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Synthesis and characterization of μ_4-S-containing double- and triple-butterfly iron carbonyl complexes. Crystal structures of (μ-EtS)[μ-PhC(O)S][$Fe_2(CO)_6$]$_3$(μ_4-S)$_2$ and (μ-t-BuS)$_2$[$Fe_2(CO)_6$]$_3$(μ_4-S)$_2$

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Abstract

The [MgBr]$^+$ salts of the μ_4-S-containing double-butterfly anions {(μ-RS)(μ-CO)[$Fe_2(CO)_6$]$_2$(μ_4-S)}$^-$ (**1**, R = Ph, p-MeC_6H_4) react in situ with CS_2 followed by treatment of the corresponding intermediate [MgBr]$^+$ salts of anions {(μ-RS)(μ-S=CS)[$Fe_2(CO)_6$]$_2$(μ_4-S)}$^-$ (**m$_1$**) with $ClCH_2CO_2Et$ to give μ_4-S-containing double-butterfly iron carbonyl complexes (μ-RS)(μ-EtO_2CCH_2SC=S)[$Fe_2(CO)_6$]$_2$(μ_4-S) (**2a**, R = Ph; **2b**, R = p-MeC_6H_4), whereas the in situ reaction of the [MgX]$^+$ (X = I, Br) salts of anions **1** (R = Me, Et) with μ-$S_2Fe_2(CO)_6$ followed by treatment of the corresponding intermediate salts of anions {(μ-RS)(μ-S)[$Fe_2(CO)_6$]$_3$(μ_4-S)$_2$}$^-$ (**m$_2$**) with PhC(O)Cl produces μ_4-S-containing unsymmetrical triple-butterfly iron carbonyl complexes (μ-RS)[μ-PhC(O)S][$Fe_2(CO)_6$]$_3$(μ_4-S)$_2$ (**3a**, R = Me; **3b**, R = Et). More interestingly, the symmetrical μ_4-S-containing triple-butterfly complexes (μ-RE)$_2$[$Fe_2(CO)_6$]$_3$(μ_4-S)$_2$ (**5a**, RE = EtS; **5b**, RE = t-BuS; **5c**, RE = PhSe; **5d**, RE = p-MeC_6H_4Se) can be synthesized by reaction of an excess of the [Et_3NH]$^+$ salts of the μ-CO-containing single-butterfly anions [(μ-RE)(μ-CO)$Fe_2(CO)_6$]$^-$ (**4**) with μ-$S_2Fe_2(CO)_6$ and subsequent treatment of the resulting mixture with SO_2Cl_2. While the function of an excessive **4** for production of **5a**–**d** is proposed, products **2a**,**b**, **3a**,**b** and **5a**–**d** have been characterized by elemental analysis, and IR and ^{1}H NMR spectroscopy, as well as for **3b** and **5b** by X-ray diffraction techniques.

Keywords: μ-CO butterfly anions; μ_4-S butterfly complexes; Reactions; Synthesis; Crystal structures

1. Introduction

It is known that very few μ_4-S-containing butterfly iron carbonyl complexes of the type [(μ-RS)$Fe_2(CO)_6$]$_2$(μ_4-S) had been prepared [1–4] before 1988, when we reported a general and convenient procedure for synthesis of such μ_4-S-containing double-butterfly complexes [(μ-RS)$Fe_2(CO)_6$]$_2$(μ_4-S) (R = Me, Et, $PhCH_2$, p-MeC_6H_4, PhC≡C) in high yield (61–91%) [5]. In view of the novelty and diversity of structures and reactivities concerning μ_4-S iron carbonyl complexes, we have been interested in studying μ_4-S-forming reactions and the reactions involving μ_4-S-containing reactive intermediates, which has so far led us to obtain a variety of double-, triple- and even multiple-butterfly iron carbonyl complexes [6–10]. This paper will describe the synthesis of double- and triple-butterfly complexes (μ-RS)(μ-EtO_2CCH_2SC=S)[$Fe_2(CO)_6$]$_2$(μ_4-S) (**2a**, R = Ph; **2b**, R = p-MeC_6H_4), (μ-RS)[μ-PhC(O)S][$Fe_2(CO)_6$]$_3$(μ_4-S)$_2$ (**3a**, R = Me; **3b**, R = Et) and (μ-RE)$_2$[$Fe_2(CO)_6$]$_3$(μ_4-S)$_2$ (**5a**, RE = EtS; **5b**, RE = t-BuS; **5c**, RE = PhSe; **5d**, RE = p-MeC_6H_4Se), and the structural characterization of these new μ_4-S-containing complexes by elemental analysis, spectroscopy, and particularly for **3b** and **5b** by X-ray diffraction analysis.

