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Preparation and structural characterization of $[RSFe_2(CO)_6]_2S$. A novel route to Fe–S cluster compounds containing a sulfur atom coordinated to four metal atoms

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Abstract

The reaction of monoanions derived from $(\mu\text{-}S_2)Fe_2(CO)_6$ and RMgBr ($R = CH_3$, C_2H_5, $C_6H_5CH_2$, $p\text{-}CH_3C_6H_4$, $C_6H_5C{\equiv}C$) with di-acid chlorides at room temperature unexpectedly produced tetranuclear complexes of general formula $[RSFe_2(CO)_6]_2S$ in high yield. These complexes have been characterized by proton NMR, IR and elemental analysis. A single crystal X-ray study (for $R = C_2H_5$) has unambiguously confirmed the composition and revealed that there is a pseudotetrahedral sulfur atom bridging the four iron atoms and so joins together the two identical $[RSFe_2(CO)_6]$ fragments. This compound ($R = C_2H_5$) crystallizes in the space group $P2_12_12_1$ with a 11.875(2), b 12.920(3), c 17.020(3) Å, $Z = 4$; D_c 1.754 g cm^{-3}. Intensity data of 3550 independent reflections were collected in the range $2° < \theta < 28°$, with 1718 reflections ($I > 3\sigma(I)$) being used in the structure refinement. When the reaction was stopped at lower temperature, the diacyl groups were found to have bridged the two monoanions.

Introduction

Organolithium and Grignard reagents have been shown to cleave the S–S bond of $(\mu\text{-}S_2)Fe_2(CO)_6$ to give monoanion intermediates (**1**) that can undergo alkylation [1,2], mercuration [1], protonation [4], acylation [5] and conjugated addition with α,β-unsaturated substrates [6].

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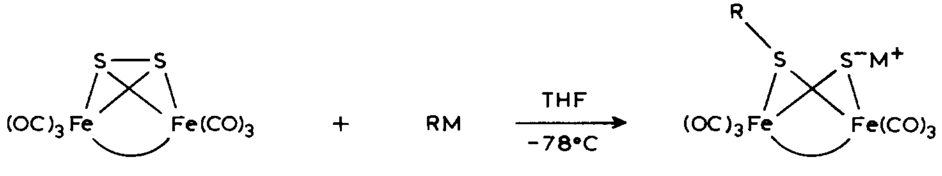


(M = Li , MgX)

(1)

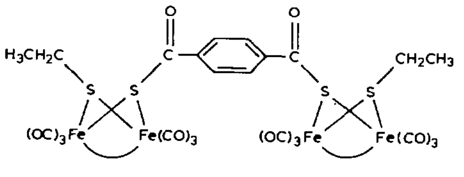
The reaction of these monoanions with di-acid chlorides gives complexes in which the diacyl groups derived from di-acid chlorides bridge the two monoanions [5]. In order to prepare more of such complexes and to investigate whether the acylation was independent of reaction temperature, reaction time and the nature of groups R and di-acid chlorides, we carried out the reaction using different Grignard reagents RMgX (R = CH_3, C_2H_5, $C_6H_5CH_2$, *p*-$CH_3C_6H_4$, $C_6H_5C{\equiv}C$) and a series of di-acid chlorides (*o*-phthaloyl, *m*-phthaloyl, *p*-phthaloyl, and succinoyl chloride). Surprisingly, we have found that in all cases at room temperature, the reaction unexpectedly produced Fe–S cluster complexes in which a central sulfur atom bridges four iron atoms. Only when the reaction was stopped at low temperature (−40 to −30 °C) were the expected di-thioacylated derivatives obtained together with small amounts of the unexpected products. Here we report the preparation, structure and some physico-chemical properties of the complexes $[RSFe_2(CO)_6]_2S$. These complexes are structurally analogous to $[(\mu_2\text{-SMe})Fe_2(CO)_6]_2(\mu_4\text{-S})$ [7], $[Fe_2(CO)_8(\mu_2\text{-Sn}(CH_3)_2]_2(\mu_4\text{-Sn})$ [8]. $[Co_4(\eta^5\text{-}C_5H_5)_4(CO)_4(\mu_4\text{-As})]^+$ [9], $[Me_3NCH_2Ph]$ $[Fe_4(CO)_{12}H(\mu_4\text{-CO})]$ [10] and $[Fe_2(CO)_8(\mu_4\text{-Sb})]_2$ $Fe_2(CO)_6$ [11], which contain quadruply bridging sulfur, tin, arsenic, carbon and antimony atoms, respectively.

