

Journal of Organometallic Chemistry, 391 (1990) 387–394
 Elsevier Sequoia S.A., Lausanne
 JOM 20953

Synthesis and structural characterization of bridged double butterfly-shaped Fe–S cluster complexes $[(\mu\text{-RS})\text{Fe}_2(\text{CO})_6]_2(\mu\text{-SCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{S}\text{-}\mu)$

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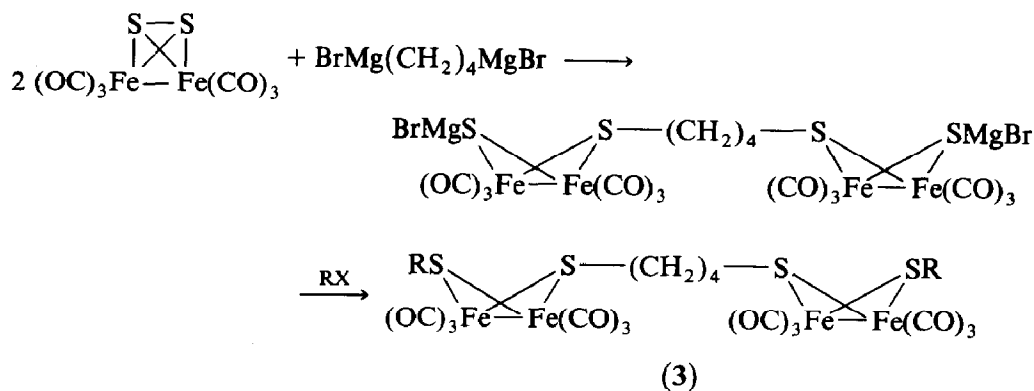
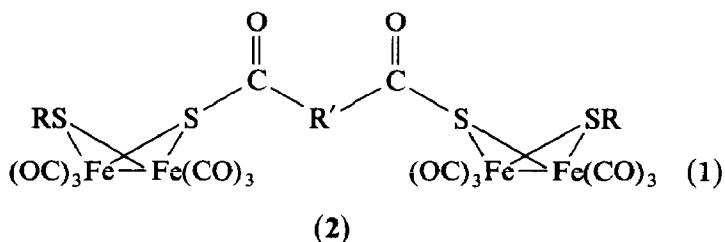
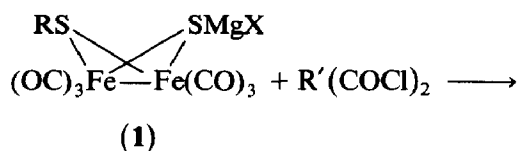
(Received July 17th, 1989; in revised form September 24th, 1989)

Abstract

The monoanions derived from $\mu\text{-S}_2\text{Fe}_2(\text{CO})_6$ and RMgX ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$) react with *o*-, *m*-, or *p*- $\text{BrCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{Br}$ in THF to give the bridged double Fe–S cluster complexes of $[(\mu\text{-RS})\text{Fe}_2(\text{CO})_6]_2[\mu\text{-S}(\textit{o}, \textit{m}, \textit{p}\text{-CH}_2\text{C}_6\text{H}_4\text{CH}_2)\text{-S}\text{-}\mu]$ in 44–87% yield. These products were characterized by IR, proton NMR and elemental analysis. A single crystal X-ray diffraction study of $[(\mu\text{-CH}_3\text{S})\text{Fe}_2(\text{CO})_6]_2[\mu\text{-S}(\textit{m}\text{-CH}_2\text{C}_6\text{H}_4\text{CH}_2)\text{-S}\text{-}\mu]$ has shown that it crystallizes in the space group $P\bar{1}$ with a 7.831(2), b 14.423(3), c 14.928(2) Å; α 68.29(1), β 87.76(2), γ 83.19(2)°; V 1555.4 Å³; D_c 1.755 g cm⁻³. Intensity data of 4154 independent reflections were collected in the range of $2 < \theta < 23^\circ$, with 3184 reflections ($I > 3\sigma(I)$) being used in the structure refinement. The final R value was 0.052.

