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Synthesis, characterization and crystal structures of carboxy-functionalized diiron propanedithiolate complexes

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ABSTRACT

Four new carboxy-functionalized diiron propanedithiolate complexes **1–4** have been successfully synthesized and fully characterized. The all-carboxyl complexes $[(\mu$ -SCH₂)₂CHCO₂CH₂CH₂Cl][Fe₂(CO)₆] (**1**) and $[(\mu$ -SCH₂)₂CHCO₂C₆H₄I-*p*][Fe₂(CO)₆] (**2**) were prepared by the condensation reaction of the known complex $[(\mu$ -SCH₂)₂CHCO₂H][Fe₂(CO)₆] (**A**) with ClCH₂CH₂OH and *p*-IC₆H₄OH in the presence of 4-dimethylaminopyridine (DMAP) and dicyclohexylcarbodiimide (DCC) in yields of 46% and 66%, whereas the phosphine-substituted complexes $[(\mu$ -SCH₂)₂CHCO₂CH₂CH₂Cl][Fe₂(CO)₅PPh₃] (**3**) and $[(\mu$ -SCH₂)₂CHCO₂-CH₂CH₂Cl][Fe₂(CO)₄(PPh₃)₂] (**4**) were further synthesized through the carbonyl substitution reaction of **1** with PPh₃ using the decarbonylating agent Me₃NO·2H₂O in yields of 44% and 41%. The new complexes **1–4** were characterized by combustion analysis, IR and ¹H, ¹³C and ³¹P NMR spectroscopic techniques. The molecular structures of **1–4** were unequivocally determined by single crystal X-ray diffraction analysis, in which the carboxy-functionalized substituent attached to the bridgehead-C atom resides in an equatorial position of the six-membered rings in the solid state.

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1. Introduction

In the 1980s, Seyferth et al. reported that the diiron propanedithiolate complex $[(\mu-SCH_2)_2CH_2][Fe_2(CO)_6]$ could be commonly prepared via two methods: by the reaction of $(\mu-\text{LiS})_2\text{Fe}_2(\text{CO})_6$ (generated in situ from $(\mu$ -S₂)Fe₂(CO)₆ and LiBEt₃H in THF at -78 °C) with BrCH₂CH₂CH₂Br [1], or by the reaction of Fe₃(CO)₁₂ with HSCH₂CH₂CH₂SH at reflux in toluene or THF [2,3]. More recently, Darensbourg and co-workers covered that the carboxycontaining diiron propanedithiolate complex $[(\mu-SCH_2)_2CHCO_2]$ $H][Fe_2(CO)_6]$ was synthesized using the same method as Seyferth's group [4], which was regarded as the active site model of [FeFe]hydrogenase that catalyzed the production/uptake of dihydrogen and featured a butterfly 2Fe2S subunit, having CO/CN ligands, a bridging dithiolate ligand as well as a cysteinyl-S-linked cubic 4Fe4S cluster [5-10]. Notably, the design of models for [FeFe]hydrogenase was of great interest in the field of bioorganometallic chemistry. This interest was attributed to the need to develop an efficient and inexpensive catalyst for the generation of hydrogen, a clean and ideal alternative to fossil fuels [11-13].

In order to extend this kind of [FeFe]-hydrogenase model, we herein report the synthesis, characterization and crystal structures of four new carboxy-functionalized diiron propanedithiolate complexes, namely $[(\mu$ -SCH₂)₂CHCO₂CH₂CH₂Cl][Fe₂(CO)₆] (**1**),

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2. Experimental

2.1. Materials and methods

All reactions and operations were carried out under a dry, oxygen-free nitrogen atmosphere with standard Schlenk and vacuumline techniques. CH₂Cl₂ and MeCN were distilled with CaH₂ under N₂. Dicyclohexylcarbodiimide (DCC), N,N-dimethylaminopyridine (DMAP), ClCH₂CH₂OH, *p*-IC₆H₄OH, Me₃NO·2H₂O, PPh₃, and other materials were commercially available and used as received. [(μ -SCH₂)₂CHCO₂H][Fe₂(CO)₆] was prepared according to the literature [4]. Preparative TLC was carried out on glass plates (25 cm × 20 cm × 0.25 cm) coated with silica gel H (10–40 mm). IR spectra were recorded on a Nicolet 670 FTIR spectrometer. ¹H, ¹³C and ³¹P NMR spectra were obtained on a Bruker Avance 400 MHz spectrometer. Elemental analyses were performed on a Perkin–Elmer 240C analyzer. Melting points were determined on a YRT-3 apparatus and are uncorrected.