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2. Results and discussion

2.1. Synthesis and characterization of (μ-RS)(μ-$EtO_2CCH_2SC{=}S$)[$Fe_2(CO)_6$]$_2$(μ_4-S) (**2a**,**b**)

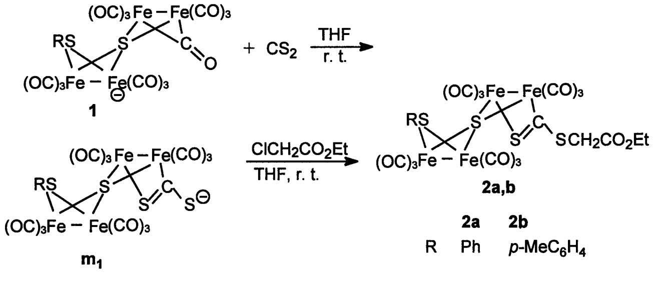
Interestingly, we have found that the μ-CO-containing double-butterfly anions {(μ-RS)(μ-CO)[$Fe_2(CO)_6$]$_2$(μ_4-S)}$^-$ (**1**, R = Ph, p-MeC_6H_4) (prepared as their [MgBr]$^+$ salts from a sequential reaction of μ-$S_2Fe_2(CO)_6$, Grignard reagents RMgBr and $Fe_3(CO)_{12}$) reacted in situ with CS_2 followed by treatment of the corresponding intermediate [MgBr]$^+$ salts of anions {(μ-RS)(μ-S=CS)[$Fe_2(CO)_6$]$_2$(μ_4-S)}$^-$ (**m$_1$**) [9] with $ClCH_2CO_2Et$ to afford the S-functionalized double-butterfly iron carbonyl complexes **2a**,**b** (Scheme 1).

Complexes **2a**,**b** are new and were characterized by elemental analysis and spectroscopy. For example, while the ^{1}H NMR spectra of **2a**,**b** displayed the corresponding resonance signals for their R and CH_2CO_2Et groups, the IR spectra showed one absorption band at 1739 and 1740 cm^{-1} for their ester carbonyls and one absorption band at 1020 and 1010 cm^{-1} for their coordinated C=S double bonds [11].

2.2. Synthesis and characterization of (μ-RS)[μ-PhC(O)S][$Fe_2(CO)_6$]$_3$(μ_4-S)$_2$ (**3a**,**b**). Crystal structure of **3b**

We have further found that the [MgX]$^+$ (X = Br, I) salts of anions (**1**, R = Me, Et) reacted in situ with μ-$S_2Fe_2(CO)_6$ followed by treatment of the corresponding intermediate [MgX]$^+$ salts of anions {(μ-RS)(μ-S)[$Fe_2(CO)_6$]$_3$(μ_4-S)$_2$}$^-$ (**m$_2$**) [9] with PhC(O)Cl to give the S-functionalized triple-butterfly iron carbonyl complexes **3a**,**b** (Scheme 2).

Products **3a**,**b** are also new and were characterized by elemental analysis, spectroscopy and crystal X-ray diffraction analysis. For example, the IR spectra of **3a**,**b** showed one absorption band at 1687 and 1684 cm^{-1} for their carbonyls in benzoyl groups, whereas the ^{1}H NMR spectra of **3a**,**b** exhibited one signal or one set of signals for their Me, Et and Ph groups. In principle, the R and PhC(O) groups in **3a**,**b** should be attached to the bridged S atoms by an equatorial type of bond, in order to avoid the sterically strong repulsions between these groups and the structural moieties axially bonded to their neighboring bridged S atoms [6,7]. Fortunately, this has been confirmed by crystal X-ray diffraction analysis of **3b**. The molecular structure of **3b** is shown in Fig. 1, whereas its selected bond lengths and angles are given in Table 1. Fig. 1 shows that **3b** contains three butterfly cores Fe(3)Fe(4)S(1)S(3), Fe(1)Fe(2)S(1)S(2) and Fe(5)Fe(6)S(2)S(4) joined together by two μ_4-S atoms of S(1) and S(2). While each of the Fe atoms from Fe(1) to Fe(6) is bound to three terminal carbonyls, the PhCO and Et groups are indeed bonded to the bridged S atoms of S(3) and S(4) by an equatorial type of bond, respectively. It is worthy of note that in the three butterfly cores the geometric parameters of the middle butterfly core are somewhat different from those of the two side butterfly cores. For example, the bond length of Fe(3)–Fe(4) (2.5156(11) Å) or Fe(5)–Fe(6) (2.5166(13) Å) is shorter than that of Fe(1)–Fe(2) (2.5699(12) Å), and the dihedral angle between Fe(3)–Fe(4)–S(1) and Fe(3)–Fe(4)–S(3) (84.54°) or Fe(5)–Fe(6)–S(2) and Fe(5)–Fe(6)–S(4) (83.77°) is larger than that between Fe(1)–Fe(2)–S(1) and Fe(1)–Fe(2)–S(2) (72.59°).



