.25 (17)	C124—C123—H123	120.2
C5—C4—Fe1	69.09 (16)	C122—C123—H123	120.2
C3—C4—H4	125.7	C125—C124—C123	119.9 (3)
C5—C4—H4	125.7	C125—C124—H124	120.0
Fe1—C4—H4	127.5	C123—C124—H124	120.0
C4—C5—C1	108.3 (3)	C124—C125—C126	121.1 (3)
C4—C5—Fe1	70.58 (17)	C124—C125—H125	119.5
C1—C5—Fe1	68.58 (16)	C126—C125—H125	119.5
C4—C5—H5	125.9	C125—C126—C121	119.9 (3)
C1—C5—H5	125.9	C125—C126—H126	120.1
Fe1—C5—H5	126.5	C121—C126—H126	120.1

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C22—H22 \cdots O1 ⁱ	0.95	2.63	3.548 (4)	164
C112—H112 \cdots S1 ⁱⁱ	0.95	2.83	3.576 (3)	136
C116—H116 \cdots S1	0.95	2.89	3.374 (3)	113
C21—H21 \cdots S1	0.95	2.87	3.604 (3)	135

Symmetry codes: (i) $-x+1, -y+2, -z+1$; (ii) $x-1, y, z$.