Although the methyl member of this Fe–S cluster series $[RSFe_2(CO)_6]_2S$ has been known for 20 years, it was prepared only in 1% yield and up to now no improved preparative method has been reported. Herein we describe, what we understand to be a novel, convenient general procedure for the synthesis, in high yield (61–91%), of this series of complexes in which sulfur donates six electrons to four metal atoms.

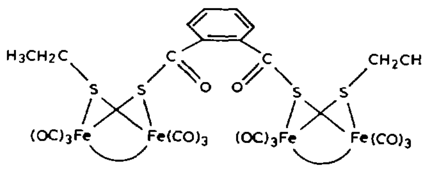
Results and discussion

The reactions of ethylmagnesium bromide/$(\mu\text{-}S_2)Fe_2(CO)_6$-derived monoanion with *o*-phthaloyl, *m*-phthaloyl, *p*-phthaloyl and succinoyl chlorides at low temperature gave complexes in which two $(\mu\text{-EtS})(\mu\text{-S})Fe_2(CO)_6$ units were linked via the corresponding difunctional organic moieties. Of these relatively unstable sticky red materials, only the *p*-phthaloyl chloride and *o*-phthaloyl chloride derivatives were isolated in a form suitable for physico-chemical characterization. The solid state IR spectrum of the *p*-phthaloyl chloride derivative indicated the presence of terminal carbonyl ligand absorption bands at 2055 s, 2050 vs, 2000s, 1995s 1990s cm^{-1} and the ester carbonyl at 1675s cm^{-1}. The 60-MHz proton NMR spectrum in $CDCl_3$ showed a triplet at δ 1.33 ppm due to the methyl protons and a quadruplet at δ 2.50 ppm which was assigned to the methylene protons whereas the singlet at δ 7.96 ppm is probably due to the protons of the disubstituted phenyl ring of the *p*-phthaloyl moiety. This complex is believed to have structure 2.

On the other hand, the solid state IR spectrum of the *o*-phthaloyl chloride derivative (structure **3**) showed terminal carbonyl ligands at 2060m, 2020s, 1990m, 1980m cm^{-1} and the ester carbonyl at 1685s cm^{-1}. The proton NMR spectrum in $CDCl_3$ showed a triplet at δ 1.39 ppm due to the methyl protons and a quadruplet at δ 2.49 ppm which was assigned to the methylene protons. A multiplet at δ 7.36–8.30 ppm is probably attributable to the phenyl ring protons.

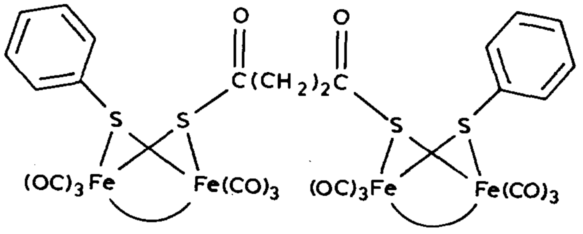


(**2**)



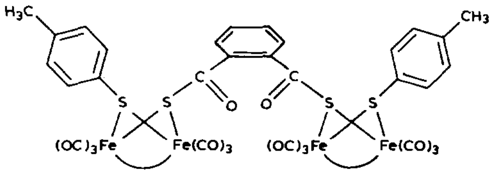
(**3**)

The reaction of phenylmagnesium bromide-derived monoanion with succinoyl chloride gave a sticky red material. Its IR spectrum revealed absorption bands by terminal carbonyl at 2050m, 2020vs, 2000s, 1990s and that of the ester carbonyl at 1695m cm^{-1}. The 60-MHz proton NMR spectrum in $CDCl_3$ revealed a multiplet at δ 3.00 ppm due to the methylene, and another multiplet at δ 7.00–7.59 ppm which was assigned to the phenyl ring protons (**4**).

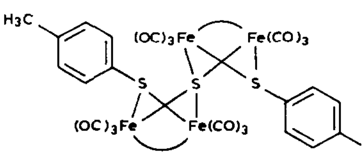


(**4**)

The reaction of the *p*-tolylmagnesium bromide/(μ-S_2)$Fe_2(CO)_6$-derived anion with *o*-phthaloyl chloride gave **5**, in which two (μ-*p*-$CH_3C_6H_4S$)(μ-S)$Fe_2(CO)_6$ units are linked via a difunctional organic moiety in 32% yield, together with the unexpected, non-acylated product **6** in 41% yield. This was the case for all of the other reactions described above; small amounts of the unexpected product were always isolated.