2.2. Synthesis of $[(\mu - SCH_2)_2 CHCO_2 CH_2 CH_2 CI][Fe_2(CO)_6]$ (1)

A CH₂Cl₂ (20 mL) solution of $[(\mu$ -SCH₂)₂CHCO₂H][Fe₂(CO)₆] (0.430 g, 1.0 mmol), DCC (0.206 g, 1.0 mmol) and DMAP (0.013 g,





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Table 1

Crystal data and structural refinements details for complexes 1-4.

Complex	1	2	3	4
Empirical formula	C ₁₂ H ₉ ClFe ₂ O ₈ S ₂	$C_{16}H_9Fe_2IO_8S_2$	C ₂₉ H ₂₄ ClFe ₂ O ₇ PS ₂	C46H39ClFe2O6P2S2
Formula weight	492.46	631.95	726.72	960.98
Temperature (K)	113(2)	113(2)	113(2)	113(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	monoclinic	triclinic
Space group	P2(1)/c	ΡĪ	P2(1)/c	ΡĪ
a (Å)	10.399(3)	7.600(5)	11.366(5)	10.929(6)
b (Å)	8.829(2)	11.525(7)	16.097(8)	14.691(7)
<i>c</i> (Å)	19.620(5)	12.378(8)	16.849(8)	15.099(7)
α (°)	90	102.320(5)	90	65.017(16)
β (°)	92.026(5)	96.523(16)	96.729(7)	81.94(3)
γ (°)	90	105.282(13)	90	87.78(3)
V (Å ³)	1800.1(8)	1005.0(11)	3061(3)	2175.2(19)
Ζ	4	2	4	2
$D_{\text{calc}} (\text{g cm}^{-3})$	1.810	2.088	1.577	1.467
$\mu (\mathrm{mm}^{-1})$	2.027	3.228	1.268	0.946
F(000)	976	612	1480	988
Crystal size (mm)	$0.20\times0.18\times0.08$	$0.20\times0.18\times0.10$	$0.24 \times 0.20 \times 0.16$	$0.30 \times 0.24 \times 0.20$
$\theta_{\min}, \theta_{\max}$ (°)	1.96, 27.83	1.71, 27.85	1.76, 27.91	1.50, 25.02
Reflections collected/unique	18181/4272	10560/4700	30899/7224	17337/7455
R _{int}	0.0416	0.0311	0.0419	0.1075
hkl Range	$-13 \leqslant h \leqslant 13$	$-9\leqslant h\leqslant 9$	$-14 \leqslant h \leqslant 14$	$-12 \leqslant h \leqslant 13$
	$-11 \leqslant k \leqslant 11$	$-15 \leqslant k \leqslant 15$	$-21 \leqslant k \leqslant 21$	$-17 \leqslant k \leqslant 17$
	$-24\leqslant l\leqslant 25$	$-16 \leqslant l \leqslant 16$	$-19 \leqslant l \leqslant 22$	$-17 \leqslant l \leqslant 17$
Completeness to θ_{max} (%)	100.0	98.7	98.9	97.1
Data/restraints/parameters	4272/20/236	4700/0/262	7224/0/379	7455/86/586
Goodness-of-fit (GOF) on F ²	0.996	1.011	1.044	1.059
$R_1/wR_2 \left[I > 2\sigma(I)\right]$	0.0273/0.0568	0.0227/0.0438	0.0231/0.0552	0.0749/0.1983
R_1/wR_2 (all data)	0.0362/0.0591	0.0296/0.0445	0.0277/0.0564	0.0831/0.2072
Largest difference peak/hole ($e A^{-3}$)	0.804/-0.474	0.626/-0.701	0.319/-0.417	0.753/-0.775



Scheme 1. Preparation of the all-carbonyl complexes 1 and 2.



Scheme 2. Preparation of the phosphine-substituted complexes 3 and 4.



Fig. 1. Molecular structure of 1 with thermal ellipsoids at 50% probability.



Fig. 2. Molecular structure of 2 with thermal ellipsoids at 50% probability.