Introduction

During recent years the interest in bridged double cluster core complexes has burgeoned [1–5]. On one hand, this is probably due to their novel structures and unique properties, and on the other hand because of their potential use, for instance as model compounds of the iron-molybdenum cofactor of nitrogenase [1–5]. Currently, it is noteworthy that the bridged double butterfly-shaped Fe–S cluster complexes, which possess a diacyl or butylene bridge, have been reported [3–5]. They can be obtained from the reaction of monoanions **1** with diacid chlorides [3,4] (eq. 1) and or from the reaction of $\mu\text{-S}_2\text{Fe}_2(\text{CO})_6$ with di-Grignard reagents [5] (eq. 2):

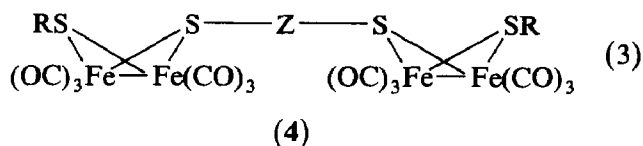
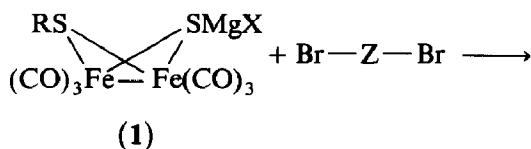


(2)

Interestingly, we have now found that the reaction of xylylene dibromides with monoanions 1 produces the third class of bridged double butterfly-shaped Fe-S cluster complexes, which are bridged by *o*-, *m*-, and *p*-CH₂C₆H₄CH₂ groups. Here we describe the results of the study.

Results and discussion

In our previous paper we pointed out that butylenebridged complexes 3 could not be obtained from monoanions 1 and 1,4-dibromobutane [5]. However, in this paper we have confirmed that the xylylene-bridged complexes, 4, can be satisfactorily obtained from the reaction of monoanions 1 with the corresponding dihalides, which are more reactive than dibromobutane (eq. 3):



(Y = CH₂C₆H₄CH₂; R = Me: Z = *o*-Y 4a, Z = *m*-Y 4b, Z = *p*-Y 4c; R = Et: Z = *o*-Y 4d, Z = *m*-Y 4e, Z = *p*-Y 4f)

The complexes **4a–4f** have been well characterized by combustion analysis, IR and ^1H NMR. From ^1H NMR data of these complexes we can see that the δ values of the methylene groups on the benzene ring are obviously shifted upfield, compared with the δ values of the methylenes of the starting material xylene dibromide ($\delta(\text{CH}_2)$: 4.66, 4.40 and 4.43 ppm in *o*-, *m*-, and *p*-(BrCH_2) $_2\text{C}_6\text{H}_4$, respectively). Interestingly, the ^1H NMR data for **4a–4f** permitted us to assign the various bond types by which the relevant sulfur atom is attached to the methyl, ethyl, and the organic bridge, and to establish further possible conformers of the complexes [5–10]. For complexes **4b** and **4e** the δ values for their CH_2 attached to the benzene ring are 3.23 and 3.30 ppm, respectively, indicating that their xylene bridges are bonded to two sulfur atoms through axial (abbreviated as *a*) bonds [8,9]. Furthermore, since the $\delta(\text{CH}_3)$ of **4b** and the $\delta(\text{CH}_2)$ of the ethyl in **4e** are 2.20 and 2.53 ppm, the two methyl groups of **4b** and the two ethyl groups of **4e** should be