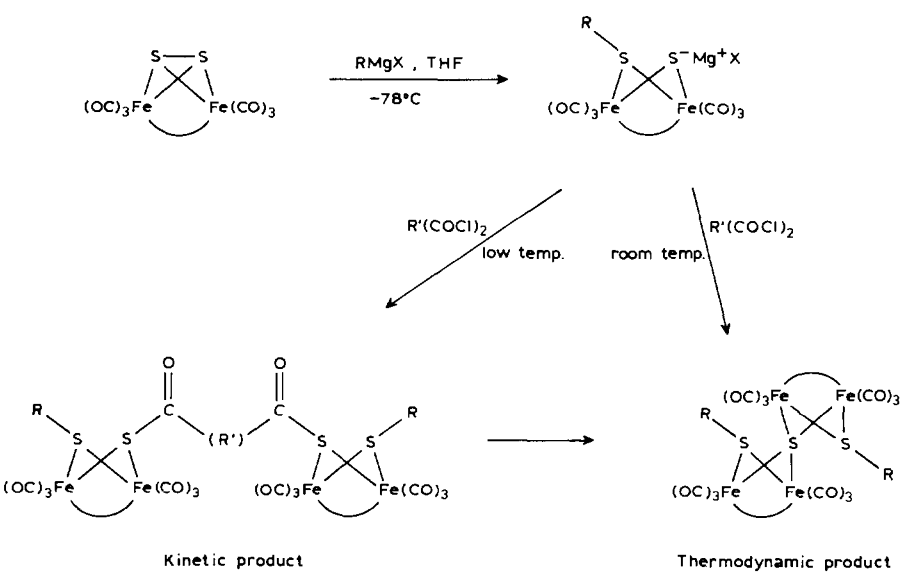


(**5**)



(**6**)

Similar reactions of ethylmagnesium bromide/(μ-S_2)$Fe_2(CO)_6$-derived monoan-



Scheme 1. R = CH_3, C_2H_5, C_6H_5, $C_6H_5CH_2$, $C_6H_5C{\equiv}C$, *p*-$CH_3C_6H_4$; R' = $(CH_2)_2$, C_6H_4; X = Br, Cl.

ion with any of the di-acid chlorides investigated, for 2 h, at room temperature resulted in the formation of a dark red crystalline complex in good yield. The solid state IR spectrum of this complex revealed only the presence of terminal carbonyls at 2070s, 2050vs, 2020vs, 1990s and 1980s cm^{-1}. The proton NMR spectrum shows a triplet at δ 1.36 ppm which can be assigned to the methyl proton resonance, and a quadruplet at δ 2.46 ppm due to the methylene proton resonance.

The reactions of the monoanion intermediates, which derive from other Grignard reagents (CH_3MgI, C_6H_5MgBr, $C_6H_5CH_2MgCl$, *p*-$CH_3C_6H_4MgBr$, $C_6H_5C{\equiv}CMgBr$), with di-acid chlorides similarly gave crystalline complexes which had no ester carbonyl present in their IR spectra. IR and proton NMR spectroscopy, elemental analysis and a single crystal X-ray study carried out on $[\mu\text{-EtSFe}_2(CO)_6]_2(\mu_4\text{-S})$ confirm that there is a a pseudotetrahedral sulfur atom coordinated to four iron atoms of the $RSFe_2(CO)_6$ moieties in these complexes. These results suggest the reaction sequence as shown in Scheme 1.

The crystal structure of this Fe–S cluster complex is depicted in Fig. 1. The final fractional coordinates with equivalent isotropic thermal parameters are listed in Table 1. Table 2 lists the most important interatomic distances, and Table 3 lists the bond angles for $[\mu\text{-EtS})Fe_2(CO)_6]_2(\mu_4\text{-S})$. It has a very similar structure to that of $[(\mu\text{-MeS})Fe_2(CO)_6]_2S$ [7]. The molecule consists of two identical $[(\mu\text{-EtS})Fe_2(CO)_6]$ moieties joined to a unique sulfur atom. In the cluster core, the unique sulfur atom is situated on the center of a distorted tetrahedron with four iron atoms at its apices.

The bond lengths between this sulfur atom and the iron atoms are almost the same (average 2.246 Å). The six intramolecular Fe–Fe distances may be divided into two equivalent bonding distances of 2.540 Å and four of 4.115 Å (average) which are non-bonding.

The two bonding Fe–Fe distances are identical with those in $[(\mu\text{-EtS})Fe(CO)_3]_2$ at 2.54 Å [12] and those in the complex $[(\mu\text{-S})Fe(CO)_3]_2$, a Fe–Fe distance of 2.55 Å [13].

