

Reactions of $[(\mu\text{-RS})(\mu\text{-S})\{\text{Fe}_2(\text{CO})_6\}_2(\mu_4\text{-S})]^-$ with acid chlorides and diacid chlorides. Crystal structure of $(\mu\text{-PhCH}_2\text{S})[\mu\text{-CH}_2=\text{C}(\text{Me})\text{COS}][\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})$

Zhong-Xia Wang ^{a,*}, Cheng-Sheng Jia ^a, Zhong-Yuan Zhou ^b, Xiang-Ge Zhou ^b

^a Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

^b Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu 610041, People's Republic of China

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Abstract

The reaction of anionic complexes $[(\mu\text{-RS})(\mu\text{-S})\{\text{Fe}_2(\text{CO})_6\}_2(\mu_4\text{-S})]^-$ (**1**) with acid chlorides R^1COCl [$\text{R}^1 = \text{Me}, \text{Ph}, \text{PhCH}=\text{CH}, \text{CH}_2=\text{C}(\text{Me})$] gives S-acylated compounds $(\mu\text{-RS})(\mu\text{-R}^1\text{COS})[\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})$ (**2a–h**). However, if R^1 in R^1COCl is an electron-withdrawing group such as EtO_2C and $p\text{-O}_2\text{NC}_6\text{H}_4$, the reaction produces $[(\mu\text{-RS})\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})$ ($\text{R} = \text{Ph}$ (**4**)), $[(\mu\text{-RS})\text{Fe}_2(\text{CO})_6(\mu_4\text{-S})]_2\text{Fe}_2(\text{CO})_6$ ($\text{R} = \text{Ph}$ (**5a**), tBu (**5b**)) and $[(\mu\text{-RS})\text{Fe}_2(\text{CO})_6]_2(\mu\text{-S-S-}\mu)$ ($\text{R} = \text{tBu}$ (**6**)). The same results were achieved in the reaction by use of diacid chlorides or SO_2Cl_2 instead of EtO_2CCOCl and $p\text{-O}_2\text{NC}_6\text{H}_4\text{COCl}$. The structure of complex $(\mu\text{-PhCH}_2\text{S})[\mu\text{-CH}_2=\text{C}(\text{Me})\text{COS}][\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})$ (**2d**) was determined by single-crystal X-ray diffraction. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Iron; Sulfur; Cluster; Synthesis; Reaction

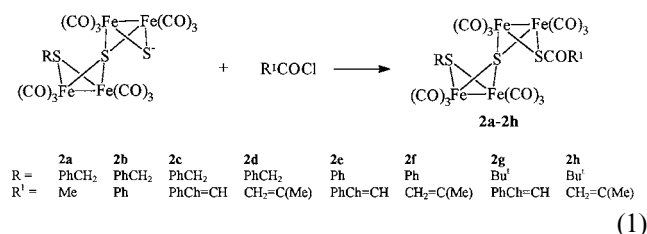
1. Introduction

We have reported synthesis of anionic complexes $[(\mu\text{-RS})(\mu\text{-S})\{\text{Fe}_2(\text{CO})_6\}_2(\mu_4\text{-S})]^-$ (**1**) and their reactions with alkyl halides, $\text{Cp}(\text{CO})_2\text{FeI}$ and acid chlorides, yielding the complexes of type $(\mu\text{-RS})(\mu\text{-R}'\text{S})[\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})$ ($\text{R}' = \text{alkyl}, \text{Cp}(\text{CO})_2\text{Fe}$ and acyl) [1]. In further studies on the reactivity of **1** towards acid chlorides, we found that the reaction products were dependent on the nature of the acid chlorides. In order to investigate how the reaction is affected by an acid chloride, we carried out the reaction using different acid chlorides. The reaction of **1** with a series of diacid chlorides was also studied. Herein we report the results.

2. Results and discussion

Anionic complexes $[(\mu\text{-RS})(\mu\text{-S})\{\text{Fe}_2(\text{CO})_6\}_2(\mu_4\text{-S})]^-$ (**1**) were prepared as described previously [1] and used

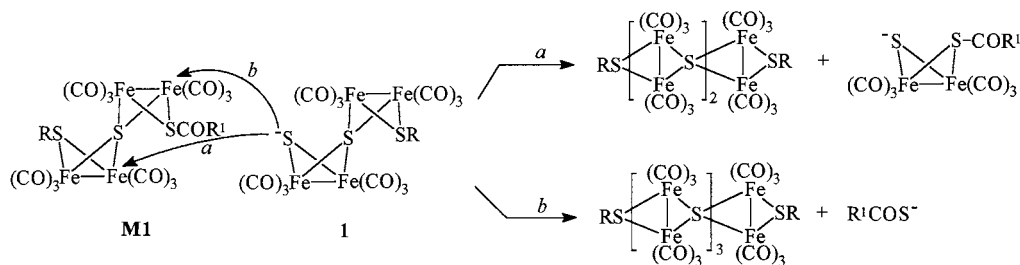
in situ at -78°C . Treatment of anions **1** with acid chlorides R^1COCl [$\text{R}^1 = \text{Me}, \text{Ph}, \text{PhCH}=\text{CH}$ and $\text{CH}_2=\text{C}(\text{Me})$] formed S-acylated products $(\mu\text{-RS})(\mu\text{-R}^1\text{COS})[\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})$ **2a–h**, see Eq. (1).