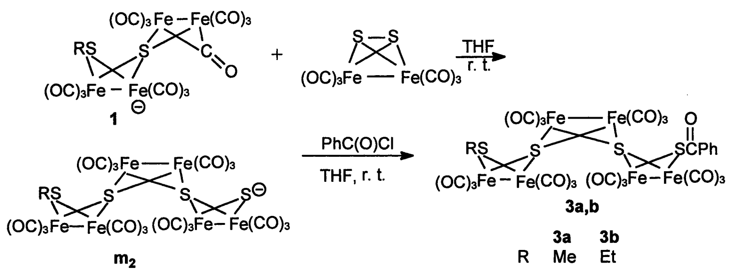
Scheme 1.

2.3. Synthesis and characterization of (μ-RE)$_2$[$Fe_2(CO)_6$]$_3$(μ_4-S)$_2$ (**5a**–**d**). Crystal structure of **5b**

More interestingly, the [Et_3NH]$^+$ salts of the μ-CO-containing single-butterfly anions [(μ-RE)(μ-CO)-$Fe_2(CO)_6$]$^-$ (**4**, RE = EtS, t-BuS, PhSe, p-MeC_6H_4Se) (prepared from corresponding REH, $Fe_3(CO)_{12}$ and Et_3N) [6,12] could react in situ with approximately 0.5 equiv. (or more less amount) of μ-$S_2Fe_2(CO)_6$ at room temperature followed by treatment with 0.5 equiv. (or more less amount) of SO_2Cl_2 from −78 °C to room temperature [8] to give symmetrically R-substituted triple-butterfly iron carbonyl complexes **5a**–**d** (Scheme 3).

In fact, this type of novel tandem reaction leading to complexes (μ-RE)$_2$[$Fe_2(CO)_6$]$_3$(μ_4-S)$_2$ (**5b**, RE = t-BuS; **5d**, RE = p-MeC_6H_4Se) was briefly described in our communication [8]. In this paper, we wish to report the experimental details and give more detailed discussion concerning the synthesis and structural characterization of **5a**–**d** all obtained from this type of reaction.

Complexes **5a**–**d** have been characterized by elemental analysis and spectroscopy. For instance, while the IR spectra of **5a**–**d** showed several absorption bands in the range 2088–1922 cm^{-1} for their terminal carbonyls, their ^{1}H NMR spectra displayed resonance signals for their respective R groups. In addition, it is worth pointing out that the two R groups in **5a**–**d**, similar to R and PhC(O) groups in **3a**,**b**, should be attached to the bridged S and/or Se atoms by an equatorial type of



Scheme 2.

bond. This is consistent with the ^{1}H NMR spectra of Et, t-Bu, Ph and p-MeC$_6$H$_4$ in **5a–d** showing one signal or one set of signals, and this has been further confirmed by the X-ray diffraction analysis of **5b**.

Fig. 2 shows the molecular structure of **5b** and Table 2 lists its selected bond lengths and angles. As seen in Fig. 2, **5b** comprises the three butterfly-shaped Fe$_2$S$_2$ subcluster cores Fe(1)Fe(2)S(1)S(2), Fe(3)Fe(3a)S(2)S(2a), and Fe(1a)Fe(2a)S(1a)S(2a). In addition, each Fe atom has three terminal CO ligands, and the two t-Bu groups are indeed bonded to S(1) and S(1a) atoms by an equatorial bond. This molecule is chiral, which has a C_2 axis passing through the two midpoints of Fe(3)–Fe(3a) and S(2)···S(2a). It is noteworthy that the geometric parameters of the middle subcluster core are somewhat different from those of the two identical side subcluster cores. For example, the dihedral angle between Fe(3)–Fe(3a)–S(2) and Fe(3)–Fe(3a)–S(2a) (73.7°) is less than that between Fe(1)–Fe(2)–S(1) and Fe(1)–Fe(2)–S(2) or Fe(1a)–Fe(2a)–S(1a) and Fe(1a)–Fe(2a)–S(2a) (86.1°), and the bond length of Fe(3)–Fe(3a) (2.563(2) Å) is longer than that of Fe(1)–Fe(2) or Fe(1a)–Fe(2a) (2.504(1) Å). In fact, this triple-butterfly cluster is very similar to cluster **3b** described above.

