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Synthesis of $[(\mu\text{-RS})(\mu\text{-S})\{Fe_2(CO)_6\}_2(\mu_4\text{-S})]^-$ and their reactivity toward electrophiles

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Abstract

Reaction of the Et_3NH^+ salts of the $[(\mu\text{-RS})(\mu\text{-CO})Fe_2(CO)_6]^-$ anions ($R = \mathrm{Bu}^t$, Ph or $PhCH_2$) with $(\mu\text{-}S_2)Fe_2(CO)_6$ gives reactive intermediates $[(\mu\text{-RS})(\mu\text{-S})\{Fe_2(CO)_6\}_2(\mu_4\text{-S})]^-$. Reactions of the latter with alkyl halides, acid chlorides and $Cp(CO)_2FeI$ have been studied. X-Ray structure of $(\mu\text{-}\mathrm{Bu}^tS)(\mu\text{-}PhCH_2S)[Fe_2(CO)_6]_2(\mu_4\text{-S})$ was determined. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Iron; Bridging-sulfur ligand; Complexes; Synthesis; Reaction

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1. Introduction

The S–S bond of $(\mu\text{-}S_2)Fe_2(CO)_6$ has been reported to be cleaved readily by nucleophiles such as RLi or RMgX, forming the monoanionic complexes $[(\mu\text{-RS})(\mu\text{-S})Fe_2(CO)_6]^-$ [1,2]. These anionic complexes showed versatile reactivities toward electrophiles or oxidation agents [2–4]. However, the reactions of $(\mu\text{-}S_2)Fe_2(CO)_6$ with metallic nucleophiles have not been explored. In this paper, we report the reaction of $(\mu\text{-}S_2)Fe_2(CO)_6$ with $[(\mu\text{-RS})(\mu\text{-CO})Fe_2(CO)_6]^-$ (**A**) and the reactivity of the resulting complexes $[(\mu\text{-RS})(\mu\text{-S})\{Fe_2(CO)_6\}_2(\mu_4\text{-S})]^-$ (**1**) toward electrophiles. These reactions provide a general route for the synthesis of Fe–S cluster series $(\mu\text{-RS})(\mu\text{-}R^1S)[Fe_2(CO)_6]_2(\mu_4\text{-S})$ and also make possible the preparation of complexes of types $(\mu\text{-RS})[\mu\text{-}R^2C(O)S][Fe_2(CO)_6]_2(\mu_4\text{-S})$ and $(\mu\text{-RS})[\mu\text{-}Cp(CO)_2FeS][Fe_2(CO)_6]_2(\mu_4\text{-S})$.

2. Results and discussion

Anionic complexes $[(\mu\text{-RS})(\mu\text{-CO})Fe_2(CO)_6]^-$ (**A**) are known to act as metal-centred nucleophiles [5]. Treatment of $(\mu\text{-}S_2)Fe_2(CO)_6$ with $[(\mu\text{-RS})(\mu\text{-CO})Fe_2(CO)_6]^-$ in THF at −78°C resulted in cleavage of the sulfur–sulfur bond of $(\mu\text{-}S_2)Fe_2(CO)_6$, forming the tetranuclear anionic complexes, presumably **1**, in which the μ-CO ligand of **A** is replaced by one of the sulfur atoms of $(\mu\text{-}S_2)Fe_2(CO)_6$, Scheme 1. The anions **1** with alkyl halides afforded $(\mu\text{-RS})(\mu\text{-}R^1S)[Fe_2(CO)_6]_2(\mu_4\text{-S})$ (**2**–**4**) and with acid chlorides gave $(\mu\text{-RS})(\mu\text{-}R^2COS)\text{–}[Fe_2(CO)_6]_2(\mu_4\text{-S})$ (**5**–**8**). When the anions **1** were treated with $Cp(CO)_2FeI$, pentanuclear iron–sulfur complexes **9**–**11** were obtained as black crystals. Complexes **2**–**11** are air-stable in solid state, but slightly air-sensitive in solution. They are very soluble in polar organic solvents such as methylene chloride and soluble in petroleum ether. Complexes **3** and **4** were previously prepared by another route and identified by comparison of their melting points, NMR and IR spectral data

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to those authentic samples [6–8]. Each of complexes **2** and **5**–**11** gave satisfactory microanalytical, as well as ^{1}H-NMR and IR spectra and the data are in good agreement with the structures. For instance, the IR spectra of complexes **2**–**11** showed terminal carbonyl ligands. For complexes **5**–**8** the absorption bands of ester carbonyls were also observed. The ^{1}H-NMR spectra of the complexes showed that each of them exists only one conformer, although there are four possible conformational isomers according to the orientations of the S–R and S–R′ to the cluster core (Scheme 2). For example, the ^{1}H-NMR spectrum of complex **2** showed a sharp Bu^t group signal at δ 1.33 ppm and benzyl signals at δ_{CH_2} 3.52 and δ_{Ph} 7.20 ppm. However, the NMR spectral data do not allow us to say which is present. It seems that structure ii–iv are unfavored by repulsions between the axial R (or R′) group and terminal carbonyls.