However, when R^1 is an electron-withdrawing group such as EtO_2C and $p\text{-NO}_2\text{C}_6\text{H}_4$, the reaction gave a mixture of several iron–sulfur clusters. For $\text{R} = \text{Ph}$, $(\mu\text{-PhS})_2\text{Fe}_2(\text{CO})_6$ (**3**), $[(\mu\text{-PhS})\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})$ (**4**) and $[(\mu\text{-PhS})\text{Fe}_2(\text{CO})_6(\mu_4\text{-S})]_2\text{Fe}_2(\text{CO})_6$ (**5a**) were obtained. For $\text{R} = \text{tBu}$, the products were $[(\mu\text{-tBuS})\text{Fe}_2(\text{CO})_6(\mu_4\text{-S})]_2\text{Fe}_2(\text{CO})_6$ (**5b**), $[(\mu\text{-tBuS})\text{Fe}_2(\text{CO})_6]_2(\mu\text{-S-S-}\mu)$ (**6**) and a minor component (**7**), which may be an $8\text{Fe}_5\text{S}$ cluster such as $[(\mu\text{-tBuS})\text{Fe}_2(\text{CO})_6(\mu_4\text{-S})\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})$. Further experiments showed that the same results could be achieved by reaction of **1** with diacid chlorides or

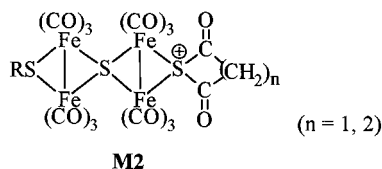
* Corresponding author. Fax: +86-0551-3631 760.

E-mail address: zwxwang@ustc.edu.cn (Z.-X. Wang)



Scheme 1.

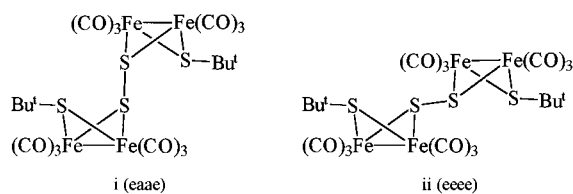
SO_2Cl_2 . After this work was finished, Song and co-workers reported the reaction of $[(\mu\text{-}^t\text{BuS})(\mu\text{-S})\{\text{Fe}_2(\text{CO})_6\}_2(\mu_4\text{-S})]^-$ with SO_2Cl_2 , yielding $[(\mu\text{-}^t\text{BuS})\text{Fe}_2(\text{CO})_6(\mu_4\text{-S})]_2\text{Fe}_2(\text{CO})_6$ [2]. The reaction mechanism of **1** with R^1COCl ($\text{R}^1 = \text{EtO}_2\text{C}$, $p\text{-NO}_2\text{C}_6\text{H}_4$) might be proposed as showed in Scheme 1 based on the reported mechanism for the reaction between $(\mu\text{-RS})(\mu\text{-R}^1\text{COS})\text{Fe}_2(\text{CO})_6$ and $[(\mu\text{-RS})(\mu\text{-S})\text{Fe}_2(\text{CO})_6]^-$ [3] and similar systems [4,5]. First, the anions **1** react with R^1COCl to form normal S-acylated products $(\mu\text{-RS})(\mu\text{-R}^1\text{COS})[\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})$ (**M1**). Then **M1** undergoes nucleophilic attack on the iron atoms by the anionic sulfur atom of excess **1** in two paths, *a* and *b*, respectively. Path *a* gives a $6\text{Fe}4\text{S}$ cluster $[(\mu\text{-RS})\text{Fe}_2(\text{CO})_6(\mu_4\text{-S})]_2\text{Fe}_2(\text{CO})_6$ and anionic fragment $[(\mu\text{-R}^1\text{COS})(\mu\text{-S})\text{Fe}_2(\text{CO})_6]^-$ which further decomposes. Path *b* yields an $8\text{Fe}5\text{S}$ cluster $[(\mu\text{-}^t\text{BuS})\text{Fe}_2(\text{CO})_6(\mu_4\text{-S})\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})$ and anion R^1COS^- . From the reaction results, it seems that the path *a* is favored. When a diacid chloride such as oxalyl chloride or fumaryl chloride is used in the reaction, the R^1 group (ClCO or $\text{ClCOCH}=\text{CH}$) in **M1** is still strongly electron withdrawing and makes the iron atoms more electrophilic. However, when malonyl dichloride or succinyl chloride is employed in the reaction, the electron-withdrawing power of the R^1 group [$\text{ClCO}(\text{CH}_2)_n$ ($n = 1, 2$)] in **M1** should be close to that of Ph and Me. While the reaction of **1** with PhCOCl or MeCOCl formed usual products $(\mu\text{-RS})(\mu\text{-R}^1\text{COS})[\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})$ only, see Eq. (1). Hence, we assume that the reaction with $\text{ClCO}(\text{CH}_2)_n\text{COCl}$ ($n = 1, 2$) proceeds through a cationic intermediate **M2**.