Table 1
Selected bond lengths (Å) and angles (°) for **3b**

Bond lengths			
Fe(1)–Fe(2)	2.5699(12)	Fe(1)–S(2)	2.2560(16)
Fe(1)–S(1)	2.2668(16)	Fe(2)–S(2)	2.2623(16)
Fe(2)–S(1)	2.2639(15)	Fe(3)–S(3)	2.2619(17)
Fe(3)–S(1)	2.2725(16)	Fe(3)–Fe(4)	2.5156(11)
Fe(4)–S(1)	2.2835(15)	Fe(5)–S(2)	2.2654(15)
Fe(5)–S(4)	2.2700(19)	Fe(5)–Fe(6)	2.5166(13)
Fe(6)–S(4)	2.262(2)	Fe(6)–S(2)	2.2772(17)
Bond angles			
S(2)–Fe(1)–S(1)	83.15(6)	S(2)–Fe(5)–S(4)	76.59(6)
S(2)–Fe(5)–Fe(6)	56.58(5)	S(2)–Fe(1)–Fe(2)	55.45(5)
S(2)–Fe(2)–S(1)	83.07(6)	S(1)–Fe(2)–Fe(1)	55.50(4)
S(3)–Fe(3)–S(1)	76.48(6)	S(1)–Fe(3)–Fe(4)	56.69(4)
S(4)–Fe(6)–Fe(5)	56.43(5)	Fe(2)–S(1)–Fe(1)	69.11(5)
Fe(2)–S(1)–Fe(3)	128.42(7)	Fe(1)–S(1)–Fe(3)	129.83(7)
Fe(1)–S(2)–Fe(2)	69.33(5)	Fe(1)–S(2)–Fe(5)	141.11(7)

Finally, it should be noted that although the reaction mechanism for the formation of **5a–d** is not completely

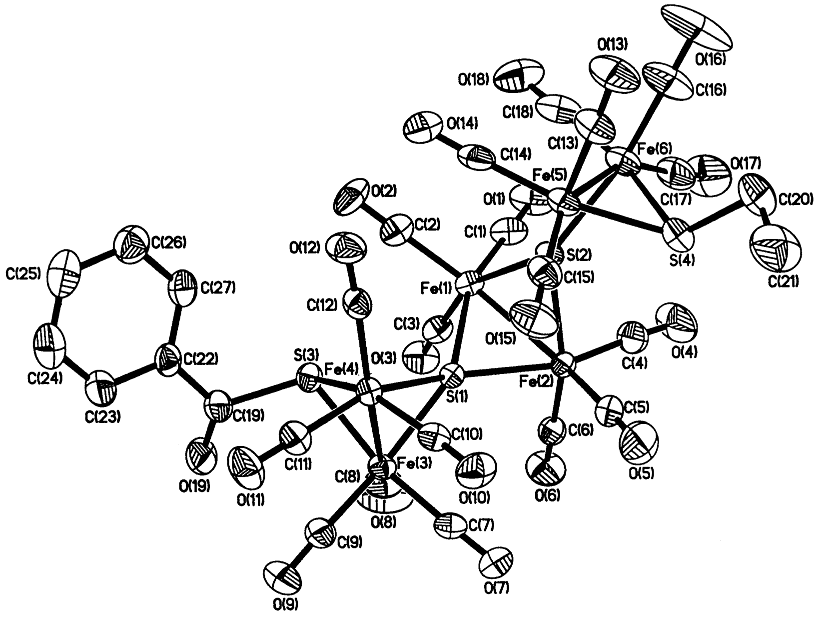
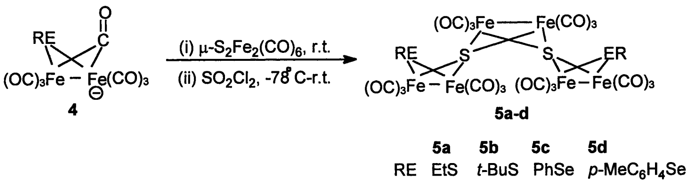


Fig. 1.



Scheme 3.

understood as yet, we might propose a possible pathway, on the basis of the well-known properties of both anions [(μ-RS)(μ-S)$Fe_2(CO)_6$]$^-$ and [(μ-RE)(μ-CO)-$Fe_2(CO)_6$]$^-$ (**4**) [6,13], to account for the production of **5a**–**d**.

This pathway, as shown in Scheme 4, actually includes three major steps: (i) the negatively charged Fe atom of anions **4** attacks the S atom of μ-$S_2Fe_2(CO)_6$, followed by loss of the μ-CO ligand from intermediates **m**$_3$ to give the S-centered intermediate anions **m**$_4$; (ii) the attack of the negatively charged S atom of **m**$_4$ at the S atom of SO_2Cl_2 gives rise to intermediates **m**$_5$; (iii) the bridged S atom attached to the SO_2Cl group in **m**$_5$ is attacked by the negatively charged Fe atom of the excess amount of anions **4**, followed by loss of the SO_2Cl group and μ-CO ligand to produce **5a**–**d**. Up to now, we have proved that when the ratio of the starting materials (anions **4**: μ-$S_2Fe_2(CO)_6$–SO_2Cl_2 is approximately 1:1:1 or less anions **4**) is used in this type of reaction, products **5a**–**d** cannot be obtained. This has not only indicated the function of an excess of anions **4** played in the formation of **5a**–**d**, but also gives an additional evidence for the suggested pathway described above.