0.1 mmol) was stirred at room temperature for 5 min. To this mixture ClCH₂CH₂OH (0.08 mL, 1.2 mmol) was added, and the new mixture was stirred at room temperature for 12 h. The solvent was removed on a rotary evaporator and the residue was subjected to preparative TLC separation using CH₂Cl₂/petroleum ether (v/v = 1:2) as the eluent. From the main red band, complex **1** (0.226 g, 46%) was obtained as a red solid. Mp: 70–71 °C. *Anal.* Calc.



Fig. 3. Molecular structure of 3 with thermal ellipsoids at 50% probability.

for $C_{12}H_9CIFe_2O_8S_2$: C, 29.27; H, 1.84. Found: C, 29.48; H, 2.10%. IR (KBr disk, cm⁻¹): $v_{C=0}$ 2076 (vs), 2033 (vs), 1993 (vs); $v_{C(O)O}$ 1738 (s). ¹H NMR (400 MHz, CDCl₃, TMS, ppm): 4.31 (s, 2H, OCH₂), 3.65 (s, 2H, CH₂Cl), 2.90 (s, 2H, 2SCH_aH_e), 2.17 (s, 1H, CH), 1.75 (s, 2H, 2SCH_aH_e). ¹³C NMR (100.6 MHz, CDCl₃, TMS, ppm): 207.39 (s, FeCO), 170.61 (s, C(O)O), 64.69 (s, OCH₂), 48.00 (s, CH), 41.27 (s, CH₂Cl), 24.68 (s, SCH₂).

2.3. Synthesis of $[(\mu - SCH_2)_2 CHCO_2 C_6 H_4 I - p][Fe_2(CO)_6]$ (2)

The procedure was similar to that of **1** except *p*-IC₆H₄OH (0.264 g, 1.2 mmol) was used instead of ClCH₂CH₂OH (0.1 mL, 1.5 mmol). Complex **2** (0.419 g, 66%) was obtained as a red solid. Mp: 140–141 °C. *Anal.* Calc. for C₁₆H₉Fe₂IO₈S₂: C, 30.41; H, 1.44. Found: C, 30.55; H, 1.70%. IR (KBr disk, cm⁻¹): $v_{C=0}$ 2084 (s), 2068 (s), 2042 (vs), 2006 (vs); $v_{C(0)0}$ 1743 (s). ¹H NMR (400 MHz, CD₃COCD₃, TMS, ppm): 7.76, 6.96 (d, d, *J* = 8.8, 8.8 Hz, 2H, 2H, PhH), 3.19 (dd, *J* = 13.6, 3.6 Hz, 2H, 2SCH_aH_e), 2.54 (m, 1H, *CH*), 2.01 (d, *J* = 13.6 Hz, 2H, 2SCH_aH_e). ¹³C NMR (100.6 MHz, CD₃COCD₃, TMS, ppm): 208.76 (s, FeCO), 169.99 (s, *C*(O)O), 151.56 (s, PhC), 139.37 (s, PhCH), 124.91 (s, PhCH), 90.47 (s, PhC), 49.06 (s, CH), 25.06 (s, SCH₂).

2.4. Synthesis of [(μ-SCH₂)₂CHCO₂CH₂CH₂Cl][Fe₂(CO)₅PPh₃] (**3**) and [(μ-SCH₂)₂CHCO₂CH₂Cl][Fe₂(CO)₄(PPh₃)₂] (**4**)

A mixture of **2** (0.221 g, 0.45 mmol), PPh₃ (0.131 g, 0.50 mmol), and Me₃NO·2H₂O (0.056 g, 0.50 mmol) were dissolved in MeCN (15 mL). The mixture was stirred at room temperature for 2 h to give a black-red solution. The solvent was removed on a rotary evaporator and the residue was subjected to preparative TLC separation using CH₂Cl₂/petroleum ether (v/v = 2:3) as the eluent. Two main red bands were collected. From the first brown-red band, complex **3** (0.144 g, 44%) was obtained as a brown-red solid. Mp: 133–134 °C. *Anal.* Calc. for C₂₉H₂₄ClFe₂O₇PS₂: C, 47.93; H, 3.33. Found: C, 48.17; H, 3.19%. IR (KBr disk, cm⁻¹): v_{C=0} 2045 (vs), 1983 (vs), 1936 (vs); v_{C(O)O} 1736 (m). ¹H NMR (400 MHz, CDCl₃, TMS, ppm): 7.67 (s, 6H, 3*m*-PhH), 7.45 (s, 9H, 3*o*, *p*-PhH), 4.05 (s,



Fig. 4. Molecular structure of 4 with thermal ellipsoids at 50% probability.

