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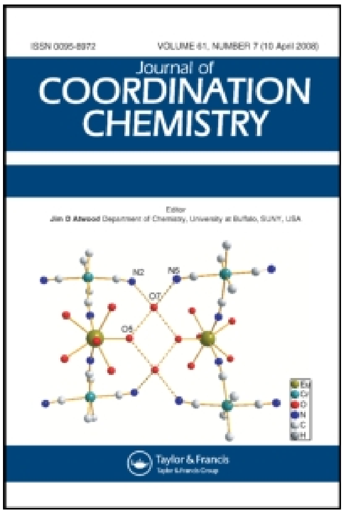

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Synthesis and structural characterization of a diiron propanedithiolate complex $[(\mu\text{-PDT})Fe_2(CO)_5]_2[(\eta^5\text{-}Ph_2PC_5H_4)_2Fe]$ containing a bidentate phosphine ligand 1,1'-bis(diphenylphosphino)ferrocene

Xu-Feng Liu[a]; Bang-Shao Yin[b]
[a] Department of Chemical Engineering, Ningbo University of Technology, Ningbo 315016, China [b] College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, China

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Synthesis and structural characterization of a diiron propanedithiolate complex $[(\mu\text{-PDT})Fe_2(CO)_5]_2[(\eta^5\text{-}Ph_2PC_5H_4)_2Fe]$ containing a bidentate phosphine ligand 1,1′-bis(diphenylphosphino)ferrocene

XU-FENG LIU*† and BANG-SHAO YIN‡

†Department of Chemical Engineering, Ningbo University of Technology,
Ningbo 315016, China
‡College of Chemistry and Chemical Engineering, Hunan Normal University,
Changsha 410081, China

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The reaction of $(\mu\text{-PDT})Fe_2(CO)_6$ (PDT = $SCH_2CH_2CH_2S$) with 1,1′-bis(diphenylphosphino) ferrocene in the presence of the decarbonylating agent $Me_3NO{\cdot}2H_2O$ afforded $[(\mu\text{-PDT})Fe_2(CO)_5]_2[(\eta^5\text{-}Ph_2PC_5H_4)_2Fe]$ (**1**) in 80% yield. The new complex **1** was characterized by elemental analysis, IR, and ^1H-(^{31}P-, ^{13}C-) NMR spectroscopies. The structure of **1** was determined by single crystal X-ray diffraction analysis; the molecule is centrosymmetric and two cyclopentadienyl (Cp) rings reside in a staggered conformation.

Keywords: Diiron propanedithiolate; dppf; Synthesis; Crystal structure

1. Introduction

Diiron propanedithiolate complex $(\mu\text{-PDT})Fe_2(CO)_6$ was prepared either by the reaction of $(\mu\text{-LiS})_2Fe_2(CO)_6$ (generated *in situ* from $(\mu\text{-}S_2)Fe_2(CO)_6$ and $LiBEt_3H$) with $BrCH_2CH_2CH_2Br$ [1, 2], or by the reaction of $Fe_3(CO)_{12}$ and $HSCH_2CH_2CH_2SH$ [3] as Seyferth's group reported in 1980 and 1987, respectively. Since 1999, diiron propanedithiolate complexes of the type $(\mu\text{-PDT})Fe_2(CO)_{6-n}L_n$ (L, ligand), such as $(\mu\text{-PDT})Fe_2(CO)_4(CN)_2$ [4], $[(\mu\text{-PDT})Fe_2(CO)_5]_2$(dppe) (dppe = $Ph_2PCH_2CH_2PPh_2$) [5], and $(\mu\text{-PDT})Fe_2(CO)_5(CpFe(CO)_2PPh_2)$ [6], were obtained from the reaction of $(\mu\text{-PDT})Fe_2(CO)_6$ with various ligands [7–9]. Due to the electron donor properties of ferrocene, we initiated our studies on the reaction of $(\mu\text{-PDT})Fe_2(CO)_6$ with the

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*Corresponding author. Email: nkxfliu@yahoo.com.cn

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bidentate ligand dppf. Herein, we report the synthesis, characterization, and crystal structure of $[(\mu\text{-PDT})Fe_2(CO)_5]_2[(\eta^5\text{-}Ph_2PC_5H_4)_2Fe]$ (**1**).