3. Experimental

All reactions were carried out under an atmosphere of prepurified nitrogen using standard Schlenk and vacuum-line techniques. Tetrahydrofuran (THF) was distilled from Na/benzophenone ketyl under nitrogen. $Fe_3(CO)_{12}$ [14], μ-$S_2Fe_2(CO)_6$ [15] and Grignard reagents RMgX [16] were prepared according to literature procedures, whereas the others used in this paper were of commercial origin and used without further purification. Preparative TLC was carried out on glass plates (26 × 20 × 0.25 cm) coated with silica gel H (10–40 μm). IR spectra were recorded on a Bruker Vector 22 infrared spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker AC-P200 NMR spectrometer. C/H analyses were performed on an Elementar Vario EL analyzer. M.p.s were determined on a Yanaco MP-500 apparatus and were uncorrected.

Table 2
Selected bond lengths (Å) and angles (°) for **5b**

Bond lengths			
Fe(1)–Fe(2)	2.504(1)	Fe(1)–S(2)	2.277(2)
Fe(1)–S(1)	2.275(2)	Fe(2)–S(1)	2.260(2)
Fe(2)–S(2)	2.270(2)	Fe(3)–S(2)	2.253(2)
Fe(3)–S(2a)	2.256(1)	Fe(3)–Fe(3a)	2.563(2)
Fe(3a)–S(2)	2.256(1)	S(1)–C(11)	1.879(11)
Bond angles			
Fe(2)–S(2)–Fe(3)	130.3(1)	Fe(2)–S(1)–Fe(1)	67.0(1)
S(2)–Fe(1)–S(1)	74.9(1)	Fe(1)–Fe(2)–S(2)	56.7(1)
S(1)–Fe(2)–S(2)	75.3(1)	S(2)–Fe(1)–Fe(2)	56.5(1)
S(2)–Fe(3)–Fe(3a)	55.4(1)	S(1)–Fe(2)–Fe(1)	56.8(1)
S(2)–Fe(3)–S(2a)	82.3(1)	Fe(3a)–Fe(3)–S(2a)	55.3(1)
Fe(1)–S(2)–Fe(2)	66.8(1)	Fe(1)–S(2)–Fe(3)	139.8(1)

*3.1. Preparation of (μ-PhS)(μ-EtO_2CCH_2SC=S)[$Fe_2(CO)_6$]$_2$(μ-S) (**2a**)*

A 100 ml two-necked flask equipped with a stir-bar, a N_2 inlet tube, and a serum cap was charged with 0.172 g (0.5 mmol) of μ-$S_2Fe_2(CO)_6$ and 20 ml of THF. The resulting red solution was stirred and cooled to −78 °C using a dry ice/C_3H_6O bath. To this solution was

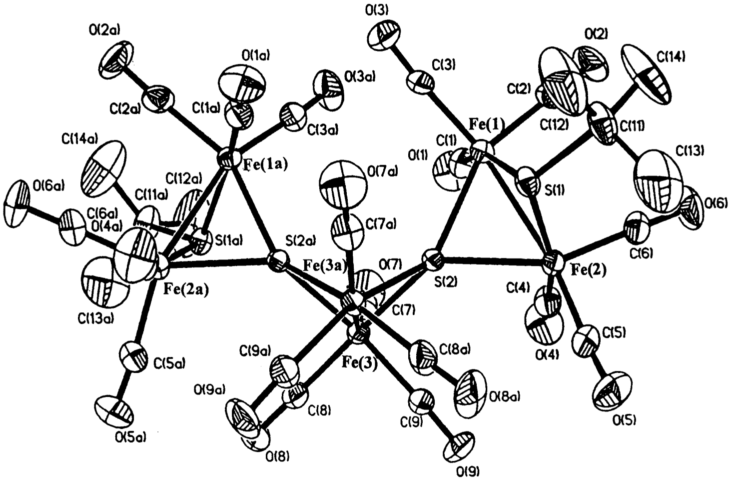
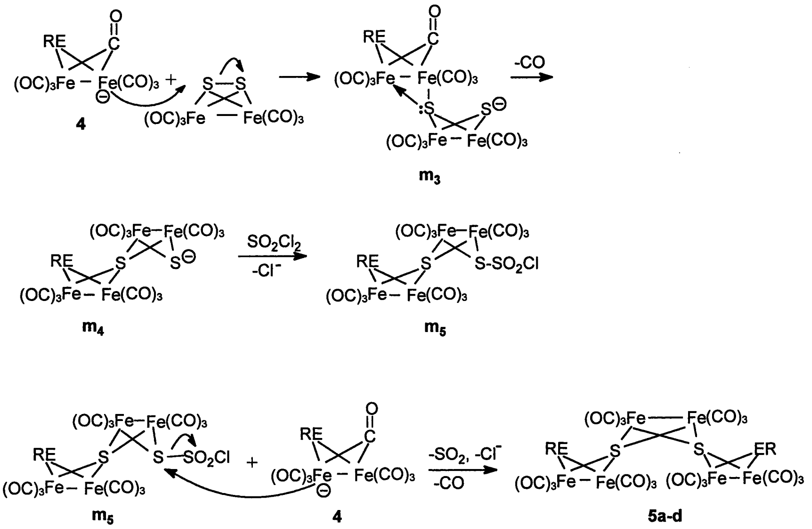


Fig. 2.