2H, OCH₂), 3.46 (s, 2H, CH₂Cl), 2.27 (d, J = 11.2 Hz, 2H, 2SCH_aH_e), 1.69 (br s, 3H, 2SCH_aH_e, CH). ¹³C NMR (100.6 MHz, CDCl₃, TMS, ppm): 213.50 (d, ²J_{PC} = 9.9 Hz, PFeCO), 208.85 (s, FeCO), 170.96 (s, *C*(O)O), 135.82 (d, ¹*J*_{PC} = 40.2 Hz, *ipso*-PhC), 133.32 (d, ²*J*_{PC} = 10.9 Hz, o-PhCH), 130.40 (s, p-PhCH), 128.68 (d, ³J_{PC} = 9.5 Hz, m-PhCH), 64.11 (s, OCH₂), 47.43 (s, CH), 41.27 (s, CH₂Cl), 24.92 (s, SCH₂). ³¹P NMR (161.9 MHz, CDCl₃, 85% H₃PO₄, ppm): 63.47 (s). From the second dark-red band, complex 4 (0.189 g, 41%) was obtained as a dark-red solid. Mp: 173-174 °C. Anal. Calc. for C46H39ClFe2O6-PS₂: C, 57.49; H, 4.09. Found: C, 57.23; H, 4.38%. IR (KBr disk, cm⁻¹): $v_{C=0}$ 1997 (vs), 1954 (vs), 1935 (vs); $v_{C(0)0}$ 1734 (m). ¹H NMR (400 MHz, CDCl₃, TMS, ppm): 7.72 (s, 12H, 6m-PhH), 7.39 (s, 18H, 6o, p-PhH), 3.81 (s, 2H, OCH₂), 3.28 (s, 2H, CH₂Cl), 1.76 (br s, 5H, 2SCH₂, CH). ¹³C NMR (100.6 MHz, CDCl₃, TMS, ppm): 215.62, 214.66 (2d, ²J_{PC} = 10.9, 9.7 Hz, PFeCO), 171.31 (s, C(O)O), 136.79, 136.23 (2d, ${}^{1}J_{PC}$ = 36.3, 35.9 Hz, *ipso-PhC*), 133.48 (d, ${}^{3}J_{PC}$ = 9.3 Hz, *m*-PhCH), 129.87 (s, *p*-PhCH), 128.57 (d, ${}^{2}J_{PC}$ = 9.5 Hz, o-PhCH), 63.56 (s, OCH₂), 47.47 (s, CH), 41.21 (s, CH₂Cl), 22.75 (s, SCH₂). ³¹P NMR (161.9 MHz, CDCl₃, 85% H₃PO₄, ppm): 61.68 (s), 60.49 (s).

2.5. X-ray structure determination

Single crystals of **1–4** suitable for X-ray diffraction analysis were grown by slow evaporation of a $CH_2Cl_2/hexane$ solution at 5 °C. Single crystals of **1–4** were mounted on a Rigaku MM-007 CCD diffractometer. Data were collected at 113 (2) K by using a graphite monochromator with Mo K α radiation (λ = 0.71073 Å) in the ω - φ scanning mode. Data collection, reduction and absorption corrections were performed by the CRYSTALCLEAR program [14]. The structures were solved by direct methods using the SHELXS-97 program [15] and refined by full-matrix least-squares techniques (SHEIXL-97) [16] on F^2 . Hydrogen atoms were located using the geometric method. A summary of the cell parameters, data collection and structure refinement is list in Table 1.

3. Results and discussion

3.1. Synthesis and spectroscopic characterization of the all-carbonyl complexes **1** and **2**

As shown in Scheme 1, treatment of the starting material $[(\mu-SCH_2)_2CHCO_2H][Fe_2(CO)_6]$ (**A**) with 0.1 equiv. of DMAP in the

presence of DCC as a dehydrating agent in CH₂Cl₂ followed by the addition of 1.2 equiv. of ClCH₂CH₂OH or p-IC₆H₄OH afforded the carboxy-functionalized all-carboxyl complex [(μ -SCH₂)₂-CHCO₂CH₂CH₂Cl][Fe₂(CO)₆] (**1**) or [(μ -SCH₂)₂CHCO₂C₆H₄I-p][Fe₂(-CO)₆] (**2**) in 46% or 66% yield, respectively.