Complexes **2a–h** are all red solids, soluble in methylene dichloride and petroleum ether. They have been characterized by elemental analyses, $^1\text{H-NMR}$ and IR spectroscopy. The IR spectrum of each of the compounds exhibited terminal carbonyl and thiocarboxylato group absorption bands. The $^1\text{H-NMR}$ spectra showed respective organic groups. The structure of

2d was further characterized by single-crystal X-ray diffraction (see below).

Complexes **3**, **4** and **6** are known [6–8] and have been identified by mass spectra (for **6**), elemental analyses (for **3**, **4** and **6**) and by comparison of their melting points, $^1\text{H-NMR}$ and IR spectral data with those of authentic samples. It is worth pointing out that complex **6** exists only as a diequatorial- ^tBu isomer according to its $^1\text{H-NMR}$ spectrum (unique signal at δ 1.46 ppm), rather than as a mixture of two conformational isomers due to *tert*-butyl groups in the axial or equatorial positions as indicated in the literature [8]. On the basis of the built relationship between the structure of $(\mu\text{-RS})_2\text{Fe}_2(\text{CO})_6$ and $^1\text{H-NMR}$ spectral data [8], **6** may exist as either *i* or *ii*.



Complex **5a** has been characterized by elemental analysis and IR, $^1\text{H-NMR}$ and mass spectra. Its IR spectrum showed terminal carbonyl absorption bands and the mass spectrum gave reasonable fragment ions such as $\text{M}^+ - n\text{CO}$, $\text{M}^+ - n\text{CO} - \text{PhS}$ and Fe_6S_4 . Complex **5b** gave satisfactory microanalytical, as well as $^1\text{H-NMR}$ and IR spectra. Its structure was also further characterized by single-crystal X-ray diffraction, which showed almost the same geometrical features and bond lengths and angles as those reported in literature [2].

Complex **7** has been incompletely characterized. Its $^1\text{H-NMR}$ spectrum gave an equatorial ^tBu signal and the IR spectrum showed the presence of terminal carbonyls. The elemental analysis supposed it to be an $8\text{Fe}5\text{S}$ cluster $[(\mu\text{-}^t\text{BuS})\text{Fe}_2(\text{CO})_6(\mu_4\text{-S})\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})$. The mass spectrum gave only small fragment ions such as $\text{M}^+ - 24\text{CO} - ^t\text{Bu}$ and $\text{Fe}_6\text{S}_2\text{CMe}_2^+$. Attempts to grow single crystals for X-ray diffraction analysis were unsuccessful.

2.1. Structure of complex **2d**

In order to further confirm the structures of complexes **2a–h** mentioned above, an X-ray diffraction

analysis for one representative compound, **2d**, was undertaken. Table 1 lists the selected bond lengths and angles. Fig. 1 shows its molecular structure. As seen from Fig. 1, the molecule consists of two $\text{Fe}_2(\text{CO})_6$ units joined to a spiral sulfur atom, with one of the $\text{Fe}_2(\text{CO})_6$ units also being bridged by a PhCH_2S ligand and the other by a $\text{CH}_2=\text{C}(\text{Me})\text{COS}$ ligand. Each $\text{S}_2\text{Fe}_2(\text{CO})_6$ unit is butterfly shaped. The four-coordinated sulfur atom is distortedly tetrahedral and hence the two $\text{Fe}_2(\text{CO})_6$ units are oriented approximately at right angles to each other. The orientations of both PhCH_2 and $\text{CH}_2=\text{C}(\text{Me})\text{CO}$ groups are equatorial. The molecular geometry and the basic geometric parameters are very similar to those of complexes $(\mu\text{-}^t\text{BuS})(\mu\text{-PhCH}_2\text{S})[\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})$ [1], $(\mu\text{-PhC}\equiv\text{CS})(\mu\text{-EtS})[\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})$ [5] and $(\mu\text{-PhS})(\mu\text{-EtS})[\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})$ [9].

Table 1
Selected bond distances (Å) and bond angles (°) for complex **2d**

Bond distances

| | | | |
|-------------|------------|-------------|-----------|
| Fe(1)–S(1) | 2.2450(11) | Fe(3)–S(1) | 2.2384(8) |
| Fe(1)–S(2) | 2.2618(8) | Fe(3)–S(3) | 2.2695(9) |
| Fe(1)–Fe(2) | 2.5399(8) | Fe(3)–Fe(4) | 2.5422(8) |
| Fe(2)–S(1) | 2.2525(7) | Fe(4)–S(1) | 2.2620(8) |
| Fe(2)–S(2) | 2.2770(8) | Fe(4)–S(3) | 2.2907(7) |