2. Experimental

2.1. *Materials and methods*

All reactions were performed using standard Schlenk and vacuum-line techniques under N_2. Acetonitrile was distilled over CaH_2 under N_2. $Me_3NO{\cdot}2H_2O$ and other materials were available commercially and used as received. $(\mu\text{-PDT})Fe_2(CO)_6$ [2] and dppf [10] were prepared according to literature procedures. IR spectra were recorded on a Nicolet MAGNA 560 FT-IR spectrometer. ^1H-(^{31}P-, ^{13}C-) NMR spectra were obtained on a Bruker Avance 500 MHz spectrometer. Elemental analysis was performed by a Perkin-Elmer 240C analyzer.

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2.2. *Synthesis of 1*

To a solution of $(\mu\text{-PDT})Fe_2(CO)_6$ (0.200 g, 0.52 mmol) in MeCN (20 mL), a solution of $Me_3NO{\cdot}2H_2O$ (0.058 g, 0.52 mmol) in MeCN (10 mL) was added. The mixture was stirred at room temperature for 15 min and then $(\eta^5\text{-}Ph_2PC_5H_4)_2Fe$ (dppf) (0.144 g, 0.26 mmol) was added. The new mixture was stirred for 1 h to give a red solution. The solvent was reduced *in vacuo* and the residue was subjected to TLC separation using CH_2Cl_2/petroleum ether ($v/v = 1:3$) as eluent. Collecting the main red band afforded 0.263 g (80%) of **1** as a dark red solid. Anal. Calcd for $C_{50}H_{40}Fe_5O_{10}P_2S_4$ (%): C, 47.28; H, 3.17. Found: C, 46.99; H, 3.44. IR (KBr disc): $\nu_{C\equiv O}$ 2037 (vs), 1975 (vs), 1926 (vs) cm^{-1}. ^1H-NMR (500 MHz, $CDCl_3$): 7.52, 7.39 (2s, 20H, $4C_6H_5$), 4.30, 4.26 (2s, 8H, $2C_5H_4$), 1.69–1.68 (m, 4H, $2SCH_2CH_2CH_2S$), 1.54 (s, 8H, $4SCH_2$) ppm. ^{31}P-NMR (200 MHz, $CDCl_3$, 85% H_3PO_4): 54.97 (s) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): 214.40 (d, $J_{P\text{–}C} = 10.7$ Hz, PFeCO), 209.32 (s, FeCO), 138.41 (d, $J_{P\text{–}C} = 41.2$ Hz, *i*-PhC), 132.89 (d, $J_{P\text{–}C} = 10.6$ Hz, *o*-PhC), 129.94 (s, *p*-PhC), 128.01 (d, $J_{P\text{–}C} = 9.4$ Hz, *m*-PhC), 80.17 (d, $J_{P\text{–}C} = 41.4$ Hz, *i*-CpC), 75.02 (d, $J_{P\text{–}C} = 10.7$ Hz, α-CpC), 73.93 (d, $J_{P\text{–}C} = 6.9$ Hz, β-CpC), 29.97 (s, SCH_2), 21.70 (s, $SCH_2CH_2CH_2S$) ppm.

2.3. *X-ray structure determination*

Single crystals of $\mathbf{1}{\cdot}2CH_2Cl_2$ suitable for X-ray diffraction analysis were grown by slow evaporation of CH_2Cl_2/hexane solution at 4°C. A single crystal of $\mathbf{1}{\cdot}2CH_2Cl_2$ was mounted on a Rigaku SCX-mini CCD diffractometer. Data were collected at room temperature using a graphite monochromator with Mo-Kα radiation ($\lambda = 0.71073$ Å) in the ω–ϕ scanning mode. Absorption correction was performed by SADABS [11]. The structure was solved by direct methods using the SHELXS-97 program [12] and refined by full-matrix least-squares (SHELXL-97) [13] on F^2. Hydrogens were located using the geometric method. Details of crystal data, data collections, and structure refinement are summarized in table 1.

Table 1. Crystal data and structure refinements details for **1**·$2CH_2Cl_2$.