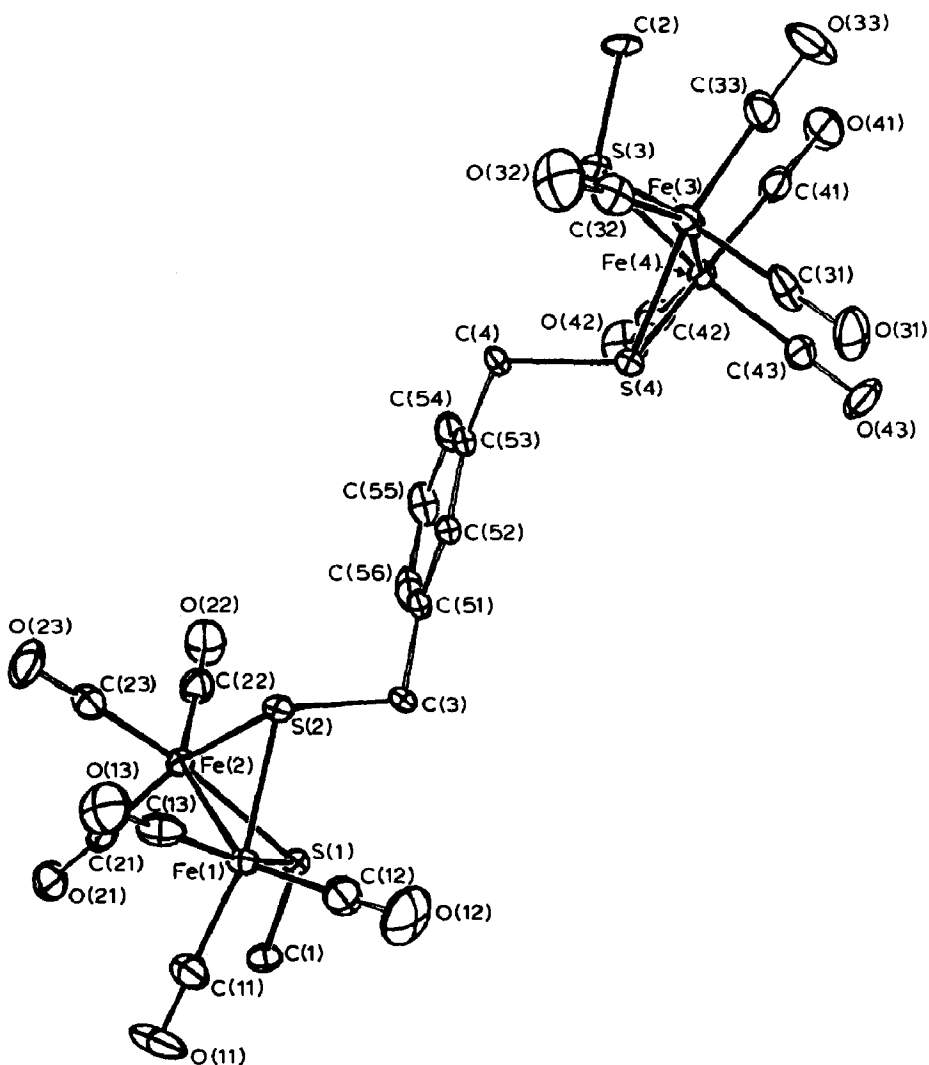
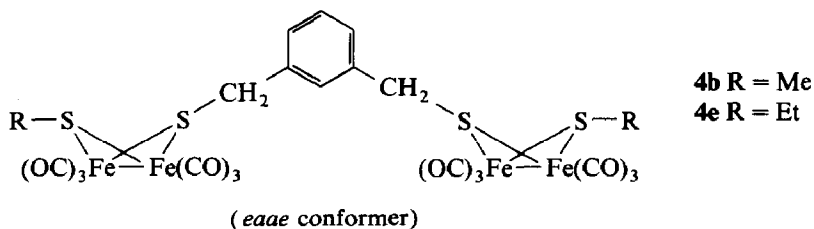


Fig. 1. Crystal structure of $[(\mu\text{-CH}_3\text{S})\text{Fe}_2(\text{CO})_6]_2[\mu\text{-S-(}m\text{-CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{)-S-}\mu]$.

attached to the sulfur atoms via equatorial (abbreviated as *e*) bonds [7–9]. Thus, by the nomenclature of Shaver et al. [6], we can see both **4b** and **4e** exist only as the *eaee* conformer [5–10]:



Unfortunately, we could not establish the conformers of the other complexes in this series, because they have two NMR peaks for CH₂ of xylylene bridge and the integrated values for the two peaks are different.

In order to confirm unambiguously the spacial structures for the complexes of this series, a single crystal X-ray diffraction study of **4b** was undertaken. The final positional parameters for the atoms are given in Table 1. Tables 2 and 3 contain the interatomic distances and bond angles. Figure 1 shows a perspective view of the molecular structure of **4b**. From Fig. 1, it can be clearly seen that in **4b** contains an organic moiety, CH₂C₆H₄CH₂, which bridges the two Fe₂S₂ butterfly-shaped skeletons and a pseudo symmetric center which lies in the central part of the benzene ring of bridge CH₂C₆H₄CH₂. It should be noted that the average bond length of Fe(1)–Fe(2) and Fe(3)–Fe(4) is 2.510(1) Å, which is close to the Fe–Fe bond lengths in (μ-EtS)₂Fe₂(CO)₆, 2.54 Å [11], and μ-S₂Fe₂(CO)₆, 2.55 Å [12]. In addition, the angles S(2) ··· S(1)–C(1) and S(4) ··· S(3)–C(2) are 159.2 and 158.9°, respectively, indicating that the methyl group is attached to the sulfur atom by an *e*-type bond; the angles of S(1) ··· S(2)–C(3) and S(3) ··· S(4)–C(4) are 78.2 and 78.8°, indicating that the two methylene groups of CH₂C₆H₄CH₂ are bonded to the sulfur atoms by *a*-type bond. Therefore, the results of X-ray diffraction study are in good agreement with the assignments based on the ¹H NMR data, namely **4b** contains one *eaee* conformer.