Bond angles

| | | | |
|------------------|----------|------------------|-----------|
| S(1)–Fe(1)–S(2) | 76.36(3) | S(1)–Fe(4)–Fe(3) | 55.17(2) |
| S(1)–Fe(1)–Fe(2) | 55.76(2) | S(3)–Fe(4)–Fe(3) | 55.72(3) |
| S(2)–Fe(1)–Fe(2) | 56.26(3) | Fe(3)–S(1)–Fe(1) | 134.33(3) |
| S(1)–Fe(2)–S(2) | 75.91(3) | Fe(3)–S(1)–Fe(2) | 137.53(3) |
| S(1)–Fe(2)–Fe(1) | 55.48(3) | Fe(1)–S(1)–Fe(2) | 68.77(3) |
| S(2)–Fe(2)–Fe(1) | 55.69(2) | Fe(3)–S(1)–Fe(4) | 68.79(3) |
| S(1)–Fe(3)–S(3) | 77.98(3) | Fe(1)–S(1)–Fe(4) | 134.09(3) |
| S(1)–Fe(3)–Fe(4) | 56.05(3) | Fe(2)–S(1)–Fe(4) | 125.48(3) |
| S(3)–Fe(3)–Fe(4) | 56.52(2) | Fe(1)–S(2)–Fe(2) | 68.05(3) |
| S(1)–Fe(4)–S(3) | 77.07(4) | Fe(3)–S(3)–Fe(4) | 67.76(3) |

3. Experimental

All reactions were carried out under an atmosphere of pure nitrogen using standard Schlenk techniques. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Triiron dodecacarbonyl [10] and $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ [11] were prepared by published procedures. Infrared spectra (KBr, disk) were obtained by using a VECTOR22 spectrometer. $^1\text{H-NMR}$ spectra were recorded on either a Varian EM360L or a Bruker DMX500 spectrometer with CDCl_3 as solvent. Mass spectra were taken on a HP5989A instrument. Elemental analyses were performed with a Perkin–Elmer 240C analyzer. Melting points were uncorrected.

*3.1. Synthesis of $[(\mu\text{-RS})(\mu\text{-R}^1\text{COS})[\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})]$ [**2a**, $R = \text{PhCH}_2$, $R^1 = \text{Me}$; **2b**, $R = \text{PhCH}_2$, $R^1 = \text{Ph}$; **2c**, $R = \text{PhCH}_2$, $R^1 = \text{PhCH}=\text{CH}$; **2d**, $R = \text{PhCH}_2$, $R^1 = \text{CH}_2=\text{C}(\text{Me})$; **2e**, $R = \text{Ph}$, $R^1 = \text{PhCH}=\text{CH}$; **2f**, $R = \text{Ph}$, $R^1 = \text{CH}_2=\text{C}(\text{Me})$; **2g**, $R = ^t\text{Bu}$, $R^1 = \text{PhCH}=\text{CH}$; **2h**, $R = ^t\text{Bu}$, $R^1 = \text{CH}_2=\text{C}(\text{Me})]$*

A solution of triethylammonium salt of $[(\mu\text{-PhCH}_2\text{S})(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]^-$ was generated by addition of PhCH_2SH (0.21 ml, 1.79 mmol) and Et_3N (0.25 ml, 1.79 mmol) to a THF (30 ml) solution of $\text{Fe}_3(\text{CO})_{12}$ (0.90 g, 1.78 mmol) at room temperature (r.t.). The solution was cooled to -78°C . To the solution was added $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ (0.58 g, 1.68 mmol) and stirred for 30 min at -78°C . Subsequently CH_3COCl (0.15 ml, 2.11 mmol) was added to the mixture. After stirring overnight at r.t., the solvent was removed at reduced pressure and the residue extracted with petroleum ether. After removal of the solvent, the material remaining was subjected to filtration chromatography (silica gel). Petroleum ether eluted a minor purple band which was not collected. Further elution with 1:9 (v/v) CH_2Cl_2 –petroleum ether afforded a red solid after evaporation of the solvent, which was recrystallized from petroleum ether to give red crystals of **2a** (0.78 g, 67%), m.p. $132\text{--}134^\circ\text{C}$. Anal. Found: C, 31.96; H, 1.36. $\text{C}_{21}\text{H}_{10}\text{Fe}_4\text{O}_{13}\text{S}_3$ requires: C, 31.93; H, 1.28%. $^1\text{H-NMR}$ (60 MHz): δ (ppm) 2.50 (s, 3H, CH_3), 3.46 (s, 2H, CH_2), 7.10 (s, 5H, Ph). IR: ν (cm^{-1}) 2089s, 2057s, 2031vs, 1991s (Fe–CO), 1720m (CO).

Complexes **2b–h** were prepared similarly. **2b**, red crystals in 62% yield, m.p. 140°C (dec.). Anal. Found: C, 36.63; H, 1.47. $\text{C}_{26}\text{H}_{12}\text{Fe}_4\text{O}_{13}\text{S}_3$ requires: C, 36.65; H, 1.42%. $^1\text{H-NMR}$ (60 MHz): δ (ppm) 3.65 (s, 2H, CH_2), 7.27–8.10 (m, 10H, Ph). IR: ν (cm^{-1}) 2085s, 2061s, 2036vs, 2000s, 1989s, 1981s (Fe–CO), 1677m (CO). **2c**, deep red crystals in 46% yield, m.p. $157\text{--}158^\circ\text{C}$. Anal. Found: C, 38.73; H, 1.77. $\text{C}_{28}\text{H}_{14}\text{Fe}_4\text{O}_{13}\text{S}_3$ requires: C, 38.30; H, 1.61%. $^1\text{H-NMR}$ (500 MHz): δ (ppm) 3.63, 3.72 (s, s, 2H, CH_2), 6.75 (s, 1H, CH), 7.26–7.54 (m, 10H, Ph), 7.84 (s, 1H, CH). IR: ν (cm^{-1}) 2084s, 2052s,