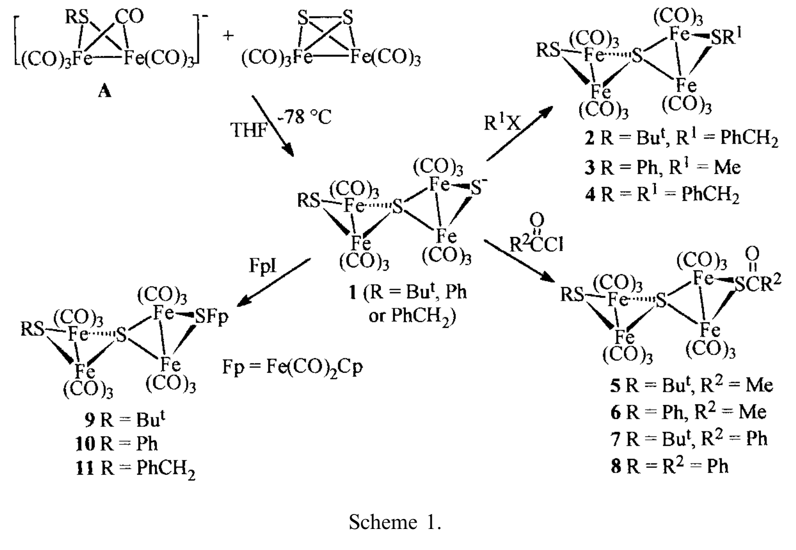
Complex **2** was characterised further by single crystal X-ray diffraction. It crystallises in the triclinic crystal system. The structure is presented in Fig. 1. Crystal data and refinement are given in Table 1; selected bond lengths and bond angles are listed in Table 2. The structure shows that the molecule consists of doubly-bridged $Fe_2(CO)_6$ units sharing a common central sulfur atom ligand. The two $Fe_2(CO)_6$ units also bridge by SBu^t ligand and SCH_2Ph ligand, respectively , and the orientations of both Bu^t and CH_2Ph are equatorial. The coordination about the central sulfur atom is distortedly tetrahedral. The molecular geometry is very similar to those of the previously reported complexes, namely symmetrical $[(\mu\text{-RS})Fe_2(CO)_6]_2(\mu_4\text{-S})$ (R = Me [9], Et [6]) and the unsymmetrical $(\mu\text{-RS})(\mu\text{-R}^1S)[Fe_2(CO)_6]_2(\mu_4\text{-S})$ (R = ferrocenylmethyl, R^1 = Me [10]; R = Ph, R^1 = Et [7] and R = Ph, R^1 = Bu^n [8]).

3. Experimental

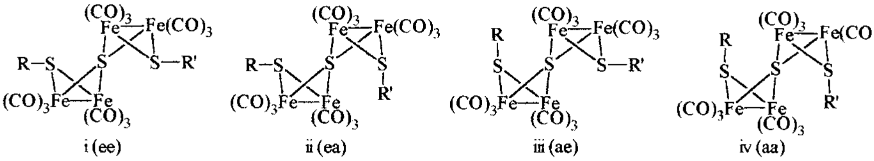
All reactions were carried out under nitrogen using standard Schlenk techniques. Tetra-hydrofuran (THF) was distilled from sodium benzophenone ketyl. $[Et_3NH]^+$ $[(\mu\text{-RS})(\mu\text{-CO})\text{–}Fe_2(CO)_6]^-$ [11] and $(\mu\text{-}S_2)Fe_2(CO)_6$ [12] were prepared by published procedures. The progress of all reactions was monitored by thin-layer chromatography. Infrared spectra (KBr disc) were obtained by using a VECTOR22 spectrometer. ^{1}H-NMR spectra were recorded on either a Varian EM360L or a Bruker DMX500 spectrometer with a $CDCl_3$ solvent. Elemental analyses were performed with a 240C analyzer.