Experimental

All reactions were carried out in flame-dried flasks under highly purified nitrogen. THF and Et₂O were rigorously dried by distillation from Na-benzophenone ketyl. Chromatographic silica gel was about 300 mesh. *o*-, *m*- and *p*-(BrCH₂)₂C₆H₄ were prepared by previously published procedures [13]. Standard procedures were followed for the preparation of the Grignard reagents [14] and μ-S₂Fe₂(CO)₆ [9]. The course of the reaction was monitored by TLC. The IR spectra were recorded with a Nicolet FT-IR 5DX spectrophotometer, and the ¹H NMR spectra with JEOL JNMPMX 60 Si NMR spectrometer. Elemental analysis and melting point determinations were performed with a 204C analyzer and PHMK-3003 instruments, respectively.

Preparation of 4a–4f

A 250-ml two-necked flask, fitted with a magnetic stir-bar, an air-tight septum and a nitrogen inlet, was flame-dried and then charged with 1.00 g (2.91 mmol) of

Table 1

Positional parameters and equivalent isotropic thermal factors for **4b**

Atom	x	y	z	B_{eq} (Å ²)
Fe(1)	0.2299(2)	0.2411(1)	0.2012(1)	3.46(3)
Fe(2)	0.3712(2)	0.1676(1)	0.3646(1)	3.12(3)
Fe(3)	1.1686(2)	0.7692(1)	0.1054(1)	3.47(3)
Fe(4)	1.0241(2)	0.7797(1)	0.2547(1)	3.31(3)
S(1)	0.1327(3)	0.2800(2)	0.3284(2)	3.33(6)
S(2)	0.4724(3)	0.2914(2)	0.2375(2)	3.83(6)
S(3)	1.2676(3)	0.6780(2)	0.2559(2)	3.37(6)
S(4)	0.9322(3)	0.6941(2)	0.1683(2)	3.42(6)
O(11)	-0.063(1)	0.1294(7)	0.2122(7)	9.1(3)
O(12)	0.135(2)	0.4153(9)	0.0263(8)	11.0(4)
O(13)	0.448(1)	0.1240(7)	0.1077(7)	8.3(3)
O(21)	0.175(1)	-0.0020(6)	0.4588(7)	6.8(3)
O(22)	0.508(1)	0.1870(7)	0.5364(6)	7.8(3)
O(23)	0.648(1)	0.0263(6)	0.3355(7)	7.1(3)
O(31)	0.943(1)	0.9214(6)	-0.0424(6)	7.3(3)
O(32)	1.326(2)	0.6450(7)	0.0003(7)	9.0(3)
O(33)	1.423(1)	0.9116(6)	0.0709(7)	8.1(3)
O(41)	1.216(1)	0.9275(6)	0.2849(7)	8.2(3)
O(42)	0.875(1)	0.6885(7)	0.4461(6)	7.7(3)
O(43)	0.745(1)	0.9382(6)	0.1674(8)	8.1(3)
C(1)	-0.065(1)	0.2274(8)	0.3837(9)	4.7(3)
C(2)	1.467(1)	0.7184(8)	0.2874(9)	5.1(3)
C(3)	0.421(1)	0.4196(7)	0.238(1)	6.0(3)
C(4)	0.986(1)	0.5561(7)	0.2216(9)	4.1(3)
C(11)	0.052(2)	0.1722(8)	0.2068(9)	5.2(3)
C(12)	0.168(2)	0.3485(9)	0.0953(9)	5.7(3)
C(13)	0.362(1)	0.1703(9)	0.1443(8)	5.4(3)
C(21)	0.251(1)	0.0660(8)	0.4226(8)	4.3(3)
C(22)	0.456(2)	0.1809(8)	0.4701(8)	4.8(3)
C(23)	0.542(1)	0.0824(8)	0.3456(8)	4.5(3)
C(31)	1.033(2)	0.8611(7)	0.0141(8)	4.9(3)
C(32)	1.266(2)	0.6963(9)	0.0403(8)	5.0(3)
C(33)	1.326(2)	0.8555(8)	0.0837(9)	5.1(3)
C(41)	1.141(1)	0.8693(8)	0.2755(9)	5.3(3)
C(42)	0.937(1)	0.7253(8)	0.3698(8)	5.0(3)
C(43)	0.849(2)	0.8773(8)	0.2001(9)	5.4(3)
C(51)	0.563(1)	0.4447(6)	0.2893(8)	3.9(3)
C(52)	0.704(1)	0.4861(7)	0.2339(8)	3.7(3)
C(53)	0.837(1)	0.5102(6)	0.2815(8)	3.4(2)
C(54)	0.829(2)	0.4905(7)	0.3781(8)	4.6(3)
C(55)	0.687(2)	0.4503(8)	0.4334(9)	5.5(3)
C(56)	0.554(2)	0.4282(8)	0.3867(9)	5.4(3)