Empirical formula	$C_{50}H_{40}Fe_5O_{10}P_2S_4 \cdot 2CH_2Cl_2$
Formula weight	1440.10
Temperature (°C)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions (Å, °)	
a	9.5230(19)
b	12.909(3)
c	13.587(3)
α	99.30(3)
β	105.74(3)
γ	101.17(3)
Volume (Å^3), Z	1536.1(5), 1
Calculated density (g cm^{-3})	1.557
Absorption coefficient, μ (mm^{-1})	1.566
F(000)	728
Crystal size (mm^3)	0.29 × 0.26 × 0.22
θ range for data collection (°)	2.99–25.10
Limiting indices	$-11 \le h \le 11$; $-15 \le k \le 15$; $-16 \le l \le 15$
Reflections collected	8910
Independent reflection	5400 [R(int) = 0.0542]
Completeness to θ = 25.10 (%)	98.6
Data/restraints/parameters	5400/11/359
Goodness-of-fit on F^2	1.033
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0773$, $wR_2 = 0.1914$
R indices (all data)	$R_1 = 0.1301$, $wR_2 = 0.2159$
Largest difference peak and hole (e Å^{-3})	1.453 and −0.877

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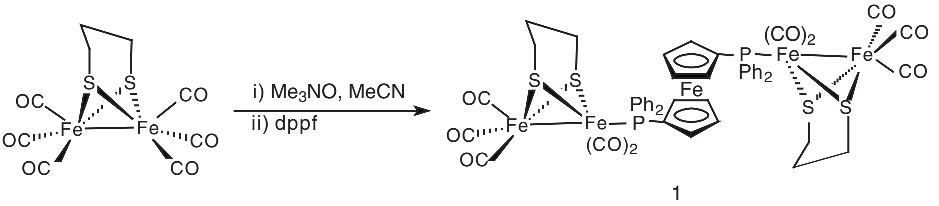
3. Results and discussion

3.1. *Synthesis and characterization*

The synthetic route to **1** is illustrated in scheme 1. Treatment of the starting material (μ-PDT)$Fe_2(CO)_6$ with 1 equivalent of $Me_3NO \cdot 2H_2O$ in MeCN at room temperature followed by addition of dppf resulted in the formation of **1** in 80% yield.

Complex **1** was characterized by elemental analysis, IR, and ^{1}H-(^{31}P-, ^{13}C-) NMR spectroscopies. The IR spectra showed three absorption bands at 2037, 1975, and 1926 cm^{-1} for its terminal carbonyls and $\nu_{C\equiv O}$ values markedly shifted to lower frequencies relative to (μ-PDT)$Fe_2(CO)_6$ (2072, 2033, 1993 cm^{-1}) [14] but very similar to diiron dithiolate complexes with phosphine ligands, such as [(μ-PDT)$Fe_2(CO)_5$]$_2$(dppe) (2040, 1982, 1922 cm^{-1}) [5]. The ^{1}H-NMR spectra displayed two singlets at δ 4.30 and 4.26 ppm for its two Cp ring hydrogens. The ^{31}P-NMR spectra have a singlet at δ 54.97 ppm for the two P atoms of dppf, each one coordinated to one Fe of the diiron subsite. In addition, the ^{13}C-NMR spectra exhibited a doublet at δ 214.40 ppm with a coupling constant $J_{P\text{–}C} = 10.7$ Hz and a singlet at δ 209.32 ppm for its terminal carbonyls, three doublets at δ 138.41, 132.89, and 128.01 ppm and a singlet at δ 129.94 ppm for its phenyl carbons, and three doublets at δ 80.17, 75.02, and 73.93 ppm for its Cp ring carbons. The NMR data we obtained were consistent with its symmetrical structure.



Scheme 1. Preparation of **1**.