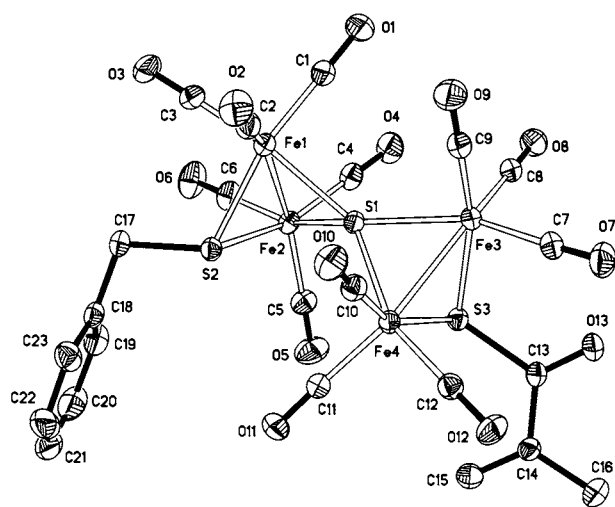


Fig. 1. ORTEP view of **2d**, drawn with 30% probability ellipsoids.

2036vs, 1998s, 1985s (Fe–CO), 1666m (CO). **2d**, red crystals in 51% yield, m.p. 165–167°C. Anal. Found: C, 33.70; H, 1.52. $C_{23}H_{12}Fe_4O_{13}S_3$ requires: C, 33.86; H, 1.48%. 1H -NMR (500 MHz): δ (ppm) 1.95 (s, 3H, CH_3), 3.63, 3.74 (s, s, 2H, CH_2), 6.04, 6.53 (s, s, 2H, $=CH_2$), 7.38 (s, 5H, Ph). IR: ν (cm^{-1}) 2087s, 2054s, 2029vs, 1990s (Fe–CO), 1681m (CO). **2e**, deep red crystals in 48% yield, m.p. 130–131°C. Anal. Found: C, 37.76; H, 1.47. $C_{27}H_{12}Fe_4O_{13}S_3$ requires: C, 37.53; H, 1.40%. 1H -NMR (500 MHz): δ (ppm) 6.72 (d, $J = 11.5$ Hz, 1H, CH), 7.19, 7.30 (s, s, 5H, Ph), 7.39, 7.51 (s, s, 5H, Ph), 7.85 (d, $J = 12.0$ Hz, 1H, CH). IR: ν (cm^{-1}) 2086s, 2060s, 2036vs, 2001s, 1979s (Fe–CO), 1665m (CO). **2f**, red crystals in 54% yield, m.p. 90–92°C. Anal. Found: C, 32.57; H, 1.35. $C_{22}H_{10}Fe_4O_{13}S_3$ requires: C, 32.95; H, 1.26%. 1H -NMR (500 MHz): δ (ppm) 1.96 (s, 3H, CH_3), 6.07, 6.59 (s, s, 2H, $=CH_2$), 7.25, 7.35 (s, s, 5H, Ph). IR: ν (cm^{-1}) 2086s, 2063s, 2039vs, 1996s (Fe–CO), 1677m (CO). **2g**, red crystals in 47% yield, m.p. 155–157°C. Anal. Found: C, 35.92; H, 1.94. $C_{25}H_{16}Fe_4O_{13}S_3$ requires: C, 35.58; H, 1.91%. 1H -NMR (500 MHz): δ (ppm) 1.44 (s, 9H, 'Bu), 6.70 (d, $J = 15.0$ Hz, 1H, CH), 7.39, 7.50 (s, s, 5H, Ph), 7.83 (d, $J = 14.6$ Hz, 1H, CH). IR: ν (cm^{-1}) 2084s, 2053s, 2037vs, 2002s, 1988s, 1980s (Fe–CO), 1660m (CO). **2h**, deep red crystals in 81% yield, m.p. 168–170°C. Anal. Found: C, 30.52; H, 1.78. $C_{20}H_{14}Fe_4O_{13}S_3$ requires: C, 30.72; H, 1.80%. 1H -NMR (500 MHz): δ (ppm) 1.48 (s, 9H, 'Bu), 1.94 (s, 3H, Me), 6.03, 6.55 (s, s, 2H, $=CH_2$). IR: ν (cm^{-1}) 2084s, 2053s, 2032vs, 2013s, 1990s, 1980s (Fe–CO), 1681m (CO).

