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Chemical reactivity of $[(\mu\text{-RSe})(\mu\text{-S})\{Fe_2(CO)_6\}_2(\mu_4\text{-S})]^-$: synthesis and characterization of $(\mu\text{-RSe})(\mu\text{-R}'\text{S})\{Fe_2(CO)_6\}_2(\mu_4\text{-S})$ and $(\mu_3\text{-S})_2Fe_3(CO)_8[Se(Ph)Fe(CO)_2Cp]$

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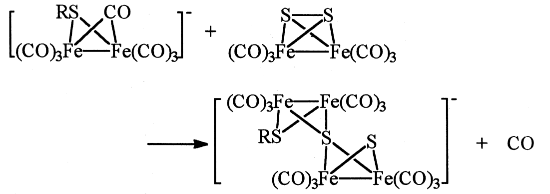
Abstract

The reaction of $(\mu\text{-S}_2)Fe_2(CO)_6$ with $[(\mu\text{-RSe})(\mu\text{-CO})Fe_2(CO)_6]^-$ gives the anionic complexes $[(\mu\text{-RSe})(\mu\text{-S})\{Fe_2(CO)_6\}_2(\mu_4\text{-S})]^-$ (**1**). Reactions of **1** with electrophiles such as alkyl halides, acid chlorides and PhN_2BF_4 form neutral complexes $(\mu\text{-RSe})(\mu\text{-R}'\text{S})[Fe_2(CO)_6]_2(\mu_4\text{-S})$ (R = Ph, R′ = Me **2a**; R = Ph, R′ = $PhCH_2$ **2b**; R = Et, R′ = Me **2c**; R = Ph, R′ = $CH_3C(O)$ **3a**; R = Ph, R′ = PhC(O) **3b**; R = Et, R′ = PhC(O) **3c**; R = R′ = Ph **4**). Treatment of **1** with $Cp(CO)_2FeI$ affords pentanuclear iron complexes $(\mu\text{-RSe})[\mu\text{-Cp(CO)}_2\text{FeS}][Fe_2(CO)_6]_2(\mu_4\text{-S})$ (R = Ph **5a**; R = Et **5b**). From the reaction mixture of **1** (R = Ph) and $Cp(CO)_2FeI$, $(\mu_3\text{-S})_2Fe_3(CO)_8[Se(Ph)Fe(CO)_2Cp]$ (**6**) was also obtained. The structure of complex **6** was determined by single-crystal X-ray analysis.

Keywords: Iron; Selenium; Sulfur; Synthesis; Reaction

1. Introduction

The chemical reactivities of $[(\mu\text{-RS})(\mu\text{-CO})Fe_2(CO)_6]^-$ and $[(\mu\text{-RSe})(\mu\text{-CO})Fe_2(CO)_6]^-$ have been studied extensively [1–17]. However, most studies concentrated mainly on reactions with organic reagents. Studies of the reactivities toward organometallic compounds, especially cluster complexes, are relatively rare. Available examples include the reactions with organomercury [3–5], organogold [15], organoiridium [16], organorhenium and organomanganese [17] compounds. Recently we reported the reaction of $[(\mu\text{-RS})(\mu\text{-CO})Fe_2(CO)_6]^-$ with $(\mu\text{-S}_2)Fe_2(CO)_6$, yielding anionic complexes $[(\mu\text{-RS})(\mu\text{-S})\{Fe_2(CO)_6\}_2(\mu_4\text{-S})]^-$ (see Eq. (1)) [18], which reacted readily with electrophiles to form neutral complexes of the type $(\mu\text{-RS})(\mu\text{-R}'\text{S})[Fe_2(CO)_6]_2(\mu_4\text{-S})$. To compare the reactivity of $[(\mu\text{-RSe})(\mu\text{-CO})Fe_2(CO)_6]^-$ with that of $[(\mu\text{-RS})(\mu\text{-CO})Fe_2(CO)_6]^-$, we have investigated the reaction of $[(\mu\text{-RSe})(\mu\text{-CO})Fe_2(CO)_6]^-$ with $(\mu\text{-S}_2)Fe_2(CO)_6$, and the reactivity of the resulting complexes $[(\mu\text{-RSe})(\mu\text{-S})\{Fe_2(CO)_6\}_2(\mu_4\text{-S})]^-$ toward electrophiles. Herein we report the results.



(1)

2. Experimental

All reactions were carried out under nitrogen using standard Schlenk techniques. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone ketyl. PhSeH [19], PhN_2BF_4 [20], $Fe_3(CO)_{12}$ [21], $Cp(CO)_2FeI$ [22] and $(\mu\text{-S}_2)Fe_2(CO)_6$ [23] were prepared by published procedures. The solution of $[(\mu\text{-RSe})(\mu\text{-CO})Fe_2(CO)_6]^-$ (R = Ph, Et) was prepared by the method described in the literature [8,14]. The progress of all reactions was monitored by thin-layer chromatography. Infrared spectra (KBr disk) were obtained using a VECTOR22 spectrometer. ^{1}H NMR spectra were recorded on either a Varian EM360L or a JEOL FX-90Q spectrometer. Elemental analyses were performed with a 240C analyzer.