Each iron is similarly connected to another iron, and surrounded by three carbonyl ligands and two sulfur atoms.

The coordination polyhedron around the iron is a distorted tetragonal bipyramid with two carbonyls and two sulfur atoms at equatorial positions and the other carbonyl and iron atoms at axial positions. As expected, the four iron atoms are displaced by about the same 0.37 Å (av.) (i.e., 0.34, 0.39, 0.36 and 0.38 Å) from their respective equatorial planes in the direction of their axial carbonyl groups. Similar displacements of the iron atoms were also observed in $[(\mu\text{-EtS})Fe(CO)_3]_2$ (0.38 Å for both irons) [12] and $[(\mu\text{-MeS})Fe_2(CO)_6]_2S$ (0.36 Å for four irons) [7]. The four

Table 1

Positional parameters and equivalent isotropic thermal factors for $[(\mu\text{-SEt})Fe_2(CO)_6]_2(\mu_4\text{-S})$

Atom	x	y	z	B_{eq} (Å$)^2$)
Fe(1)	0.7380(1)	0.0786(1)	0.83463(9)	3.30(3)
Fe(2)	0.7395(1)	−0.0390(1)	0.9543(1)	3.86(3)
Fe(3)	1.0379(1)	−0.0668(1)	0.8283(1)	3.44(3)
Fe(4)	1.0606(1)	0.0767(1)	0.9289(1)	4.06(3)
S(1)	0.8940(2)	0.0129(2)	0.8900(2)	3.14(5)
S(2)	0.7051(2)	−0.0948(2)	0.8309(2)	4.07(6)
S(3)	1.0642(2)	0.1024(2)	0.7974(2)	3.74(6)
C(11)	0.782(1)	0.1018(9)	0.7374(7)	4.1(3)
O(11)	0.8116(9)	0.1141(8)	0.6720(5)	7.1(3)
C(12)	0.590(1)	0.108(1)	0.8237(9)	5.2(3)
O(12)	0.5013(8)	0.1283(9)	0.8190(8)	9.4(4)
C(13)	0.767(1)	0.207(1)	0.8729(7)	5.1(3)
O(13)	0.781(1)	0.2881(7)	0.8952(7)	8.1(3)
C(21)	0.595(1)	−0.037(1)	0.9828(8)	5.0(3)
O(21)	0.5044(7)	−0.0359(7)	1.0018(6)	7.3(3)
C(22)	0.770(1)	0.055(1)	1.0316(8)	5.9(3)
O(22)	0.791(1)	0.1146(9)	1.0776(6)	9.2(3)
C(23)	0.778(1)	−0.158(1)	1.0035(7)	5.2(3)
O(23)	0.7965(9)	−0.2364(8)	1.0307(6)	8.3(3)
C(31)	1.182(1)	−0.102(1)	0.8085(8)	4.9(3)
O(31)	1.2732(7)	−0.1235(8)	0.7962(7)	7.9(3)
C(32)	0.973(1)	−0.1111(9)	0.7344(8)	4.8(3)
O(32)	0.9351(9)	−0.1342(8)	0.6780(5)	7.1(3)
C(33)	1.022(1)	−0.182(1)	0.8882(9)	5.5(3)
O(33)	1.015(1)	−0.2492(7)	0.9301(7)	8.2(3)
C(41)	1.034(1)	0.206(1)	0.9683(8)	5.1(3)
O(41)	1.020(1)	0.2814(7)	0.9967(7)	8.1(3)
C(42)	1.050(1)	0.006(1)	1.0204(8)	6.1(4)
O(42)	1.042(1)	−0.041(1)	1.0751(6)	10.4(4)
C(43)	1.211(1)	0.081(1)	0.9369(8)	6.7(4)
O(43)	1.3058(8)	0.083(1)	0.9406(7)	11.4(4)
C(51)	0.558(1)	−0.133(1)	0.8136(8)	5.8(3)
C(52)	0.535(2)	−0.133(2)	0.724(2)	13.7(9)
C(61)	1.203(1)	0.129(1)	0.7547(9)	5.6(3)
C(62)	1.190(1)	0.100(1)	0.6649(8)	7.6(4)