3.1. Preparation of *(μ-RS)(μ-R^{1}S)[Fe$_2$(CO)$_6$]$_2$(μ$_4$-S)* (**2**, *R = Bu^t, R^1 = PhCH$_2$;* **3**, *R = Ph, R^1 = Me;* **4**, *R=R^1 = PhCH$_2$)*

A solution of triethylammonium salt of anion **A** was generated by addition $Fe_3(CO)_{12}$ (1.83 g, 3.63 mmol), Bu^{t}SH (0.41 ml, 3.63 mmol) and Et_3N (0.51 ml, 3.66 mmol) in THF (50 ml) at room temperature under nitrogen. The solution was cooled to −78°C. To the solution was added $(\mu\text{-}S_2)Fe_2(CO)_6$ (1.25 g, 3.63 mmol) and stirred for 30 min at −78°C. Subsequently benzyl chloride (0.46 g, 3.64 mmol) was syringed. The mixture was warmed to room temperature and stirred overnight. Solvent was removed at reduced pressure and the residue extracted with petroleum ether. Filtration chromatography (silica gel; 10% CH_2Cl_2-petroleum ether) gave red solid after evaporation of the solvent, which was recrystallized from petroleum ether to give red crystals of **2** (1.10 g, 38%). Anal. Found: C, 34.51; H, 2.22. $C_{23}H_{16}Fe_4O_{12}S_3$ requires: C, 34.36; H, 2.01. m.p. 152–153°C. ^{1}H-NMR: δ (ppm) 1.33(s, 9H,



Scheme 1.



Scheme 2.

Bu^t), 3.52(s, 2H, CH_2), 7.20(s, 5H, Ph). IR: ν (cm^{-1}) 2080s, 2033vs, 2016vs, 1993vs, 1981vs (Fe–CO).

Complex **3** was obtained similarly as red crystals in 84% yield, m.p. 136–138°C (lit.[5] 134.5–135.5°C). ^1H-NMR: δ (ppm) 2.19(s, 3H, Me), 7.20(s, 5H, Ph). IR: ν 2083s, 2050vs, 2035vs, 1989vs, 1971vs cm^{-1} (Fe–CO).

Complex **4** was prepared similarly as red crystals in 62% yield, m.p. 128–130°C (lit.[6] 128–130°C). ^1H-NMR: δ (ppm) 3.57(s, 2H, CH_2), 7.21(s, 5H, Ph). IR: ν (cm^{-1}) 2083s, 2035vs, 2011s, 1986vs (Fe–CO).

*3.2. Preparation of (μ-RS)[μ-$R^2C(O)S$][$Fe_2(CO)_6$]$_2$-(μ_4-S) (**5**, R = Bu^t, R^2 = Me; **6**, R = Ph, R^2 = Me; **7**, R = Bu^t, R^2 = Ph; **8**, R=R^2 = Ph)*

To a cooled solution of [Et_3NH][(μ-Bu^tS)(μ-CO)$Fe_2(CO)_6$] generated from $Fe_3(CO)_{12}$ (1.50 g, 2.98 mmol), Bu^tSH (0.34 ml, 2.98 mmol) and Et_3N (0.41 ml, 2.99 mmol) in THF (30 ml) was added (μ-S_2)$Fe_2(CO)_6$ (1.00 g, 2.91 mmol) and stirred for 30 min at −78°C. Subsequently $CH_3C(O)Cl$ (0.4 ml, 3.64 mmol) was syringed. The mixture was warmed to room temperature and stirred overnight. Work-up as described in Section 3.1 gave red solid of complex **5** in 49% yield. Anal. Found: C, 28.84; H, 1.69. $C_{18}H_{12}Fe_4O_{13}S_3$ requires: C, 28.60; H, 1.60. m.p. 129–130°C. ^1H-NMR: δ (ppm) 1.45(s, 9H, Bu^t), 2.54(s, 3H, Me). IR: ν (cm^{-1}) 2085s, 2055vs, 2035vs, 2014vs, 1989vs, 1981vs (Fe–CO), 1731s (CH_3CO).