μ -S₂Fe₂(CO)₆ in 50 ml of dry THF. The resulting red solution was cooled to -78 °C with a dry ice-acetone bath. An amount of MeMgI or EtMgBr in Et₂O was injected in by syringe until the solution turned a deep green. The green solution was stirred at -78 °C for 15 min and then 0.384 g (1.455 mmol) of C₆H₄(CH₂Br)₂ was added. After 30 min the reaction mixture became red and the cooling bath was removed. Stirring was continued for 3 h at room temperature and the solvent removed by rotary evaporator under reduced pressure. The residue was fully

Table 2. Bond lengths (Å) for 4b.

Fe(1)–Fe(2)	2.514(1)	S(2)–C(3)	1.846(8)
Fe(1)–S(1)	2.252(3)	S(3)–C(2)	1.865(7)
Fe(1)–S(2)	2.264(2)	S(4)–C(4)	1.852(6)
Fe(1)–C(11)	1.785(8)	O(11)–C(11)	1.13(2)
Fe(1)–C(12)	1.789(9)	O(12)–C(12)	1.13(1)
Fe(1)–C(13)	1.777(9)	O(13)–C(13)	1.152(9)
Fe(2)–S(1)	2.263(2)	O(21)–C(21)	1.152(8)
Fe(2)–S(2)	2.264(2)	O(22)–C(22)	1.123(8)
Fe(2)–C(21)	1.763(8)	O(23)–C(23)	1.14(2)
Fe(2)–C(22)	1.815(8)	O(31)–C(31)	1.153(9)
Fe(2)–C(23)	1.792(8)	O(32)–C(32)	1.16(1)
Fe(3)–Fe(4)	2.506(1)	O(33)–C(33)	1.135(8)
Fe(3)–S(3)	2.255(2)	O(41)–C(41)	1.135(8)
Fe(3)–S(4)	2.251(2)	O(42)–C(42)	1.18(1)
Fe(3)–C(31)	1.785(9)	O(43)–C(43)	1.104(9)
Fe(3)–C(32)	1.770(9)	C(3)–C(51)	1.53(2)
Fe(3)–C(33)	1.792(8)	C(4)–C(53)	1.503(9)
Fe(4)–S(3)	2.260(2)	C(51)–C(52)	1.403(9)
Fe(4)–S(4)	2.272(2)	C(51)–C(56)	1.38(2)
Fe(4)–C(41)	1.790(8)	C(52)–C(53)	1.429(9)
Fe(4)–C(42)	1.752(9)	C(53)–C(54)	1.36(1)
Fe(4)–C(43)	1.819(8)	C(54)–C(55)	1.40(2)
S(1)–C(1)	1.836(7)	C(55)–C(56)	1.41(1)

extracted with petroleum ether. The extracts were concentrated to about 10 ml and then subjected to column chromatography, with 5% (v/v) CH_2Cl_2 /petroleum ether as eluant, to give 4a–4f:

4a: $[(\mu\text{-CH}_3\text{S})\text{Fe}_2(\text{CO})_6]_2[\mu\text{-S-(o-CH}_2\text{C}_6\text{H}_4\text{CH}_2)\text{-S-}\mu]$, 53% yield. red crystals, m.p. 149–150 °C (dec.). Anal. Found: C, 32.15; H, 1.73. $\text{C}_{22}\text{H}_{14}\text{Fe}_4\text{O}_{12}\text{S}_4$ calcd.: C, 32.15; H, 1.72%. IR (KBr disc): terminal $\text{C}\equiv\text{O}$, 2073s, 2032s, 1975s cm^{-1} . ^1H NMR (CDCl_3): δ 2.09, 2.17(e, e, s, s, 6H, 2 CH_3), 3.33, 3.66(a, e, s, s, 4H, 2 CH_2), 7.09–7.40(m, 4H, C_6H_4) ppm.

4b: $[(\mu\text{-CH}_3\text{S})\text{Fe}_2(\text{CO})_6]_2[\mu\text{-S-(m-CH}_2\text{C}_6\text{H}_4\text{CH}_2)\text{-S-}\mu]$, 45% yield. red crystals, m.p. 124–126 °C (dec.). Anal. Found: C, 32.48; H, 1.52. $\text{C}_{22}\text{H}_{14}\text{Fe}_4\text{O}_{12}\text{S}_4$ calcd.: C, 32.15, H, 1.72%. IR (KBr disc): terminal $\text{C}\equiv\text{O}$, 2073s, 2032s, 1991s cm^{-1} . ^1H NMR (CDCl_3): δ 2.20(e, s, 6H, 2 CH_3), 3.23(a, s, 4H, 2 CH_2), 7.13–7.43(m, 4H, C_6H_4) ppm.

4c: $[(\mu\text{-CH}_3\text{S})\text{Fe}_2(\text{CO})_6]_2[\mu\text{-S-(p-CH}_2\text{C}_6\text{H}_4\text{CH}_2)\text{-S-}\mu]$, 44% yield. red crystals, m.p. 148–150 °C (dec.). Anal. Found: C, 32.30; H, 1.71. $\text{C}_{22}\text{H}_{14}\text{Fe}_4\text{O}_{12}\text{S}_4$ calcd.: C, 32.15; H, 1.72%. IR (KBr disc): terminal $\text{C}\equiv\text{O}$, 2073s, 2032s, 1983s, 1960s cm^{-1} . ^1H NMR (CDCl_3): δ 2.20(e, s, 6H, 2 CH_3), 3.30, 3.63(a, e, s, s, 4H, 2 CH_2), 7.06–7.42(m, 4H, C_6H_4) ppm.

4d: $[(\mu\text{-C}_2\text{H}_5\text{S})\text{Fe}_2(\text{CO})_6]_2[\mu\text{-S-(o-CH}_2\text{C}_6\text{H}_4\text{CH}_2)\text{-S-}\mu]$, 67% yield. red oil. Anal. Found: C, 33.93; H, 2.38. $\text{C}_{24}\text{H}_{18}\text{Fe}_4\text{O}_{12}\text{S}_4$ calcd.: C, 33.91; H, 2.13%. IR (KBr disc): terminal $\text{C}\equiv\text{O}$, 2073s, 2040s, 1991s cm^{-1} . ^1H NMR (CDCl_3): δ 1.46(t, J 8 Hz, 6H, 2 CH_2CH_3), 2.56(e, q, J 8 Hz, 4H, 2 CH_2CH_3), 3.43, 3.73(a, e, s, s, 4H, 2 CH_2), 7.10–7.56(m, 4H, C_6H_4) ppm.

4e: $[(\mu\text{-C}_2\text{H}_5\text{S})\text{Fe}_2(\text{CO})_6]_2[\mu\text{-S-(m-CH}_2\text{C}_6\text{H}_4\text{CH}_2)\text{-S-}\mu]$, 87% yield. red crystals, m.p. 102–104 °C. Anal. Found: C, 34.23; H, 2.15. $\text{C}_{24}\text{H}_{18}\text{Fe}_4\text{O}_{12}\text{S}_4$ calcd.: C, 33.91; H, 2.13%. IR (KBr disc): terminal $\text{C}\equiv\text{O}$, 2073s, 2040s, 1975s cm^{-1} . ^1H

Table 3. Bond angles (°) for 4b.