Complexes **1** and **2** are stable in air and are soluble in most organic solvents, such as dichloromethane, acetone and ethyl acetate etc., and they have been fully characterized by elemental analysis, IR, ¹H NMR and ¹³C NMR spectroscopy. The IR spectra of **1** and **2** display three or four strong absorption bands in the range 2084– 1993 cm⁻¹ for their terminal carbonyls and one absorption band at 1738 or 1743 cm⁻¹ for their ester carbonyl.

The ¹H NMR spectra display a singlet at 2.17 ppm for **1** and 2.54 ppm for **2**, ascribed to the methine proton attached to the bridgehead-C atom of their propanedithiolate moieties. The ¹H NMR spectra show two singlets at 2.90 and 1.75 ppm for **1** and a double-doublet as well as a doublet at 3.19 and 2.01 ppm for **2**, which are assigned to the equatorial and axial protons for their SCH₂ groups. Meanwhile, the ¹H NMR spectrum of **1** exhibits two singlets at 4.31 and 3.65 ppm for the methylene protons in its ClCH₂CH₂O group, whereas that of **2** displays two doublets at 7.76 and 6.96 ppm for the aryl protons in its *p*-lC₆H₄O group. Additionally, the ¹³C NMR spectra of **1** and **2** demonstrate a singlet at about 208 ppm for their terminal coordinated carbonyls and a singlet at approximately 170 ppm for their ester carbonyls.

3.2. Synthesis and spectroscopic characterization of the phosphinesubstituted complexes **3** and **4**

As shown in Scheme 2, reaction of the parent complex $[(\mu - SCH_2)_2CHCO_2CH_2CI][Fe_2(CO)_6]$ (1) with 1.0 equiv. of Me₃₋NO·2H₂O in MeCN followed by addition of 1.1 equiv. of PPh₃ at room temperature gave the PPh₃-monosubstituted complex $[(\mu - SCH_2)_2CHCO_2CH_2CI][Fe_2(CO)_5PPh_3]$ (3) and the PPh₃-disubstituted complex $[(\mu - SCH_2)_2CHCO_2CH_2CI][Fe_2(CO)_4(PPh_3)_2]$ (4) in 44% and 41% yields, respectively.

Complex **3** is an air-stable brown-red solid, whereas complex **4** is a slightly air-sensitive dark-red solid. Their molecular structures were fully characterized by elemental analysis, IR, ¹H NMR, ¹³C NMR and ³¹P NMR spectroscopy. While the IR spectrum of **3** displays three strong absorption bands in the range 2045–1936 cm⁻¹ for its terminal carbonyls, that of **4** exhibits three strong absorption bands in the lower range of 1997–1935 cm⁻¹ for its