3.2. Reaction of $[(\mu-PhS)(\mu-S)\{Fe_2(CO)_6\}_2(\mu_4-S)]^-$ with $p-NO_2C_6H_4COCl$ and EtO_2CCOCl

$[(\mu-PhS)(\mu-S)\{Fe_2(CO)_6\}_2(\mu_4-S)]^-$ was prepared according to the same procedure as described above from $(\mu-S_2)Fe_2(CO)_6$ (0.48 g, 1.40 mmol) and $[(\mu-PhS)(\mu-CO)Fe_2(CO)_6]^-$ derived from $Fe_3(CO)_{12}$ (0.74 g, 1.45 mmol), PhSH (0.15 ml, 1.46 mmol) and Et_3N (0.20 ml, 1.43 mmol) in THF (30 ml). To the solution was added $p-NO_2C_6H_4COCl$ (0.27 g, 1.45 mmol) at $-78^\circ C$. The mixture was warmed to r.t. and stirred overnight. The solvent was removed at reduced pressure and the residue extracted with petroleum ether. After removal of the solvent, the material remaining was subjected to filtration chromatography (silica gel). Petroleum ether eluted a minor purple band which was not collected. Further elution with petroleum ether and 1:9 (v/v) CH_2Cl_2 –petroleum ether developed three red bands successively. The first band gave red crystalline $(\mu-PhS)_2Fe_2(CO)_6$ (**3**) (0.11 g, 32%). The second band gave $[(\mu-PhS)Fe_2(CO)_6]_2(\mu_4-S)$ (**4**) (0.08 g, 14%) as red crystals. The third band gave red–brown crystals of $[(\mu-PhS)Fe_2(CO)_6(\mu_4-S)]_2Fe_2(CO)_6$ (**5a**) (0.06 g, 8%). **3**: m.p. 130–132°C. Anal. Found: C, 43.40; H, 2.14.

$C_{18}H_{10}Fe_2O_6S_2$ requires: C, 43.41; H, 2.02%. 1H -NMR (60 MHz): δ (ppm) 7.13 (s, 10H, Ph). IR: ν (cm^{-1}) 2074s, 2036vs, 2008s, 1982vs, 1971s. **4**: m.p. 150°C(dec.). Anal. Found: C, 35.30; H, 1.36. $C_{24}H_{10}Fe_4O_{12}S_3$ requires: C, 35.59; H, 1.24%. 1H -NMR (60 MHz): δ (ppm) 7.20 (s, 10H, Ph). IR: ν (cm^{-1}) 2085s, 2058s, 2039vs, 1996s, 1978s. **5a**: m.p. 150°C(dec.). Anal. Found: C, 31.94; H, 1.05. $C_{30}H_{10}Fe_6O_{18}S_4$ requires: C, 32.12; H, 0.90%. 1H -NMR (60 MHz): δ (ppm) 7.12 (s, 10H, Ph). IR: ν (cm^{-1}) 2088w, 2073s, 2060s, 2044vs, 1999vs, 1977s. MS (EI), m/z (relative intensity): 956 ($M^+ - 2CO - PhS - 1$, 0.11), 928 ($M^+ - 3CO - PhS - 1$, 0.13), 872 ($M^+ - 5CO - PhS - 1$, 0.20), 787 ($M^+ - 12CO + 1$, 0.54), 759 ($M^+ - 13CO + 1$, 0.15), 731 ($M^+ - 14CO + 1$, 0.33), 703 ($M^+ - 15CO + 1$, 0.19), 675 ($M^+ - 16CO + 1$, 0.17), 647 ($M^+ - 17CO + 1$, 0.12), 619 ($M^+ - 18CO + 1$, 0.62), 561 ($M^+ - 9CO - Ph - Fe_3S_2$, 0.16), 464 ($Fe_6S_4^+$, 1.11), 329 ($Fe_2(CO)_5Ph^+$, 1.19), 242 ($FeSPh_2^+$, 0.58), 186 (SPh_2^+ , 100), 154 (Ph_2^+ , 36.10), 77 (Ph^+ , 18.67), 65 ($C_3H_3^+$, 9.84), 56 (Fe^+ , 5.90), 51 ($C_4H_3^+$, 20.78).

The reaction of $[(\mu-PhS)(\mu-S)\{Fe_2(CO)_6\}_2(\mu_4-S)]^-$ with EtO_2CCOCl followed the same procedure as described above. After work-up, complexes **3** (39%), **4** (10%) and **5a** (6%) were obtained.

3.3. Reaction of $[(\mu-PhS)(\mu-S)\{Fe_2(CO)_6\}_2(\mu_4-S)]^-$ with organic diacid chlorides

(i) $[(\mu-PhS)(\mu-S)\{Fe_2(CO)_6\}_2(\mu_4-S)]^-$ was prepared according to the same procedure as described above from $(\mu-S_2)Fe_2(CO)_6$ (0.48 g, 1.40 mmol) and $[(\mu-PhS)(\mu-CO)Fe_2(CO)_6]^-$ derived from $Fe_3(CO)_{12}$ (0.73 g, 1.45 mmol), PhSH (0.15 ml, 1.46 mmol) and Et_3N (0.20 ml, 1.43 mmol) in THF (30 ml). To the solution was added oxalyl chloride (0.06 ml, 0.68 mmol) at $-78^\circ C$ and stirred overnight at r.t. After the same work-up as described above, complexes **3** (0.16 g, 47%), **4** (0.08 g, 15%) and **5a** (0.07 g, 9%) were obtained.

(ii) The reaction of $[(\mu-PhS)(\mu-S)\{Fe_2(CO)_6\}_2(\mu_4-S)]^-$ with fumaryl chloride followed the same procedure as described above, but fumaryl chloride was used instead of oxalyl chloride. After work-up, complexes **3** (69%), **4** (12%) and **5a** (2%) were obtained.