Fe(2)–Fe(1)–S(1)	56.35(6)	S(2)–Fe(2)–C(22)	104.9(3)
Fe(2)–Fe(1)–S(2)	56.28(5)	S(2)–Fe(2)–C(23)	88.0(2)
Fe(2)–Fe(1)–C(11)	106.8(3)	C(21)–Fe(2)–C(22)	99.2(3)
Fe(2)–Fe(1)–C(12)	149.3(3)	C(21)–Fe(2)–C(23)	89.6(3)
Fe(2)–Fe(1)–C(13)	98.2(2)	C(22)–Fe(2)–C(23)	99.3(3)
S(1)–Fe(1)–S(2)	80.99(7)	Fe(4)–Fe(3)–S(3)	56.37(5)
S(1)–Fe(1)–C(11)	91.9(3)	Fe(4)–Fe(3)–S(4)	56.74(5)
S(1)–Fe(1)–C(12)	106.9(3)	Fe(4)–Fe(3)–C(31)	100.9(3)
S(1)–Fe(1)–C(13)	154.2(3)	Fe(4)–Fe(3)–C(32)	150.0(2)
S(2)–Fe(1)–C(11)	162.8(3)	Fe(4)–Fe(3)–C(33)	102.1(3)
S(2)–Fe(1)–C(12)	98.4(3)	S(3)–Fe(3)–S(4)	81.00(7)
S(2)–Fe(1)–C(13)	87.8(2)	S(3)–Fe(3)–C(31)	157.2(3)
C(11)–Fe(1)–C(12)	98.7(4)	S(3)–Fe(3)–C(32)	101.4(3)
C(11)–Fe(1)–C(13)	92.2(4)	S(3)–Fe(3)–C(33)	92.8(2)
C(12)–Fe(1)–C(13)	97.8(4)	S(4)–Fe(3)–C(31)	87.7(2)
Fe(1)–Fe(2)–S(1)	55.95(5)	S(4)–Fe(3)–C(32)	103.5(3)
Fe(1)–Fe(2)–S(2)	56.27(5)	S(4)–Fe(3)–C(33)	157.8(3)
Fe(1)–Fe(2)–C(21)	100.9(2)	C(31)–Fe(3)–C(32)	100.4(4)
Fe(1)–Fe(2)–C(22)	151.3(2)	C(31)–Fe(3)–C(33)	90.3(3)
Fe(1)–Fe(2)–C(23)	101.2(2)	C(32)–Fe(3)–C(33)	98.6(4)
S(1)–Fe(2)–S(2)	80.76(7)	Fe(3)–Fe(4)–S(3)	56.19(5)
S(1)–Fe(2)–C(21)	92.5(2)	Fe(3)–Fe(4)–S(4)	55.96(5)
S(1)–Fe(2)–C(22)	103.0(2)	Fe(3)–Fe(4)–C(41)	101.0(3)
S(1)–Fe(2)–C(23)	157.1(3)	Fe(3)–Fe(4)–C(42)	152.4(3)
S(2)–Fe(2)–C(21)	155.9(2)	Fe(3)–Fe(4)–C(43)	99.7(3)
S(3)–Fe(4)–S(4)	80.44(6)	S(4)–C(4)–C(53)	109.1(4)
S(3)–Fe(4)–C(41)	92.1(2)	Fe(1)–C(11)–O(11)	178.1(8)
S(3)–Fe(4)–C(42)	104.4(3)	Fe(1)–C(12)–O(12)	177.1(9)
S(3)–Fe(4)–C(43)	155.8(4)	Fe(1)–C(13)–O(13)	179.6(9)
S(4)–Fe(4)–C(41)	155.9(3)	Fe(2)–C(21)–O(21)	177.9(8)
S(4)–Fe(4)–C(42)	104.8(3)	Fe(2)–C(22)–O(22)	178.5(7)
S(4)–Fe(4)–C(43)	87.6(2)	Fe(2)–C(23)–O(23)	178.1(6)
C(41)–Fe(4)–C(42)	99.3(4)	Fe(3)–C(31)–O(31)	177.6(8)
C(41)–Fe(4)–C(43)	90.3(3)	Fe(3)–C(32)–O(32)	177.0(7)
C(42)–Fe(4)–C(43)	99.0(4)	Fe(3)–C(33)–O(33)	178.3(9)
Fe(1)–S(1)–Fe(2)	67.70(6)	Fe(4)–C(41)–O(41)	177.3(9)
Fe(1)–S(1)–C(1)	115.6(3)	Fe(4)–C(42)–O(42)	178.4(7)
Fe(2)–S(1)–C(1)	114.2(2)	Fe(4)–C(43)–O(43)	178.3(7)
Fe(1)–S(2)–Fe(2)	67.45(5)	C(3)–C(51)–C(52)	117.5(7)
Fe(1)–S(2)–C(3)	108.3(2)	C(3)–C(51)–C(56)	121.4(7)
Fe(2)–S(2)–C(3)	115.4(3)	C(52)–C(51)–C(56)	121.2(7)
Fe(3)–S(3)–Fe(4)	67.43(6)	C(51)–C(52)–C(53)	117.9(7)
Fe(3)–S(3)–C(2)	114.1(3)	C(4)–C(53)–C(52)	117.7(6)
Fe(4)–S(3)–C(2)	115.0(2)	C(4)–C(53)–C(54)	122.0(6)
Fe(3)–S(4)–Fe(4)	67.29(5)	C(52)–C(53)–C(54)	120.4(6)
Fe(3)–S(4)–C(4)	110.4(3)	C(53)–C(54)–C(55)	121.8(8)
Fe(4)–S(4)–C(4)	115.1(2)	C(54)–C(55)–C(56)	118.1(8)
S(2)–C(3)–C(51)	109.9(4)	C(51)–C(56)–C(55)	120.7(7)