Table 2
Selected bond lengths (Å) and angles (°) for 1-4

C			
Complex 1			
Fe(1)-Fe(2)	2.498(7)	Fe(1)-C(2)	1.796(2)
Fe(1) - S(1)	2.260(7)	Fe(1) - C(3)	1.798(2)
$E_{\alpha}(1) = S(2)$	2 262 (7)	$F_{0}(1) - C(1)$	1 820(2)
$\Gamma(1) = J(2)$	2.202 (7)	$\Gamma(1) = C(1)$	1.020(2)
Fe(2) - S(2)	2.253(8)	Fe(2)-C(6)	1.796(2)
Fe(2)-S(1)	2.259 (7)	Fe(2)-C(4)	1.798(2)
O(1) - C(1)	1136(2)	Fe(2)-C(5)	1.807(2)
O(1) C(1)	1.130(2)	P(2) = C(3)	1.142(2)
O(2) = C(2)	1.159(2)	O(0) - C(0)	1.145(5)
O(3) - C(3)	1.142(2)	O(7) - C(10)	1.212(3)
O(4) - C(4)	1.144(2)	O(8) - C(10)	1.327(3)
O(5) - C(5)	1 141(2)	O(8) - C(11)	1 444(2)
C(1) = C(1) = C(2)	0.4.05(2)	C(0) = C(11)	1. 111 (2)
S(1) - Fe(1) - S(2)	84.85(3)	S(2)-Fe(2)-Fe(1)	56.60(2)
S(1)-Fe(1)-Fe(2)	56.43(2)	S(1)-Fe(2)-Fe(1)	56.47(2)
S(2) - Fe(1) - Fe(2)	56.24(2)	Fe(2)-S(1)-Fe(1)	67.11(2)
S(2) = S(2) = S(1)	85 00(2)	$E_0(2) S(2) E_0(1)$	67 16(2)
3(2) - 12(2) - 3(1)	85.09(2)	12(2) - 3(2) - 12(1)	07.10(2)
Complex 2			
Fe(1) - Fe(2)	2518(2)	Fe(1)-C(1)	1 796(3)
$\Gamma_{c}(1) \Gamma_{c}(2)$	2.210(2)	$\Gamma_{2}(1) C(2)$	1,709(3)
Fe(1) = S(1)	2.234(2)	re(1) - C(3)	1.796(5)
Fe(1)-S(2)	2.243(2)	Fe(1)-C(2)	1.805(3)
Fe(2)-S(1)	2.238(2)	Fe(2)-C(4)	1.792(3)
Fe(2) - S(2)	2 247(2)	Fe(2) = C(5)	1 803(3)
O(1) C(1)	1 1 4 2 (2)	$\Gamma_{c}(2) = C(3)$	1.005(5)
O(1) - C(1)	1.142(3)	Fe(2) = C(6)	1.809(3)
O(2) - C(2)	1.137(3)	O(6) - C(6)	1.137(3)
O(3) - C(3)	1.144(3)	O(7) - C(10)	1.188(3)
O(4) - C(4)	1 1/1(3)	O(8) - C(10)	1344(3)
	1.141(3)	O(0) C(10)	1.344(3)
O(5) - C(5)	1.142(3)	O(8) - C(11)	1.411(3)
S(1)-Fe(1)-S(2)	85.08(4)	S(2)-Fe(1)-Fe(2)	55.95(4)
S(1) - Fe(1) - Fe(2)	55 81(3)	S(2) - Fe(2) - Fe(1)	55.82(2)
$S(1) = E_0(1) = S(2)$	84.00(4)	$E_{2}(1) = E_{1}(1) = E_{2}(1)$	69 EE(A)
S(1) - Fe(2) - S(2)	84.90(4)	re(1) - 3(1) - re(2)	08.55(4)
S(1) - Fe(2) - Fe(1)	55.64(5)	Fe(1)-S(2)-Fe(2)	68.23(5)
Complex 3			
$\Gamma_{1}(1)$ $\Gamma_{2}(2)$	2 510(0)	F-(1) P(1)	2 252(0)
Fe(1)-Fe(2)	2.518(9)	Pe(1)-P(1)	2.253(9)
Fe(1)-S(1)	2.270(9)	Fe(1)-C(4)	1.769(2)
Fe(1)-S(2)	2.276(1)	Fe(1) - C(5)	1.778(2)
Fe(2) = C(1)	1 793(2)	$F_{e}(2) = S(2)$	2 249(1)
$\Gamma(2) C(1)$	1.755(2)	$\Gamma(2) = S(2)$	2.243(1)
Fe(2)-C(3)	1.795(2)	Fe(2) - S(1)	2.266(9)
Fe(2)-C(2)	1.806(2)	Cl(1)-C(11)	1.787(2)
O(1) - C(1)	1144(2)	O(5) - C(5)	1151(2)
O(2) C(2)	1 1 45(2)	O(6) C(0)	1 205(2)
O(2) = C(2)	1.145(2)	O(0) - C(9)	1.205(2)
O(3) - C(3)	1.140(2)	O(7) - C(9)	1.344(2)
O(4) - C(4)	1.155(2)	O(7) - C(10)	1.453(2)
S(1) - Fe(1) - S(2)	84.18(2)	Fe(2) - S(1) - Fe(1)	67.44(3)
S(1) - Fe(1) - Fe(2)	56.21(2)	Fe(2)-S(2)-Fe(1)	67.63(2)
S(2) - Fe(1) - Fe(2)	55 68(2)	P(1) - Fe(1) - S(1)	111 27(3)
$S(2) = F_{c}(1) = F_{c}(2)$	94.00(2)	$P(1) = F_{1}(1) = F_{1}(1)$	100.04(2)
S(2) - Fe(2) - S(1)	04.09(Z)	P(1) - P(1) - S(2)	108.04(2)
S(2) - Fe(2) - Fe(1)	56.69(3)	P(1) - Fe(1) - Fe(2)	157.82(2)
S(1)-Fe(2)-Fe(1)	56.35(2)	C(9)-O(7)-C(10)	115.48(1)
Complex A			
E_{1}	0.50.4(0)		1 50 4(5)
re(1)-re(2)	2.534(2)	Fe(1)-C(2)	1.764(5)
Fe(2)–C(3)	1.766(5)	Fe(1)–C(1)	1.779(5)
Fe(2) - C(4)	1,775(6)	Fe(1) - P(1)	2.244(2)
$E_{0}(2) = P(2)$	2 2 E C (2)	$E_0(1) S(2)$	2.211(2)
$\Gamma(2) = \Gamma(2)$	2.230(2)	F(1) = 3(2)	2.237(2)
Fe(2) - S(2)	2.265(2)	Fe(1) - S(1)	2.279(2)
Fe(2)-S(1)	2.292(2)	C(10)-Cl(1)	1.782(8)
O(1) - C(1)	1.150(6)	O(5) - C(8)	1,198(7)
O(2) = C(2)	1 156(6)	O(6) - C(8)	1 301(7)
O(2) - C(2)	1.130(0)		1.501(7)
O(3) - C(3)	1.165(6)	O(6) - C(9)	1.444(8)
O(4) - C(4)	1.151(6)	O(6)-C(9')	1.467(9)
C(D) E (4) C(1)	0.1.1.		405 66/5
S(2) - Fe(1) - S(1)	84.14(5)	P(1) - Fe(1) - S(2)	107.39(5)
S(2)-Fe(1)-Fe(2)	56.06(4)	P(1)-Fe(1)-S(1)	106.41(6)
S(1) = Fe(1) = Fe(2)	56 56(5)	P(1) - Fe(1) - Fe(2)	154 71(4)
S(1) = S(1) = S(2) S(2) = S(2) = S(2)		$D(2) = E_0(2) = C(2)$	101 C4(C)
J(Z) = FE(Z) = FE(T)	55.77(5)	r(2) - re(2) - S(2)	101.04(0)
S(1) - Fe(2)Fe(1)	56.09(4)	P(2)-Fe(2)-S(1)	114.07(6)
S(2)-Fe(2)-S(1)	83.68(5)	P(2) - Fe(2) - Fe(1)	154.15(5)