Complexes **6**–**8** were synthesized similarly. Complex **6**, dark red crystals in 42% yield. Anal. Found: C, 31.03; H, 1.16. $C_{20}H_8Fe_4O_{13}S_3$ requires: C, 30.96; H, 1.04. m.p. 130–132°C. ^1H-NMR: δ (ppm) 2.55 (s, 3H, CH_3), 7.20 (s, 5H, Ph). IR: ν (cm^{-1}) 2087s, 2036vs, 1998s, 1978s, 1969s (Fe–CO), 1732s (CH_3CO). Complex **7**, dark red crystals in 68% yield. Anal. Found: C, 34.04; H, 1.80. $C_{22}H_{14}Fe_4O_{13}S_3$ requires: C, 33.77; H, 1.73. m.p. 130–131°C. ^1H-NMR: δ (ppm) 1.47 (s, 9H, Bu^t), 7.17–7.60, 7.95–8.15 (m, 5H, Ph). IR: ν (cm^{-1}) 2085s, 2036vs, 1996vs, 1976s, (Fe–CO), 1680m (CH_3CO). Complex **8**, red crystals in 40% yield. Anal. Found: C, 36.30; H, 1.37. $C_{23}H_{14}Fe_4O_{13}S_3$ requires: C, 35.84; H, 1.19. m.p. 170–172°C. ^1H-NMR: δ (ppm) 7.20–7.55, 7.90–8.20(m, 10H, Ph). IR: ν (cm^{-1}) 2087s, 2055vs, 2038vs, 2005vs, 1991vs (Fe–CO), 1683m (PhCO).

*3.3. Preparation of (μ-RS)[μ-Cp(CO)$_2$FeS)-[$Fe_2(CO)_6$]$_2$(μ_4-S) (**9**, R = Bu^t; **10**, R = Ph; **11**, R = $PhCH_2$)*

To a cooled solution of [Et_3NH][(μ-Bu^tS)(μ-CO)Fe_2 $(CO)_6$] [generated from $Fe_3(CO)_{12}$ (0.64 g, 1.27 mmol), Bu^tSH (0.14 ml, 1.24 mmol) and Et_3N (0.20 ml, 1.43 mmol) in THF (30 ml) at room temperature] was added (μ-S_2)$Fe_2(CO)_6$ (0.42 g, 1.22 mmol) and stirred for 30 min at −78°C. Subsequently $Cp(CO)_2FeI$ (0.37 g, 1.38 mmol) was added. The reaction was carried out and work-up as described in Section 3.1. Complex **9** (0.30 g, 28%) was obtained as black crystals. Anal. Found: C, 30.56; H, 1.60. $C_{23}H_{14}Fe_5O_{14}S_3$ requires: C, 31.05; H, 1.59. m.p. 154–155°C. ^1H-NMR: δ (ppm) 1.43(s, 9H, Bu^t), 5.10(s, 5H, Cp). IR: ν (cm^{-1}) 2076s, 2053s, 2023vs, 1985s, 1967vs (Fe–CO).

Complexes **10** and **11** were prepared similarly. Complex **10**, black crystals in 24% yield. Anal. Found: C, 33.13; H, 1.16. $C_{25}H_{10}Fe_5O_{14}S_3$ requires: C, 33.02; H, 1.11. m.p. 130–131°C. ^1H-NMR: δ (ppm)

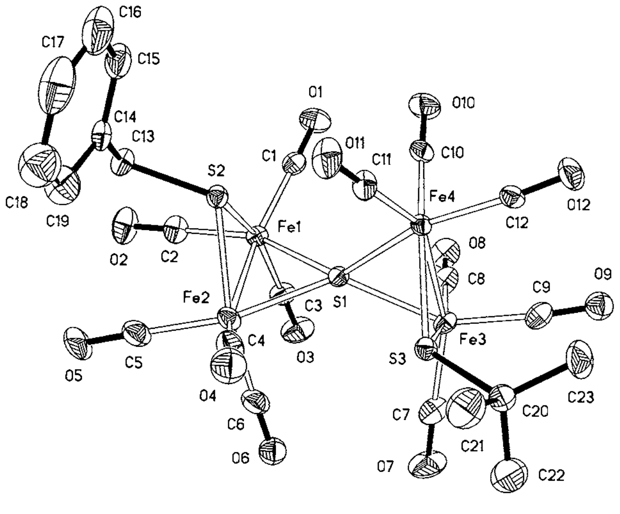


Fig. 1. ORTEP representation of the molecular structure of complex **2**.

