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Key indicators

Single-crystal X-ray study
 T = 298 K
 Mean $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$
 R factor = 0.041
 wR factor = 0.122
 Data-to-parameter ratio = 14.8

For details of how these key indicators were
 automatically derived from the article, see
<http://journals.iucr.org/e>.

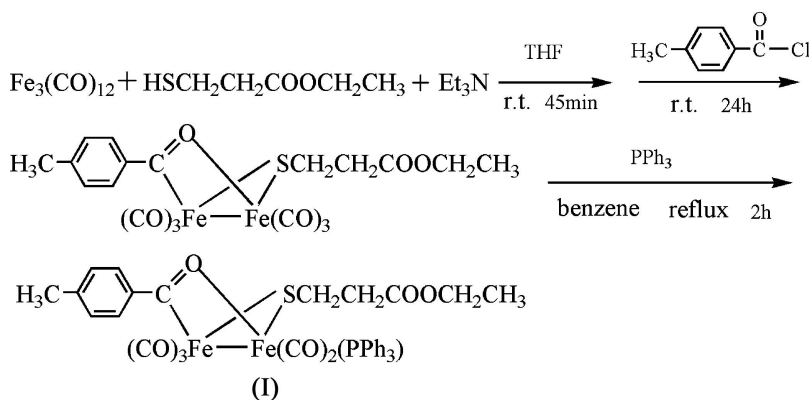
Pentacarbonyl- $1\kappa^2\text{C}, 2\kappa^3\text{C}$ -(μ -ethyl 3-mercapto-
 propionato- $1\kappa\text{S}:2\kappa\text{S}$)(μ -4-methylbenzoyl-
 $1\kappa\text{O}:2\kappa\text{C}$)(triphenylphosphine- $1\kappa\text{P}$)-
 diiron($\text{Fe}-\text{Fe}$)

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In the molecule of the title compound, $[\text{Fe}_2(\text{C}_8\text{H}_7\text{O})-(\text{C}_5\text{H}_9\text{O}_2\text{S})(\text{C}_{18}\text{H}_{15}\text{P})(\text{CO})_5]$, the two Fe atoms are bridged by the ethyl 3-mercaptopropionate and 4-methylbenzoyl ligands. The central structural Fe_2COS fragment adopts an envelope conformation. Each Fe atom is in a pseudo-square pyramidal coordination. In addition, the crystal structure is stabilized by intermolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds.

Comment

As an efficient catalyst for the production of hydrogen, the active site of Fe-only hydrogenase has attracted intensive attention in recent years (Evans *et al.*, 2003; Darensbourg *et al.*, 2000). Gloaguen *et al.* (2001) have proved that simple analogues of Fe-only containing phosphane ligands can be effective catalysts. In this paper, we report a diiron mono(triphenylphosphine)pentacarbonyl complex, (I), with bridging ethyl 3-mercaptopropionate and 4-methylbenzoyl ligands (Fig. 1).



The central Fe_2COS unit is in an envelope conformation with S1 at the flap position. Each Fe atom has a pseudo-square-pyramidal coordination. Triphenylphosphine has replaced CO at Fe1, which is connected to Fe2 through a bridging acyl group (Seyferth *et al.*, 1986). Furthermore, the triphenylphosphine ligand is bound to Fe1 in the apical position (Lyon *et al.*, 1999). In addition, the $\text{C1}-\text{O1}$ [1.253 (3) Å] bond in the bridging acyl group is somewhat longer than those in the terminal acyl complex $\text{N}(\text{CH}_2\text{CH}_3)_4^+[(\text{CO})_3(\text{C}_6\text{H}_5\text{O})_3\text{PFeCOCH}_3]^-$ [1.226 (5) Å; Casey *et al.*, 1985] and the IR spectrum of the title compound shows that the characteristic absorption band of the acyl bridging ligand is at 1460 cm^{-1} , which is probably due to the coordination of the acyl bridging ligand to the diiron unit. Meanwhile, the crystal structure is stabilized by the intermolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds, as shown in Fig. 2 and Table 1.

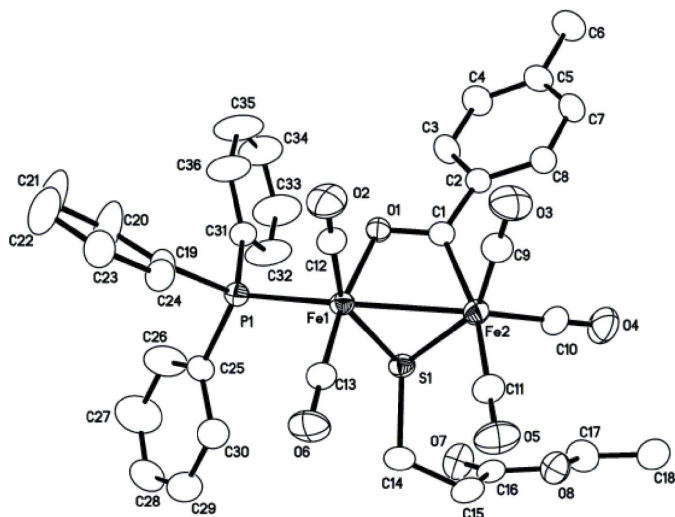


Figure 1
A view of the title compound, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted.