terminal carbonyls. Obviously, the highest $v_{C=0}$ values of **3** and **4** are shifted by 31 and 99 cm⁻¹ toward lower frequencies relative to that of their precursor **1**, respectively. This is because PPh₃ is a stronger electron-donating ligand than CO [17]. The ¹H NMR spectra of **3** and **4** show that in addition to the corresponding organic groups of their precursor **1**, the surplus two singlets at about

7.70 and 7.40 ppm are attributed to the phenyl protons of the PPh₃ ligand. Furthermore, the ³¹P NMR spectra demonstrate one singlet at 64.37 ppm for the phosphorus atom of the PPh₃ ligand in **3** and two singlets at 61.68 and 60.49 ppm for the two phosphorus atoms of the two PPh₃ ligands in **4** [18]. In addition, the ¹³C NMR spectrum of **3** exhibits a doublet at 213.50 ppm with a coupling constant ${}^{2}J_{P-C} = 9.9$ Hz for the PFe(CO)₂ coordinated carbonyls and a singlet at 208.85 ppm for the terminal carbonyls of Fe(CO)₃ [19], whereas that of **4** displays two doublets at 215.62 and 214.66 ppm with the corresponding coupling constant ${}^{2}J_{P-C} = 10.9$ and 9.7 Hz for the PFe(CO)₂ coordinated to the two iron atoms of the diiron subsite [20].

3.3. Crystal structures of complexes 1-4

The molecular structures of **1–4** have been further confirmed by single crystal X-ray diffraction analysis. ORTEP views of **1–4** are illustrated in Figs. 1–4 and selected bond lengths as well as angles are given in Table 2.