(iii) The reaction of $[(\mu-PhS)(\mu-S)\{Fe_2(CO)_6\}_2(\mu_4-S)]^-$ with malonyl dichloride followed the same procedure as described in (i), but malonyl dichloride was used instead of oxalyl chloride. After the same work-up as described above, complexes **3** (62%), **4** (16%) and **5a** (3%) were obtained.

(iv) The reaction of $[(\mu-PhS)(\mu-S)\{Fe_2(CO)_6\}_2(\mu_4-S)]^-$ with succinyl chloride was carried out according to the same procedure as described in (i), but succinyl chloride was used instead of oxalyl chloride. After the same work-up, complexes **3** (43%), **4** (12%) and **5a** (3%) were obtained.

3.4. Reaction of $[(\mu\text{-}^t\text{BuS})(\mu\text{-S})\{\text{Fe}_2(\text{CO})_6\}_2(\mu_4\text{-S})]^-$ with EtO_2CCOCl

A solution of triethylammonium salt of $[(\mu\text{-}^t\text{BuS})(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]^-$ was generated by addition of $^t\text{BuSH}$ (0.16 ml, 1.42 mmol) and Et_3N (0.20 ml, 1.43 mmol) to a THF (30 ml) solution of $\text{Fe}_3(\text{CO})_{12}$ (0.72 g, 1.43 mmol) at r.t. The solution was cooled to -78°C . To the solution was added $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ (0.48 g, 1.40 mmol) and stirred for 30 min at -78°C . Subsequently EtO_2CCOCl (0.16 ml, 1.43 mmol) was added to the mixture. After stirring overnight at r.t., the solvent was removed at reduced pressure and the residue extracted with petroleum ether. After removal of the solvent, the material remaining was subjected to filtration chromatography (silica gel). Petroleum ether eluted a minor purple band which was not collected. Further elution with petroleum ether and then 1:9 (v/v) CH_2Cl_2 –petroleum ether moved three red bands successively. The first band gave $[(\mu\text{-}^t\text{BuS})\text{Fe}_2(\text{CO})_6]_2(\mu\text{-S-S-}\mu)$ (**6**) (0.05 g, 9%) as purplish–red crystals. The second band gave red–purple crystals $[(\mu\text{-}^t\text{BuS})\text{Fe}_2(\text{CO})_6(\mu_4\text{-S})]_2\text{-Fe}_2(\text{CO})_6$ (**5b**) (0.12 g, 16%) and the third band afforded **7** (0.07 g, 7%) as a red powder. **6**: m.p. 137–138°C. Anal. Found: C, 29.58; H, 2.27. $\text{C}_{20}\text{H}_{18}\text{Fe}_4\text{O}_{12}\text{S}_4$ requires: C, 29.95; H, 2.26%. $^1\text{H-NMR}$ (60 MHz): δ (ppm) 1.47 (s, 18H, ^tBu). IR: ν (cm^{-1}) 2081m, 2056s, 2037vs, 2016s, 1990vs, 1974s. MS (EI), m/z (relative intensity): 634 ($\text{M}^+ - 6\text{CO}$, 0.12), 606 ($\text{M}^+ - 7\text{CO}$, 0.14), 578 ($\text{M}^+ - 8\text{CO}$, 0.24), 550 ($\text{M}^+ - 9\text{CO}$, 0.19), 522 ($\text{M}^+ - 10\text{CO}$, 0.27), 494 ($\text{M}^+ - 11\text{CO}$, 0.85), 466 ($\text{M}^+ - 12\text{CO}$, 0.35), 409 ($\text{M}^+ - 12\text{CO} - ^t\text{Bu}$, 0.23), 352 ($\text{M}^+ - 12\text{CO} - 2^t\text{Bu}$, 1.64), 320 ($\text{M}^+ - 12\text{CO} - 2^t\text{Bu} - \text{S}$, 0.82), 207 ($\text{M}^+ - 12\text{CO} - 2^t\text{Bu} - \text{SFe}_2$, 0.58), 176 ($\text{M}^+ - 12\text{CO} - 2^t\text{Bu} - \text{S}_2\text{Fe}_2$, 0.68), 90 ($^t\text{BuSH}^+$, 6.93), 75 ($^t\text{BuSH}^+ - \text{Me}$, 3.89), 56 (Fe^+ , 44.99), 41 (C_3H_5^+ , 100). **5b**: m.p. 170°C (dec.). Anal. Found: C, 28.64; H, 1.69. $\text{C}_{26}\text{H}_{18}\text{Fe}_6\text{O}_{18}\text{S}_4$ requires: C, 28.87; H, 1.68%. $^1\text{H-NMR}$ (60 MHz): δ (ppm) 1.48 (s, 18H, ^tBu). IR: ν (cm^{-1}) 2087w, 2066vs, 2041vs, 1989vs, 1975s. **7**: m.p. 190°C (dec.). Anal. Found: C, 27.28; H, 1.50. $\text{C}_{32}\text{H}_{18}\text{Fe}_8\text{O}_{24}\text{S}_5$ requires: C, 27.58; H, 1.30%. $^1\text{H-NMR}$ (60 MHz): δ (ppm) 1.42 (s, 18H, ^tBu). IR: ν (cm^{-1}) 2091w, 2080m, 2057vs, 2039vs, 2022s, 1988vs. MS (EI), m/z (relative intensity): 665 ($\text{M}^+ - 24\text{CO} - ^t\text{Bu}$, 0.97), 442 ($\text{M}^+ - 20\text{CO} - ^t\text{Bu} - \text{Fe}_4\text{S}_3$, 0.71), 315 ($\text{Fe}_2\text{S}_2(\text{CO})_4\text{CMe}^+$, 0.65), 244 ($\text{Fe}_2\text{S}_2(\text{CO})_2\text{C}^+$, 2.29), 147 ($^t\text{Bu}_2\text{S}^+ + 1$, 2.97), 84 ($\text{Fe}(\text{CO})^+$, 26.38), 71 ($\text{C}_3\text{H}_{11}^+$, 28.66), 57 ($^t\text{Bu}^+$, 89.76), 41 (C_3H_5^+ , 100).