Scheme 4.

injected a given amount of Grignard reagent PhMgBr in Et_2O by a syringe until the solution turned to emerald green. To this solution was added 0.252 g (0.5 mmol) of $Fe_3(CO)_{12}$ and then the mixture was warmed to room temperature (r.t.). The mixture was stirred at this temperature for 1 h to give a solution of the $[MgBr]^+$ salt of anion $\{(\mu\text{-PhS})(\mu\text{-CO})[Fe_2(CO)_6]_2(\mu_4\text{-S})\}^-$. To this solution was added 0.10 ml (1.8 mmol) of CS_2 and the mixture was stirred at r.t. for 1 h to give a red–brown solution. To this solution was added 0.1 ml (0.9 mmol) of $ClCH_2CO_2Et$ and the mixture was stirred at this temperature for 12 h. Solvent was removed under reduced pressure and the residue was subjected to TLC separation using CH_2Cl_2/petroleum ether (v/v = 2:5) as eluent. From the main orange–red band 0.200 g (46%) of **2a** was obtained as a red solid. M.p. 35–36 °C. *Anal.* Found: C, 31.98; H, 1.61. Calc. for $C_{23}H_{12}Fe_4O_{14}S_4$: C, 31.97; H, 1.40%. IR (KBr disk, cm^{-1}): $\nu_{(C\equiv O)}$ 2083(s), 2059(vs), 2036(vs), 1997(vs); $\nu_{(C=O)}$ 1739(s); $\nu_{(C=S)}$ 1020(s). ^1H NMR ($C_3H_6O\text{-}d_6$, δ, ppm): 1.23 (t, $J = 7.6$ Hz, 3H, CH_3), 4.05–4.39 (m, 4H, $2CH_2$), 7.20–7.59 (m, 5H, C_6H_5).

3.2. Preparation of *(μ-p-MeC_6H_4S)(μ-EtO_2CCH_2SC=S)[$Fe_2(CO)_6$]$_2$(μ_4-S) (**2b**)*

The same procedure as that for **2a** was followed, but the $[MgBr]^+$ salt of anion $\{(\mu\text{-p-MeC}_6H_4S)(\mu\text{-CO})[Fe_2(CO)_6]_2(\mu_4\text{-S})\}^-$ prepared from p-MeC_6H_4MgBr, μ-$S_2Fe_2(CO)_6$ and $Fe_3(CO)_{12}$ was used instead of the $[MgBr]^+$ salt of anion $\{(\mu\text{-PhS})(\mu\text{-CO})[Fe_2(CO)_6]_2(\mu_4\text{-S})\}^-$. From the main orange–red band 0.178 g (41%) of **2b** was obtained as a red solid. M.p. 61–63 °C. *Anal.* Found: C, 33.10; H, 1.61. Calc. for $C_{24}H_{14}Fe_4O_{14}S_4$: C, 32.83; H, 1.61%. IR (KBr disk, cm^{-1}): $\nu_{(C\equiv O)}$ 2090(s), 2065(vs), 2042(vs), 1993(vs); $\nu_{(C=O))}$ 1740(s); $\nu_{(C=S)}$ 1010(s). ^1H NMR ($C_3H_6O\text{-}d_6$, δ, ppm): 1.24 (br.s, 3H, CH_3), 2.28 (s, 3H, $ArCH_3$), 4.05–4.40 (m, 4H, $2CH_2$), 7.07–7.50 (m, 4H, C_6H_4).

3.3. Preparation of *(μ-MeS)[μ-PhC(O)S][$Fe_2(CO)_6$]$_3$ (μ_4-S)$_2$ (**3a**)*

To the $[MgI]^+$ salt of anion $\{(\mu\text{-MeS})(\mu\text{-CO})[Fe_2(CO)_6]_2(\mu_4\text{-S})\}^-$ prepared from MeMgI, μ-$S_2Fe_2(CO)_6$ and $Fe_3(CO)_{12}$ was added 0.172 g (0.5 mmol) of μ-$S_2Fe_2(CO)_6$. The mixture was stirred for 2 h at r.t. and then 0.16 ml (1.3 mmol) of PhC(O)Cl was added. The new mixture was stirred at this temperature for 10 h. Solvent was removed under reduced pressure and the residue was subjected to TLC separation using petroleum ether as eluent. From the main red band 0.161 g (30%) of **3a** was obtained as a brown–red solid. M.p. 143 °C (dec.). *Anal.* Found: C, 28.52; H, 0.92. Calc. for $C_{26}H_8Fe_6O_{19}S_4$: C, 28.71; H, 0.74%. IR (KBr disk, cm^{-1}): $\nu_{(C\equiv O)}$ 2060(s), 2043(vs), 2007(s); $\nu_{(C=O)}$ 1687(m). ^1H NMR ($C_3H_6O\text{-}d_6$, δ, ppm): 2.36 (s, 3H, CH_3), 7.34–8.20 (m, 5H, C_6H_5).