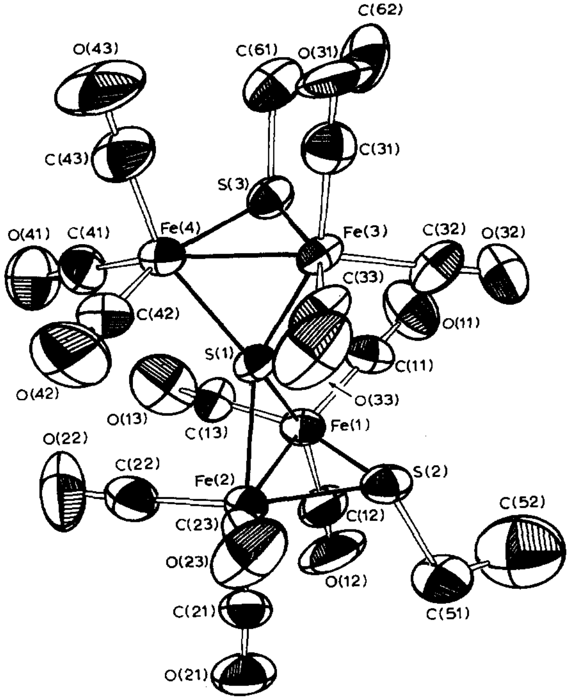


Fig. 1. Crystal structure of $[(\mu\text{-EtS})Fe_2(CO)_6]_2(\mu_4\text{-S})$.

Table 2

Bond lengths (Å) for $[(\mu\text{-SEt})Fe_2(CO)_6]_2(\mu_4\text{-S})$

Fe(1)-Fe(2)	2.542(2)	Fe(1)-S(1)	2.245(2)
Fe(1)-S(2)	2.275(2)	Fe(1)-C(11)	1.805(9)
Fe(1)-C(12)	1.803(9)	Fe(1)-C(13)	1.815(10)
Fe(2)-S(1)	2.240(2)	Fe(2)-S(2)	2.259(3)
Fe(2)-C(21)	1.778(9)	Fe(2)-C(22)	1.828(10)
Fe(2)-C(23)	1.814(11)	Fe(3)-Fe(4)	2.538(2)
Fe(3)-S(1)	2.254(2)	Fe(3)-S(3)	2.270(2)
Fe(3)-C(31)	1.798(10)	Fe(3)-C(32)	1.866(10)
Fe(3)-C(33)	1.815(12)	Fe(4)-S(1)	2.244(2)
Fe(4)-S(3)	2.264(3)	Fe(4)-C(41)	1.824(10)
Fe(4)-C(42)	1.810(12)	Fe(4)-C(43)	1.794(10)
S(2)-C(51)	1.844(10)	S(3)-C(61)	1.836(11)
C(11)-O(11)	1.134(10)	C(12)-O(12)	1.093(11)
C(13)-O(13)	1.127(14)	C(21)-O(21)	1.129(10)
C(22)-O(22)	1.126(12)	C(23)-O(23)	1.130(14)
C(31)-O(31)	1.141(12)	C(32)-O(32)	1.100(12)
C(33)-O(33)	1.125(12)	C(41)-O(41)	1.105(10)
C(42)-O(42)	1.114(11)	C(43)-O(43)	1.125(11)
C(51)-C(52)	1.54(2)	C(61)-C(62)	1.575(14)