3.5. Reaction of $[(\mu\text{-}^t\text{BuS})(\mu\text{-S})\{\text{Fe}_2(\text{CO})_6\}_2(\mu_4\text{-S})]^-$ with organic diacid chlorides

(i) $[(\mu\text{-}^t\text{BuS})(\mu\text{-S})\{\text{Fe}_2(\text{CO})_6\}_2(\mu_4\text{-S})]^-$ was prepared according to the same procedure as described above from $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ (0.59 g, 1.71 mmol) and $[(\mu\text{-}$

$^t\text{BuS})(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]^-$ derived from $\text{Fe}_3(\text{CO})_{12}$ (0.87 g, 1.73 mmol), $^t\text{BuSH}$ (0.20 ml, 1.77 mmol) and Et_3N (0.25 ml, 1.79 mmol) in THF (30 ml). To the solution was added oxalyl chloride (0.08 ml, 0.9 mmol) at -78°C and stirred overnight at r.t. After the same work-up as described above, complexes **6** (0.06 g, 9%), **5b** (0.33 g, 36%) and **7** (0.06 g, 5%) were obtained.

(ii) The reaction of $[(\mu\text{-}^t\text{BuS})(\mu\text{-S})\{\text{Fe}_2(\text{CO})_6\}_2(\mu_4\text{-S})]^-$ with fumaryl chloride followed the same procedure as described above. After work-up, complexes **6** (26%), **5b** (25%) and **7** (6%) were obtained.

(iii) The THF solution of $[(\mu\text{-}^t\text{BuS})(\mu\text{-S})\{\text{Fe}_2(\text{CO})_6\}_2(\mu_4\text{-S})]^-$ was treated with malonyl dichloride according to the procedure described above to give, after work-up, **5b** (19%), **6** (12%) and **7** (10%).

(iv) The reaction of $[(\mu\text{-}^t\text{BuS})(\mu\text{-S})\{\text{Fe}_2(\text{CO})_6\}_2(\mu_4\text{-S})]^-$ with succinyl chloride was carried out similarly. After the same work-up, complexes **5b** (32%), **6** (18%) and **7** (8%) were obtained.

3.6. Crystal structure determination of complex **2d**

Suitable crystals of complex **2d** were grown from petroleum ether– CH_2Cl_2 solution at r.t. Data were collected on a Siemens P4 four-circle diffractometer using monochromated Mo– K_α radiation. A semi-empirical absorption correction was applied to the data. A summary of data collection details and crystal data is given in Table 2. The structure was solved by direct

Table 2
Crystal data and refinement for complex **2d**

| | |
|--|--|
| Formula | $\text{C}_{23}\text{H}_{13}\text{Fe}_4\text{O}_{13}\text{S}_3$ |
| Formula weight | 816.91 |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| Unit cell dimensions | |
| a (Å) | 9.181(2) |
| b (Å) | 11.455(2) |
| c (Å) | 15.795(3) |
| α (°) | 74.03(3) |
| β (°) | 74.53(3) |
| γ (°) | 84.77(3) |
| V (Å ³) | 4072.5(9) |
| Z | 2 |
| Crystal size (mm) | $0.26 \times 0.22 \times 0.20$ |
| Radiation λ (Å) | 0.71073 |
| μ (Mo– K_α) (mm^{-1}) | 2.112 |
| Temperature (K) | 294(2) |
| Total reflections | 4832 |
| Independent reflections | 4827 |
| Reflections with $I > 2\sigma(I)$ | 4441 |
| Scan type | ω scan |
| $2\theta_{\text{max}}$ (°) | 50.11 |
| R_1 | 0.0518 |
| wR_2 | 0.1546 |
| Largest differences peak and hole ($e \text{ \AA}^{-3}$) | 0.422 and -0.469 |

$$^a R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

$$^b wR_2 = \frac{[\sum w(F_o^2 - F_c^2)^2]}{[\sum wF_o^4]^{1/2}}$$

methods and was refined by full-matrix least-squares on F^2 with the positional and anisotropic thermal parameters for non-hydrogen atoms on a PC using SHELXS 86 [12] and SHELXL 93 [13] software packages, respectively.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 136814. 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; email: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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