3.4. Preparation of *(μ-EtS)[μ-PhC(O)S][$Fe_2(CO)_6$]$_3$(μ_4-S)$_2$ (**3b**)*

The same procedure as that for **3a** was followed, but the $[MgBr]^+$ salt of anion $(\mu\text{-EtS})(\mu\text{-CO})[Fe_2(CO)_6]_2(\mu_4\text{-S})^-$ prepared from EtMgBr, μ-$S_2Fe_2(CO)_6$ and $Fe_3(CO)_{12}$ was used instead of the $[MgI]^+$ salt of anion $(\mu\text{-MeS})(\mu\text{-CO})[Fe_2(CO)_6]_2(\mu_4\text{-S})^-$. From the main red band 0.082 g (15%) of **3b** was obtained as a black solid. M.p. 144 °C (dec.). *Anal.* Found: C, 29.26; H, 1.22. Calc. for $C_{27}H_{10}Fe_6O_{19}S_4$: C, 29.44; H, 0.92%. IR (KBr disk, cm^{-1}): $\nu_{(C\equiv O)}$ 2058(s), 2044(vs), 1993(s); $\nu_{(C=O)}$ 1684(m). ^1H NMR ($C_3H_6O\text{-}d_6$, δ, ppm): 1.43 (t, $J = 7.4$ Hz, 3H, CH_3), 2.64 (q, $J = 7.4$ Hz, 2H, CH_2), 7.57–8.16 (m, 5H, C_6H_5).

3.5. Preparation of $(\mu\text{-EtS})_2[Fe_2(CO)_6]_3(\mu_4\text{-S})_2$ (**5a**)

A 100 ml two-necked flask with a stir-bar, a N_2 inlet tube, and a serum cap was charged with 0.504 g (1.0 mmol) of $Fe_3(CO)_{12}$, 10 ml of THF, 0.08 ml (1.1 mmol) of EtSH and 0.17 ml (1.2 mmol) of Et_3N. The mixture was stirred at 25–30 °C for 0.5 h to give a yellow–brown solution containing approximately 1.0 mmol of the $[Et_3NH]^+$ salt of anion $[(\mu\text{-EtS})(\mu\text{-CO})Fe_2(CO)_6]^-$. To this solution was added 0.172 g (0.5 mmol) of $\mu\text{-}S_2Fe_2(CO)_6$ and the mixture was stirred at r.t. for 2 h to give a brown–green solution. When this solution was cooled to −78 °C, 0.05 ml (0.5 mmol) of SO_2Cl_2 was added and the solution turned to red immediately. The mixture was warmed to r.t. and stirred for an additional 2 h. Volatiles were removed in vacuo, and the residue was subjected to TLC. Petroleum ether/CH_2Cl_2 (v/v = 20:1) eluted one major band, from which 0.158 g (31%) of **5a** was obtained as a red solid. M.p. 142 °C (dec.). *Anal.* Found: C, 25.78; H, 0.97. Calc. for $C_{22}H_{10}Fe_6O_{18}S_4$: C, 25.75; H, 0.98%. IR (KBr disk, cm^{-1}): $\nu_{(C\equiv O)}$ 2088(s), 2068(vs), 2035(vs), 2011(s), 1983(s). ^1H NMR ($CDCl_3$, δ, ppm): 1.41 (t, $J = 6.4$ Hz, 6H, $2CH_3$), 2.50 (q, $J = 6.4$ Hz, 4H, $2CH_2$).

3.6. Preparation of $(\mu\text{-t-BuS})_2[Fe_2(CO)_6]_3(\mu_4\text{-S})_2$ (**5b**)

The same procedure as that for **5a** was followed, but approximately 1.0 mmol of the $[Et_3NH]^+$ salt of anion $[(\mu\text{-t-BuS})(\mu\text{-CO})Fe_2(CO)_6]^-$ [prepared from 0.504 g (1.0 mmol) of $Fe_3(CO)_{12}$, 0.11 ml (1.0 mmol) of t-BuSH and 0.14 ml (1.0 mmol) of Et_3N] was employed in place of approximately 1.0 mmol of the $[Et_3NH]^+$ salt of anion $[(\mu\text{-EtS})(\mu\text{-CO})[Fe_2(CO)_6]^-$. 0.204 g (38%) of **5b** was obtained as a red solid. M.p. 180 °C (dec.). *Anal.* Found: C, 28.84; H, 1.71. Calc. for $C_{26}H_{18}Fe_6O_{18}S_4$: C, 28.87; H, 1.68%. IR (KBr disk, cm^{-1}): $\nu_{(C\equiv O)}$ 2070(s), 2041(vs), 1989(vs), 1922(s). ^1H NMR ($CDCl_3$, δ, ppm): 1.48 (s, 18H, $2(CH_3)_3C$).