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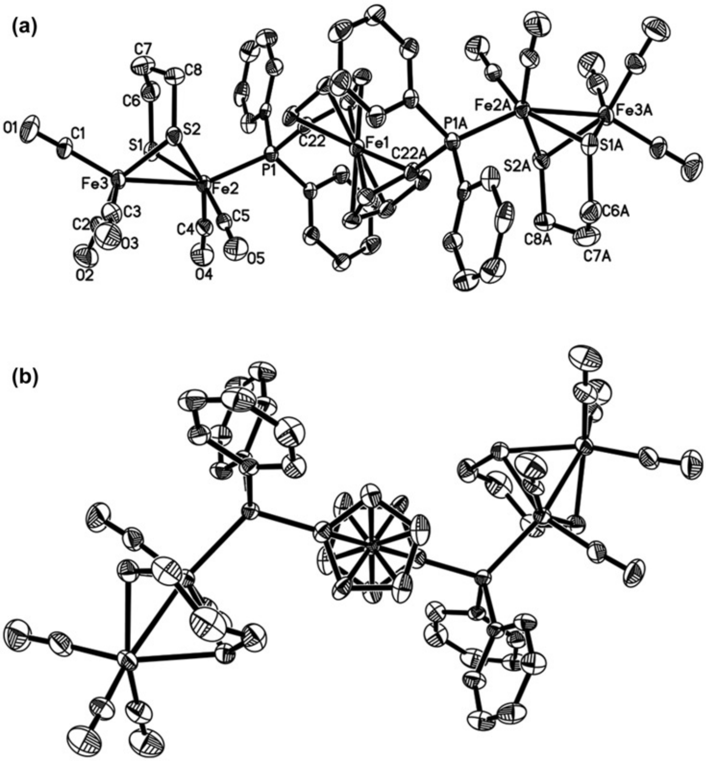

Figure 1. (a) ORTEP view of $\mathbf{1}\cdot 2CH_2Cl_2$ with 30% probability ellipsoids. Hydrogens are omitted for clarity. (b) Top view on the Cp ring.

3.2. *X-ray crystal structure*

The molecular structure of $\mathbf{1}\cdot 2CH_2Cl_2$ has been unequivocally confirmed by single crystal X-ray diffraction analysis. While the ORTEP and packing view are shown in figures 1 and 2, selected bond lengths and angles are given in table 2. The title complex $\mathbf{1}\cdot 2CH_2Cl_2$ contains two diiron propanedithiolate moieties which are joined through a dppf molecule. This molecule is centrosymmetric with Fe1 as the symmetry center, very similar to the previously reported complexes $[Fe_2(\mu\text{-}SCH_2OCH_2S\text{-}\mu)(CO)_5]_2[(\eta^5\text{-}Ph_2PC_5H_4)_2Fe]$

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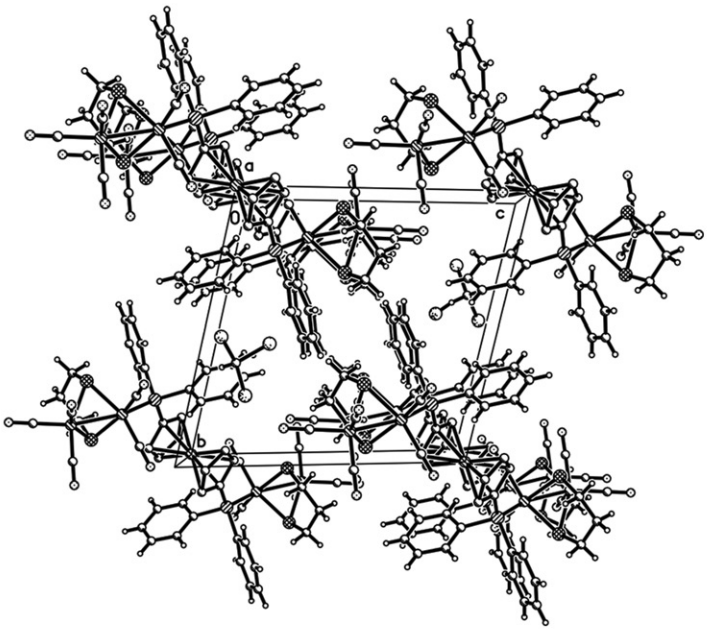

Figure 2. Crystal packing diagram of **1**·$2CH_2Cl_2$ along the *a*-axis.

Table 2. Selected bond lengths (Å) and angles (°) for **1**·$2CH_2Cl_2$.