Table 3

Bond angles (°) for $[(\mu\text{-SEt})Fe_2(CO)_6]_2(\mu_4\text{-S})$

Fe(2)-Fe(1)-S(1)	55.38(6)	Fe(2)-Fe(1)-S(2)	55.59(7)
Fe(2)-Fe(1)-C(11)	148.5(3)	Fe(2)-Fe(1)-C(12)	102.5(4)
Fe(2)-Fe(1)-C(13)	104.9(3)	S(1)-Fe(1)-S(2)	77.35(8)
S(1)-Fe(1)-C(11)	102.6(3)	S(1)-Fe(1)-C(12)	157.8(4)
S(1)-Fe(1)-C(13)	92.2(4)	S(2)-Fe(1)-C(11)	100.8(3)
S(2)-Fe(1)-C(12)	92.3(3)	S(2)-Fe(1)-C(13)	160.5(3)
C(11)-Fe(1)-C(12)	98.6(5)	C(11)-Fe(1)-C(13)	97.5(4)
C(12)-Fe(1)-C(13)	91.6(5)	Fe(1)-Fe(2)-S(1)	55.58(6)
Fe(1)-Fe(2)-S(2)	56.20(7)	Fe(1)-Fe(2)-C(21)	101.7(3)
Fe(1)-Fe(2)-C(22)	100.4(4)	Fe(1)-Fe(2)-C(23)	151.6(3)
S(1)-Fe(2)-S(2)	77.79(8)	S(1)-Fe(2)-C(21)	156.5(3)
S(1)-Fe(2)-C(22)	89.5(3)	S(1)-Fe(2)-C(23)	105.8(3)
S(2)-Fe(2)-C(21)	94.8(3)	S(2)-Fe(2)-C(22)	156.6(4)
S(2)-Fe(2)-C(23)	101.8(3)	C(21)-Fe2-C(22)	89.1(5)
C(21)-Fe(2)-C(23)	97.4(4)	C(22)-Fe(2)-C(23)	100.6(5)
Fe(4)-Fe(3)-S(1)	55.46(6)	Fe(4)-Fe(3)-S(3)	55.87(7)
Fe(4)-Fe(3)-C(31)	102.0(3)	Fe(4)-Fe(3)-C(32)	147.8(3)
Fe(4)-Fe(3)-C(33)	103.4(4)	S(1)-Fe(3)-S(3)	76.86(9)
S(1)-Fe(3)-C(31)	157.2(3)	S(1)-Fe(3)-C(32)	103.0(3)
S(1)-Fe(3)-C(33)	92.1(4)	S(3)-Fe(3)-C(31)	93.8(3)
S(3)-Fe(3)-C(32)	98.8(3)	S(3)-Fe(3)-C(33)	159.3(3)
C(31)-Fe(3)-C(32)	98.9(5)	C(31)-Fe(3)-C(33)	89.8(4)
C(32)-Fe(3)-C(33)	100.7(4)	Fe(3)-Fe(4)-S(1)	55.84(6)
Fe(3)-Fe(4)-S(3)	56.06(6)	Fe(3)-Fe(4)-C(41)	153.7(3)
Fe(3)-Fe(4)-C(42)	101.7(3)	Fe(3)-Fe(4)-C(43)	100.3(4)
S(1)-Fe(4)-S(3)	77.18(9)	S(1)-Fe(4)-C(41)	106.8(3)
S(1)-Fe(4)-C(42)	90.4(3)	S(1)-Fe(4)-C(43)	155.8(4)
S(3)-Fe(4)-C(41)	103.5(3)	S(3)-Fe(4)-C(42)	157.8(4)
S(3)-Fe(4)-C(43)	93.0(3)	C(41)-Fe(4)-C(42)	97.7(5)
C(41)-Fe(4)-C(43)	96.9(5)	C(42)-Fe(4)-C(43)	91.1(5)
Fe(1)-S(1)-Fe(2)	69.04(7)	Fe(1)-S(1)-Fe(3)	127.1(1)
Fe(1)-S(1)-Fe(4)	135.4(1)	Fe(2)-S(1)-Fe(3)	135.4(1)
Fe(2)-S(1)-Fe(4)	133.5(1)	Fe(3)-S(1)-Fe(4)	68.69(7)
Fe(1)-S(2)-Fe(2)	68.20(8)	Fe(1)-S(2)-C(51)	115.6(3)
Fe(2)-S(2)-C(51)	113.9(4)	Fe(3)-S(3)-Fe(4)	68.07(8)
Fe(3)-S(3)-C(61)	113.3(3)	Fe(4)-S(3)-C(61)	115.8(3)
Fe(1)-C(11)-O(11)	178.2(8)	Fe(1)-C(12)-O(12)	178.0(1)
Fe(1)-C(13)-O(13)	177.0(1)	Fe(2)-C(21)-O(21)	179.0(1)
Fe(2)-C(22)-O(22)	177.6(9)	Fe(2)-C(23)-O(23)	175.0(1)
Fe(3)-C(31)-O(31)	179.7(7)	Fe(3)-C(32)-O(32)	177.7(9)
Fe(3)-C(33)-O(33)	175.0(1)	Fe(4)-C(41)-O(41)	175.0(1)
Fe(4)-C(42)-O(42)	177.0(1)	Fe(4)-C(43)-O(43)	179.0(1)
S(2)-C(51)-C(52)	108.6(9)	S(3)-C(61)-C(62)	107.8(7)

bonds between irons and the carbons from the axial carbonyl groups are perpendicular to their respective equatorial planes.

Although no special molecular symmetry is demanded by the space group (i.e., all atoms are at general positions), the independent molecule possesses approximate C_2 symmetry with the twofold axis passing through the unique sulfur and the midpoint of S(2) and S(3).