3.7. Preparation of $(\mu\text{-PhSe})_2[Fe_2(CO)_6]_3(\mu_4\text{-S})_2$ (**5c**)

The same procedure as that for **5a** was followed, but approximately 1.5 mmol of the $[Et_3NH]^+$ salt of anion $[(\mu\text{-PhSe})(\mu\text{-CO})Fe_2(CO)_6]^-$ [prepared from 0.756 g (1.5 mmol) of $Fe_3(CO)_{12}$, 0.16 ml (1.5 mmol) of PhSeH and 0.23 ml (1.6 mmol) of Et_3N] was employed in place of approximately 1.0 mmol of the $[Et_3NH]^+$ salt of anion $[(\mu\text{-EtS})(\mu\text{-CO})Fe_2(CO)_6]^-$. 0.072 g (12%) of **5c** was obtained as a red solid. M.p. 173 °C (dec.). *Anal.* Found: C, 29.53; H, 1.06. Calc. for $C_{30}H_{10}Fe_6O_{18}S_2Se_2$: C, 29.64; H, 0.83%. IR (KBr disk, cm^{-1}): $\nu_{(C\equiv O)}$ 2088(s), 2069(vs), 2040(vs), 1996(s). ^1H NMR ($CDCl_3$, δ, ppm): 7.24–7.43 (m, 10H, $2C_6H_5$).

3.8. Preparation of $(\mu\text{-p-MeC}_6H_4Se)_2[Fe_2(CO)_6]_3(\mu_4\text{-S})_2$ (**5d**)

The same procedure as that for **5a** was followed, but approximately 1.5 mmol of the $[Et_3NH]^+$ salt of anion $[(\mu\text{-p-MeC}_6H_4Se)(\mu\text{-CO})[Fe_2(CO)_6]^-$ [prepared from 0.765 g (1.5 mmol) of $Fe_3(CO)_{12}$, 0.256 g (1.5 mmol) of p-MeC_6H_4SeH and 0.23 ml (1.6 mmol) of Et_3N] was employed in place of approximately 1.0 mmol of the $[Et_3NH]^+$ salt of anion $[(\mu\text{-EtS})(\mu\text{-CO})Fe_2(CO)_6]^-$. 0.145 g (23%) of **5d** was obtained as a red solid. M.p. 170 °C (dec.). *Anal.* Found: C, 30.56; H, 1.44. Calc. for $C_{32}H_{14}Fe_6O_{18}S_2Se_2$: C, 30.91; H, 1.14%. IR (KBr disk, cm^{-1}): $\nu_{(C\equiv O)}$ 2085(m), 2069(s), 2055(s), 2038(vs), 2022(s), 2006(s), 1992(vs). ^1H NMR ($CDCl_3$, δ, ppm): 231 (s, 6H, $2CH_3$), 7.17 (q, AA′BB′, $J = 8.3$ Hz, 8H, $2C_6H_4$).

3.9. Crystal X-ray structure determinations of **3b** and **5b**

Single-crystals of **3b** and **5b** suitable for X-ray diffraction analysis were grown by slow evaporation of their CH_2Cl_2/C_6H_{14} solutions at about 4 °C. Each crystal was mounted on a Bruker SMART 1000 or Enraf–Nonius CAD-4 diffractometer with a graphite monochromator with Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and

Table 3
Crystal data and structural refinements details for **3b** and **5b**

	3b	**5b**
Empirical formula	$C_{27}H_{10}Fe_6O_{19}S_4$	$C_{26}H_{18}Fe_6O_{18}S_4$
Formula weight	1101.69	1081.76
Temperature (K)	293	299
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$C2/c$ (no. 15)
a (Å)	9.2239(9)	27.454(5)
b (Å)	14.5729(13)	9.303(2)
c (Å)	16.0294(15)	20.136(4)
α (°)	79.135(2)	90
β (°)	74.749(2)	128.16(3)
γ (°)	72.965(2)	90
V (Å^3)	1973.0(3)	4044(2)
Z	2	4
D_{calc} (g cm^{-3})	1.854	1.777
Absorption coefficient (mm^{-1})	2.433	2.3627
$F(000)$	1088	2152
Scan type	ω–2θ	ω–2θ
$2\theta_{max}$ (°)	50.04	50.00
Reflections collected	8244	4002
Independent reflections	6917	3210
R_{int}	0.0309	0.068
Absorption correction	SADABS	DIFABS
R	0.0524	0.044
Rw	0.1312	0.051
Goodness-of-fit indicator	0.959	0.87
Largest difference peak and hole (e Å^{-3})	0.641 and −0.643	0.770 and −0.550

expanded by Fourier techniques. The final refinements were accomplished by the full-matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were located by using the geometric method. The calculations were performed using SHELXTL-97 program for **3b** and using the SDP-PLUS program for **5b**. Details of the crystal data, data collections and structure refinements are summarized in Table 3.

4. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 183210 and 183688 for compounds **3b** and **5b**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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