As shown in Figs. 1 and 2, complexes 1 and 2 contain a butterfly [Fe₂S₂] cluster with six carbonyl ligands and one propanedithiolate unit that is linked to the ester moiety via the bridgehead C8 atom. The ester substituent in 1 and 2 resides in the sterically-favored equatorial position of two fused six-membered Fe₂S₂C₃ rings, in which one ring (C8C9S2Fe2S1C7 for 1 or C8C9S2Fe1S1C7 for 2) has a chair conformation and the other ring (C8C9S2Fe1S1C7 for 1 or C8C9S2Fe2S1C7 for 2) adopts a boat conformation. This is good agreement with the parent complex $[(\mu-SCH_2)_2CHCO_2]$ H][Fe₂(CO)₆] [21] and other carboxy-functionalized all-carbonyl diiron propanedithiolate complexes, such as $[(\mu-SCH_2)_2]$ -CHCONHR][Fe₂(CO)₆] (R = Ph, Et, $CH_2CO_2Bu^t$) [4,21], which indicates that the carboxylic functionality does not affect the overall geometry of the diiron propanedithiolate complex. It was worth finding out that the dihedral angle between the ester group (07C1008) and the phenyl group (C11-C16) in 2 is 6.7°, demonstrating that the carboxy-functionalized substituent (p-IC₆H₄₋ C(O)O-) of **2** is almost planar. The Fe–Fe bond length of **1** (2.498(7) Å) is shorter than that of **2** (2.518(2) Å) and analogous complexes such as $[(\mu-SCH_2)_2CHCOR][Fe_2(CO)_6]$ (R = NHPh (2.514 Å), NHEt (2.517 Å), NHCH₂CO₂Bu^t (2.514 Å), and OH (2.513 Å)) [4,21], and significantly shorter than those found in the crystal structures of the natural enzymes Clostridium pasteurianum and Desulfovibrio desulfuricans (2.55–2.62 Å) [22,23].

As shown in Figs. 3 and 4, complexes 3 and 4 are composed of their precursor **1** and one or two PPh₃ ligands. The ester substituent and one hydrogen atom attached to the bridgehead-C atom in 3 and 4 occupy the equatorial and axial position of two fused sixmembered rings, respectively, which is in good agreement with the parent complex **1**. The one or two PPh₃ ligands are all located in apical positions of the square-pyramidal geometries of the Fe1 atom in **3** or Fe1 and Fe2 in **4**, which is in accordance with previous similar diiron propanedithiolate complexes with monophosphinemonosubtituted ligands such as [(µ-SCH₂)₂CH₂][Fe₂(CO)₅L] (L = PPh₃ [17], P(OEt)₃ [17], PhPMe₂ [17], Ph₂PNH(2-NH₂Ph) [24], Ph2PNH(CH2)2NMe2 [24], Ph2P(2-Me2NCH2Ph) [24], Ph2P(CH2CO2-H) [25] and Ph₂P(2-NHPy) [26]), and [(μ-SCH₂)₂CHOH][Fe₂(CO)₅₋ PPh₃ [18] or those with monophosphine-disubtituted ligands such as $[(\mu-SCH_2)_2CH_2][Fe_2(CO)_4(PPh_3)_2]$ [17] and $[(\mu-SCH_2)_2]_2$ CHOH][Fe₂(CO)₄(PPh₃)₂] [18]. It should be noted that the two PPh₃ ligands in **4** are coordinated to two Fe atoms with a symmetrically substituted apical/apical coordination configuration, which is well consistent with two doublets at 215.62 and 214.66 ppm for two kinds of terminal carbonyls in its ¹³C NMR spectrum and two singlets at 61.68 and 60.49 ppm for two phosphorus atoms coordinated to two iron atoms in its ³¹P NMR spectrum. In addition, the Fe1–Fe2 bond lengths of **3** (2.518(9)Å) and **4** (2.534(2)Å) are obviously longer than that of the precursor **1** (2.498(7)Å), demonstrating that the monophosphine-substituted ligand PPh₃ has a certain effect on the Fe–Fe bond length of the carboxy-functionalized diiron propanedithiolate complex.

In addition, the solid-state structures of **1–4** are stabilized by van der Waals' interactions and intermolecular hydrogen bonds, as observed in their crystal packing diagrams (as shown in Figs. 5–8 in the Supporting Information).

4. Conclusions

In summary, we have successfully synthesized a series of new carboxy-functionalized diiron propanedithiolate complexes, **1–4**. While the all-carboxyl complexes **1** and **2** are prepared using the condensation reaction of **A** with $ClCH_2CH_2OH$ and $p-IC_6H_4OH$ in high yields, respectively, the phosphine-substituted complexes **3** and **4** are further synthesized by the carbonyl displacement reactions of **1** with PPh₃ in moderate yields. The molecular structures of **1–4** are characterized by elemental analysis, IR and NMR spectroscopies, as well as by X-ray crystallography.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2013.01.048.

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