Experimental

All reactions were carried out in flame-dried vessels under argon. All solvents were rigorously dried. Succinoyl chloride was distilled before use (Analytical Reagent, Shanghai Chemical Plant). *o*-, *m*-, *p*-phthaloyl chlorides were prepared by adapted previously published procedures [14]. Standard procedures followed for the preparation of the Grignard reagents [15] and $(\mu\text{-}S_2)Fe_2(CO)_6$ [16].

IR spectra were recorded with a Shimadzu IR-408 spectrometer and ^{1}H NMR spectra on a JEOL JNMPMX 60 Si NMR spectrometer (U.S.A.).

Preparation and properties of $[(\mu\text{-}SEt)Fe_2(CO)_6]_2(\mu_4\text{-}S)$

A 250-ml two-necked flask, equipped with a magnetic stirbar, one air-tight septum and an argon inlet tube, was flame-dried and then charged with 1.0 g (2.91 mmol) of $(\mu\text{-}S_2)Fe_2(CO)_6$ in 50 ml of dry THF. The resulting red solution was cooled to −78 °C by a dry ice/acetone mixture. A given amount of EtMgBr in diethyl ether was added with a syringe until the solution turned deep green. The green solution was stirred at −78 °C for 10 min and then 1.455 mmol of di-acid chloride was added. The reaction mixture instantly became red and was allowed to warm to room temperature, TLC (silicic acid, petroleum ether) showed the presence of a single product. The reaction was left to proceed for 2 h at room temperature, and the residue was extracted with petroleum ether until colorless. This extract was concentrated at reduced pressure and the concentrate was chromatographed on silica column (300 mesh) and a single red band was eluted with petroleum ether. The red solid which remained after evaporation of the solvent was recrystallized from petroleum ether to give $[(\mu\text{-}SEt)Fe_2(CO)_6]_2(\mu_4\text{-}S)$ in 90% yield. The dark red crystals melt at 150–152 °C. Crystals of the complex for X-ray study were grown by slow evaporation of solvent from CH_2Cl_2/petroleum ether at room temperature.

Anal. Found: C, 27.20; H, 1.18. $C_{16}H_{12}Fe_4O_{12}S_3$ calc: C, 26.92; H, 1.41%. IR (KBr disc): terminal C≡O, 2070s, 2050vs, 2020vs, 1990s, 1980s cm^{-1}; C–S, C–H, str., 1450m, 1380m, 1255m cm^{-1}. 60 MHz ^{1}H NMR ($CDCl_3$): δ 1.36 (t, 6H, CH_3, *J* 7Hz), 2.46 ppm (q, 4H, CH_2, *J* 7 Hz).

When *p*-phthaloyl chloride was used and the reaction stopped at −40 °C, a sticky red material was obtained in 72% yield as the only product. Trituration with petroleum ether gave a red solid, which was recrystallized from CH_2Cl_2/petroleum to give **2** as red crystals, m.p. 132–133 °C. Anal. Found: C, 33.45; H, 1.61. $C_{24}H_{14}Fe_4O_{14}S_4$ calc: C, 32.83; H, 1.61%. IR (KBr disc): ester C=O, 1675s; terminal C≡O, 2055s, 2050vs, 2000s, 1995s, 1990s cm^{-1}; C–S, C–H str., 1400m, 1255m, 1195s; benzene ring substitution C–H out-of-plane bending, 860s, 830m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.33 (t, 6H, CH_3, *J* 7 Hz), 2.50 (q, 4H, CH_2, *J* 7 Hz), 7.96 (s, 4H, Ph) ppm.

Other $[(\mu\text{-}SR)Fe_2(CO)_6]_2(\mu_4\text{-}S)$ *complexes*

The same procedure as described for that of $[(\mu\text{-}SEt)Fe_2(CO)_6]_2(\mu_4\text{-}S)$ was used with other Grignard reagents. It was found that the reactions at room temperature gave identical products which were independent of the nature of the di-acid chlorides used. All these complexes were obtained in the form of red crystals.

$[(\mu\text{-}SMe)Fe_2(CO)_6]_2(\mu_4\text{-}S)$ was obtained in 89% yield and recrystallized from petroleum ether, m.p. 170–172 °C. Anal. Found: C, 24.72; H, 0.69. $C_{14}H_6Fe_4O_{12}S_3$ calc: C, 24.52; H, 0.88%. IR (KBr disc): terminal C≡O, 2060s, 2050vs, 2010s, 1980s, 1960s cm^{-1}; C–S, C–H str., 1430m, 1420m, 1305m, 950w cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.17 (s, 6H, CH_3) ppm.