Table 1
Crystal data and refinement for complex **2**

Formula	$C_{23}H_{16}Fe_4O_{12}S_3$
M	803.94
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	9.063(2)
b (Å)	11.422(3)
c (Å)	16.138(2)
α (°)	105.09(2)
β (°)	101.37(2)
γ (°)	94.87(2)
U (Å^3)	1564.9(6)
Z	2
$D_{\text{calc.}}$ (g cm^{-3})	1.706
Crystal size (mm)	$0.38 \times 0.32 \times 0.26$
Radiation λ (Å)	0.71073
F(000)	804
μ(Mo–K$_\alpha$) (mm^{-1})	2.073
Temperature (K)	293(2)
Total reflections	5657
Independent reflections	5657
Reflections with $I > 2\sigma(I)$	3675
Goodness-of-fit on F^2	0.962
Final R indices [$I > 2\sigma(I)$]	
R_1[a]	0.0457
wR_2[b]	0.1168
Largest differences peak and hole (e Å^{-3})	0.483 and −0.512

[a] $R_1 = \Sigma||F_0| - |F_c||$.

[b] $wR_2 = [\Sigma\, w(F_0^2 - F_c^2)^2 / \Sigma\, wF_0^4]^{1/2}$.

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

Distances (Å)			
Fe(1)–S(1)	2.2433(7)	Fe(3)–S(3)	2.2683(7)
Fe(1)–S(2)	2.2536(8)	Fe(3)–Fe(4)	2.5309(8)
Fe(1)–Fe(2)	2.5283(6)	Fe(4)–S(1)	2.2572(8)
Fe(2)–S(1)	2.2454(8)	Fe(4)–S(3)	2.2713(7)
Fe(2)–S(2)	2.2719(8)	S(2)–C(13)	1.853(2)
Fe(3)–S(1)	2.2411(8)	S(3)–C(20)	1.865(2)
Angles (°)			
S(1)–Fe(1)–S(2)	76.15(3)	Fe(3)–S(1)–Fe(1)	135.89(3)
S(1)–Fe(1)–Fe(2)	55.76(2)	Fe(3)–S(1)–Fe(2)	135.93(3)
S(2)–Fe(1)–Fe(2)	56.38(2)	Fe(1)–S(1)–Fe(2)	68.56(2)
S(1)–Fe(2)–S(2)	75.74(3)	Fe(3)–S(1)–Fe(4)	68.47(3)
S(1)–Fe(2)–Fe(1)	55.68(2)	Fe(1)–S(1)–Fe(4)	134.57(2)
S(2)–Fe(2)–Fe(1)	55.69(2)	Fe(2)–S(1)–Fe(4)	125.45(3)
S(1)–Fe(3)–S(3)	76.05(3)	C(13)–S(2)–Fe(1)	116.52(8)
S(1)–Fe(3)–Fe(4)	56.06(2)	C(13)–S(2)–Fe(2)	115.61(8)
S(3)–Fe(3)–Fe(4)	56.17(2)	Fe(1)–S(2)–Fe(2)	67.93(2)
S(1)–Fe(4)–S(3)	75.68(2)	C(20)–S(3)–Fe(3)	121.56(8)
S(1)–Fe(4)–Fe(3)	55.46(2)	C(20)–S(3)Fe(4)	124.48(7)
S(3)–Fe(4)–Fe(3)	56.06(2)	Fe(3)–S(3)Fe(4)	67.77(2)

5.30(s, 5H, Cp), 7.40(s, 5H, Ph). IR: ν (cm^{-1}) 2078s, 2053s, 2028vs, 1991s, 1974s (Fe–CO). Complex **11**, black crystals in 25% yield. Anal. Found: C, 34.02; H, 1.46. $C_{26}H_{12}Fe_5O_{14}S_3$ requires: C, 33.80; H, 1.31. m.p. 170 °C (dec.). ^{1}H-NMR: δ (ppm) 3.60(s, 2H, CH_2), 5.05(s, 5H, Cp), 7.20–7.26(b, 5H, Ph). IR: ν (cm^{-1}) 2075s, 2051s, 2038s, 2023vs, 2003vs, 1984s, 1972s, 1961s (Fe–CO).

3.4. Crystal data and structure determination of complex **2**

Suitable crystals of complex **2** were grown from petroleum ether = CH_2Cl_2 solution at room temperature. Data were collected on a Siemens P4 four-circle diffractometer using monochromated Mo–K$_\alpha$ radiation. A semi-empirical absorption correction was applied to the data. Structure was solved by direct method and was refined by full-matrix least-squares on F^2 with the positional and anisotropic thermal parameters on a PC using Siemens SHELXTL software package.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

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