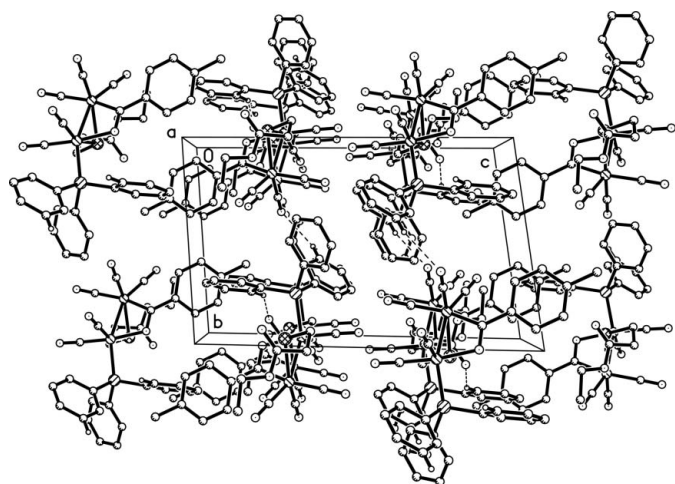


Figure 2
Crystal packing of the title compound, viewed down the *a* axis. H atoms have been omitted. Dashed lines indicate hydrogen bonds.

Experimental

A solution of $\text{Fe}_3(\text{CO})_{12}$ (1.5 g, 3.0 mmol), ethyl 3-mercaptopropionate (0.27 ml, 3.0 mmol) and triethylamine (0.5 ml, 3.6 mmol) in THF (40 ml) was reacted under an atmosphere of purified nitrogen at room temperature for 45 min to give a brown-red solution. 4-Methylbenzoyl chloride (0.53 ml, 4.0 mmol) was then added and stirred for 24 h. The solvent was removed under reduced pressure. The residue was extracted with petroleum ether/ethyl acetate (20/1 *v/v*) and then concentrated. The condensate was separated by column chromatography on silica gel with ethyl acetate-petroleum ether (1:20) as eluent. From the main band, a red oily liquid $[(\mu\text{-}4\text{-CH}_3\text{PhCO})(\mu\text{-SCH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3)\text{Fe}_2(\text{CO})_6]$ was obtained (yield 0.859 g, 54.2%). $^1\text{H NMR}$ (CDCl_3): δ 1.10–1.37 (*m*, 3H), 2.29 (*s*, 3H), 2.20–2.88 (*m*, 4H), 3.95–4.26 (*m*, 2H), 7.05–7.45 (*m*, 4H).

Subsequently, the solution of the red oily liquid (0.67 g, 1.26 mmol) and PPh_3 (0.33 g, 1.26 mmol) in benzene (20 ml) was refluxed under an atmosphere of purified nitrogen for 2 h and the color turned dark red. After the solution was concentrated by solvent evaporation in a vacuum, the crude product was purified by column chromatography on silica gel with ethyl acetate/petroleum ether (1:15 *v/v*) as eluent. Dark red crystals of $[(\mu\text{-}4\text{-CH}_3\text{PhCO})(\mu\text{-SCH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3)\text{Fe}_2(\text{CO})_5(\text{PPh}_3)]$ were obtained by recrystallization from hexane- CH_2Cl_2 (10/1 *v/v*) (yield 86%, 0.83 g; m.p. 393–395 K, decomposition). IR (KBr, $\nu\text{ cm}^{-1}$): 2031, 1972, 1942, 1922; $^1\text{H NMR}$ (CDCl_3): δ 1.14–1.22 (*m*, 3H), 2.24 (*s*, 3H), 1.78–2.36 (*m*, 4H), 3.87–4.15 (*m*, 2H), 7.03–7.67 (*m*, 19H). Analysis calculated for $\text{C}_{36}\text{H}_{31}\text{Fe}_2\text{O}_8\text{PS}$: C 56.42, H 4.08%; found: C 56.24, H 3.97%.

Crystal data

$[\text{Fe}_2(\text{C}_8\text{H}_7\text{O})(\text{C}_5\text{H}_9\text{O}_2\text{S})\text{-}(\text{C}_{18}\text{H}_{15}\text{P})(\text{CO})_5]$
 $M_r = 766.34$
Triclinic, $P\bar{1}$
 $a = 10.4846$ (8) Å
 $b = 11.2367$ (9) Å
 $c = 16.7452$ (13) Å
 $\alpha = 80.339$ (1)°
 $\beta = 79.669$ (1)°
 $\gamma = 65.918$ (1)°
 $V = 1762.0$ (2) Å³

$Z = 2$
 $D_x = 1.444$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 6455 reflections
 $\theta = 2.1\text{--}25.5^\circ$
 $\mu = 0.98$ mm⁻¹
 $T = 298$ (2) K
Plate, dark red
0.70 × 0.50 × 0.15 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
 $T_{\text{min}} = 0.548$, $T_{\text{max}} = 0.867$
9686 measured reflections

6455 independent reflections
5591 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.014$
 $\theta_{\text{max}} = 25.5^\circ$
 $h = -5 \rightarrow 12$
 $k = -13 \rightarrow 13$
 $l = -17 \rightarrow 20$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.122$
 $S = 1.10$
6455 reflections
435 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0759P)^2 + 0.4104P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.71$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.35$ e Å⁻³

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>
C21—H21···O3 ⁱ	0.93	2.48	3.308 (6)	149
C36—H36···O7 ⁱⁱ	0.93	2.45	3.254 (5)	144

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

H atoms were positioned geometrically [$\text{C—H} = 0.93$ (CH), 0.97 (CH₂) and 0.96 Å (CH₃)] and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{methyl C})$.

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-NT* (Bruker, 1998); data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-NT* (Bruker, 1998); software used to prepare material for publication: *SHELXTL-NT*.

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