$[(\mu\text{-}C_6H_5S)Fe_2(CO)_6]_2(\mu_4\text{-}S)$ was obtained in 89% yield and recrystallized from CH_2Cl_2/petroleum ether; the red crystals decomposed at 150 °C without melting. Anal. Found: C, 35.79; H, 1.01. $C_{24}H_{10}Fe_4O_{12}S_3$ calc: C, 35.59; H, 1.24%. IR (KBr disc); terminal C≡O, 2070s, 2050vs, 2030s, 1995s, 1980s; C–S str., 1570w, 1440w; benzene ring monosubstitution C–H bending, 730m, 680w cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.30 (s, 10H, Ph) ppm.

$[(\mu\text{-}SC_6H_5C{\equiv}C)Fe_2(CO)_6]_2(\mu_4\text{-}S)$ was prepared in 61% yield and recrystallized from CH_2Cl_2/petroleum ether; it decomposed at 142 °C. Anal. Found: C, 39.56; H, 1.19 $C_{28}H_{10}Fe_4O_{12}S_3$ calc: C, 39.20; H, 1.17%. IR (KBr disc): acetylene C≡C, 2150w, terminal C≡O, 2070m, 2040s, 2020vs, 1990s, 1980s; monosubstituted benzene ring C–H bending: 750m, 675m cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.30, 7.36 (s,s, 10H, Ph) ppm.

$[(\mu\text{-}C_6H_5CH_2S)Fe_2(CO)_6]_2(\mu_4\text{-}S)$ in 71% yield, recrystallization from CH_2Cl_2/petroleum ether, m.p. 128–130 °C. Anal. Found: C, 37.63; H, 1.62. $C_{26}H_{14}Fe_4O_{12}S_3$ calc: C, 37.27; H, 1.68%. IR (KBr disc): terminal C≡O, 2070s, 2050vs, 1990vs, 1980s; monosubstituted benzene ring C–H bending, 760w, 690m cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.63(s, 4H, CH_2), 7.33(s, 10H, Ph) ppm.

$[(\mu\text{-}p\text{-}CH_3C_6H_4S)Fe_2(CO)_6]_2(\mu_4\text{-}S)$ was obtained in 81% yield and recrystallized from CH_2Cl_2/petroleum ether. Decomposition occurred at 150 °C without melting. Anal. Found: C, 37.61; H, 1.45. $C_{26}H_{14}Fe_4O_{12}S_3$ calc: C, 37.27; H, 1.68%. IR (KBr disc): terminal C≡O, 2070s, 2050vs, 1985vs, C–S str., 1480m, 1395m, disubstituted benzene ring C–H bending, 800s cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.40 (s, 6H, CH_3), δ 7.20–7.59(m, 8H, Ph) ppm.

Crystal data for and structure determination of $[(\mu\text{-}SEt)Fe_2(CO)_6]_2(\mu_4\text{-}S)$

A dark red cubic crystal of $(\mu\text{-EtS})Fe_2(CO)_6(\mu_4\text{-S})Fe_2(CO)_6(\mu\text{-EtS})$ of approximate dimensions 0.3 × 0.3 × 0.3 mm was mounted on a glass fiber in an arbitrary orientation. Preliminary examination and data collection were performed with Mo-K_α radiation (λ 0.71073 Å) on an Enraf–Nonius CAD4 diffractometer equipped with a graphite monochromator. The crystals of this complex are orthorhombic, the systematic absences of $\{h00\}$ for h odd, $\{0k0\}$ for k odd, and $\{00l\}$ for l odd indicated the space group $P2_12_12_1$. The cell parameters are a 11.875(2), b 12.920(3), c 17.020(3) Å; $Z = 4$; D_c 1.754 g cm^{-3}. Intensity data of 3550 unique reflections were collected in the range $2° < \theta < 28°$, of which 1718 reflections with $I > 3\sigma(I)$ were considered observed and used in the subsequent structure refinement. The LP and absorption corrections were applied to the data.

The structure was solved by direct methods (MULTAN 82). A total of 4 Fe atoms in the molecule were located from an E-map. The remaining non-hydrogen atoms were found in subsequent difference Fourier synthesis. The final cycle of structure refinement including the coordinates and anisotropic thermal parameters of non-hydrogen atoms converged with unweighted and weighted agreement factors of $R = 0.036$ and $R_w = 0.041$. The highest peak in the final difference Fourier had a height of 0.97e/Å^3. All calculations were carried out with a PDP-11/44 computer by use of SDP-PLUS program system.

At present, a study is in progress in this laboratory on the possible mechanistic implications of this reaction, and the results of our current investigations will be published.

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