Fe(1)–C(22)	2.093(7)	Fe(2)–Fe(3)	2.5441(16)
Fe(2)–P(1)	2.264(2)	Fe(3)–S(1)	2.291(3)
Fe(2)–S(2)	2.277(2)	Fe(3)–S(2)	2.293(2)
Fe(2)–S(1)	2.293(3)	C(9)–P(1)	1.845(8)
C(22)–P(1)	1.827(8)	C(15)–P(1)	1.839(7)
C(22)#1–Fe(1)–C(22)	180.0(5)	S(1)–Fe(3)–Fe(2)	56.33(7)
P(1)–Fe(2)–Fe(3)	153.62(8)	S(2)–Fe(3)–Fe(2)	55.88(6)
S(2)–Fe(2)–Fe(3)	56.47(6)	P(1)–C(22)–Fe(1)	134.0(4)
S(1)–Fe(2)–Fe(3)	56.26(7)	C(22)–P(1)–Fe(2)	117.6(3)

Symmetry transformations used to generate equivalent atoms: #1:$-x+2$, $-y$, $-z$.

and $[Fe_2(\mu\text{-}SCH_2OCH_2S\text{-}\mu)(CO)_5]_2[(\eta^5\text{-}Ph_2PC_5H_4)_2Ru]$ [15]. The molecular structure also revealed that each [2Fe2S] unit of **1**·$2CH_2Cl_2$ has two fused six-membered rings, in which one six-membered ring C7C8S2Fe2S1C6 has a chair conformation and the other six-membered ring C7C8S2Fe3S1C6 has a boat conformation. Furthermore, each phosphorus of the diphosphine ligand resides in the axial position of the square-pyramidal coordination sphere of Fe2 and Fe2A, consistent with diiron dithiolate complexes substituted by monophosphine ligands [16–19] or by diphosphine ligands, such as $[(\mu\text{-PDT})Fe_2(CO)_5]_2(dppe)$ [5], $[\{Fe_2(CO)_5(\mu\text{-PDT})\}_2(\mu,\kappa^1,\kappa^1\text{-}Ph_2PCH_2N(n\text{-}Pr)CH_2PPh_2)]$ [20], and $[\{Fe_2(CO)_5(\mu\text{-PDT})\}_2(\mu,\kappa^1,\kappa^1\text{-}Ph_2PCH_2N(Ph)CH_2PPh_2)]$ [20]. The orientation of the phosphine ligands are in opposite positions to the bridgehead C7 and C7A in order to reduce steric repulsion between them, common in diiron azadithiolate derivatives, for example, $[\{(\mu\text{-}SCH_2)_2N(C_6H_4OMe\text{-}p)\}Fe_2(CO)_5(PPh_3)]$ [18] and $[(\mu\text{-}SCH_2N(4\text{-bromophenyl})CH_2S)Fe_2(CO)_5(PPh_3)]$ [21]. The Fe2–Fe3 bond length [2.5441(16) Å] is longer than (μ-PDT)$Fe_2(CO)_6$ [2.5103(11) Å] [14] and the analogous diiron dithiolate complexes [22–24], but shorter than those in the structures of natural enzymes *Clostridium pasteurianum* and *Desulfovibrio desulfuricans* (2.55–2.62 Å) [25, 26]. All carbons of carbonyls are about 1.79 Å apart from the iron atoms with no differences in their equatorial and axial positions. In addition, the disordered CH_2Cl_2 could give rise to the relative high R_1/wR_2 (all data) 0.1301/0.2159 for the structure of **1**.

As can be seen in figure 1(b), the top view on the Cp ring shows that two Cp rings of ferrocene adopt a staggered conformation.

As shown in figure 2, there are no non-covalent interactions in the crystal packing diagram of $\mathbf{1}\cdot 2CH_2Cl_2$ along the *a*-axis.

4. Conclusions

Complex [(μ-PDT)$Fe_2(CO)_5]_2[(\eta^5$-$Ph_2PC_5H_4)_2Fe$] was prepared by carbonyl substitution from (μ-PDT)$Fe_2(CO)_6$ and dppf in high yield. The title complex was characterized by various spectroscopic techniques as well as by X-ray crystallography.

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Supplementary material

CCDC 787958 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

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