NMR(CDCl₃): δ 1.46 (t, *J* 8 Hz, 6H, 2CH₃CH₂), 2.53 (e, q, *J* 8 Hz, 4H, 2CH₂CH₃), 3.30 (a, s, 4H, 2CH₂), 7.00–7.33 (m, 4H, C₆H₄) ppm.

4f: [(μ-C₂H₅S)Fe₂(CO)₆]₂[μ-S-(p-CH₂C₆H₄CH₂)-S-μ], 53% yield. red crystals, m.p. 122–125 °C. Anal. Found: C, 33.93; H, 2.18. C₂₄H₁₈Fe₄O₁₂S₄ calcd.: C, 33.91;

H, 2.13%. IR (KBr disc): terminal $\text{C}\equiv\text{O}$, 2073s, 2024s, 1983s cm^{-1} . ^1H NMR(CDCl_3): δ 1.44(t, J 8 Hz, 6H, 2 CH_3CH_2), 2.53 (e, q, J 8 Hz, 4H, 2 CH_2CH_3), 3.30, 3.60(a, e, s, s, 4H, 2 CH_2), 7.00–7.53(m, 4H, C_6H_4) ppm.

Crystal data and structure determination of 4b

A red crystal of **4b** having the approximate dimensions $0.1 \times 0.2 \times 0.3$ mm was mounted on a glass fiber in an arbitrary orientation. Preliminary examination and data collection were performed under Mo-K_α radiation (λ 0.71073 Å) with an Enraf–Nonius CAD4 diffractometer equipped with a graphite monochromator. A total of 4514 independent reflections were collected in the range of $2 < \theta < 23^\circ$ by ω - 2θ scan technique at room temperature, in which 3184 reflections with $I > 3\sigma(I)$ were considered observed and used in the subsequent refinement. Corrections for LP and for absorption based on a series of ψ scans were applied to the data. The crystal is triclinic, space group $P\bar{1}$, with a 7.831(2), b 14.423(3), c 14.928(2) Å; α 68.29(1), β 87.76(2), γ 83.19(2)°; V 1555.4 Å³; $MW = 821.99$; $Z = 2$; D_c 1.755 g cm^{-3} .

The structure was solved by direct method (MULTAN 82). Four Fe and four S atoms were located from an E -map. The coordinates of the remaining non-hydrogen atoms were found in subsequent difference Fourier synthesis. The hydrogen atoms were not included in the refinements. The final refinement by full matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms converged to unweighted and weighted agreement factors of .052 and 0.065. The highest peak on the final difference Fourier map had a height of 1.01 $e/\text{Å}^3$.

All calculations were performed by a PDP11/44 computer with a SDP-PLUS program system.

Acknowledgement

We are grateful to the National Science Foundation of China for support of this work.

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