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2.1. Preparation of (μ-PhSe)(μ-R^{1}S)[Fe$_2$(CO)$_6$]$_2$(μ_4-S) (**2a**, R^1 = Me; **2b**, R^1 = PhCH$_2$)

A solution of the triethylammonium salt of [(μ-PhSe)(μ-CO)Fe$_2$(CO)$_6$]$^-$ was generated by reacting 0.65 g (1.29 mmol) of Fe$_3$(CO)$_{12}$, 0.14 ml (1.32 mmol) of PhSeH and 0.19 ml (1.36 mmol) of Et$_3$N in 30 ml of THF at room temperature under nitrogen. The solution was cooled to -78°C, and 0.27 g (0.78 mmol) of (μ-S$_2$)Fe$_2$(CO)$_6$ was added with stirring for 30 min at -78°C. Subsequently 0.12 ml (1.93 mmol) of iodomethane was syringed. The mixture was warmed to room temperature 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) using petroleum ether as eluent. The first band gave 0.10 g (26% based on (μ-S$_2$)Fe$_2$(CO)$_6$) of (μ_3-S)$_2$Fe$_3$(CO)$_9$ as dark purple crystals. The second band gave 0.02 g (5% based on Fe$_3$(CO)$_{12}$) of dark red crystalline (μ-PhSe)$_2$Fe$_2$(CO)$_6$ and the third main band afforded 0.16 g (26% based on (μ-S$_2$)Fe$_2$(CO)$_6$) of red crystalline **2a**, m.p. 142–144°C. *Anal*. Found: C, 28.50; H, 0.89. Calc. for C$_{19}$H$_8$Fe$_4$O$_{12}$S$_2$Se: C, 28.72; H, 1.01%. ^{1}H NMR (CCl$_4$): δ (ppm) 2.20 (s, 3H, Me), 7.26 (s, 5H, Ph). IR: ν (cm^{-1}) 2083m, 2056s, 2031vs, 1993s, 1973s (Fe–CO).

A similar reaction was carried out, in which 1.30 mmol of benzyl chloride was added to a solution of anion **1** prepared from 1.43 mmol of Fe$_3$(CO)$_{12}$, 1.51 mmol of PhSeH and 1.50 mmol of Et$_3$N followed by addition of 1.28 mmol of (μ-S$_2$)Fe$_2$(CO)$_6$ giving, after similar work-up, 0.08 g (13% based on (μ-S$_2$)Fe$_2$(CO)$_6$) of (μ_3-S)$_2$Fe$_3$(CO)$_9$, 0.19 g (25% based on Fe$_3$(CO)$_{12}$) of (μ-PhSe)$_2$Fe$_2$(CO)$_6$ and 0.14 g (13% based on (μ-S$_2$)Fe$_2$(CO)$_6$) of dark red crystals of **2b**, m.p. 110°C (dec.). *Anal*. Found: C, 34.33; H, 1.13. Calc. for C$_{25}$H$_{12}$Fe$_4$O$_{12}$S$_2$Se: C, 34.48; H, 1.39%. ^{1}H NMR (CCl$_4$): δ (ppm) 3.60 (s, 2H, CH$_2$), 7.03–7.23 (m, 10H, Ph). IR: ν (cm^{-1}) 2082m, 2054vs, 2036vs, 2010s, 1999vs, 1990vs (Fe–CO).

2.2. Preparation of (μ-EtSe)(μ-MeS)[Fe$_2$(CO)$_6$]$_2$(μ_4-S) (**2c**)

A Schlenk tube was charged with 0.16 g (2.03 mmol) of selenium powder, 30 ml of THF and 2.00 mmol of EtMgBr in Et$_2$O. The mixture was stirred at room temperature for 20 min. To the solution was added 0.90 g (1.78 mmol) of Fe$_3$(CO)$_{12}$ and stirring was continued for 20 min, resulting in a brown–red solution of [MgBr][(μ-EtSe)(μ-CO)Fe$_2$(CO)$_6$]. The solution was cooled to -78°C, and 0.55 g (1.60 mmol) of (μ-S$_2$)Fe$_2$(CO)$_6$ was added with stirring for 30 min at -78°C. Subsequently 0.20 ml (3.21 mmol) of iodomethane was syringed. The mixture was warmed to room temperature and stirred for 3 h. Work-up as described in Section 2.1 gave 0.11 g (14% based on (μ-S$_2$)Fe$_2$(CO)$_6$) of (μ_3-S)$_2$Fe$_3$(CO)$_9$ and 0.13 g (11% based on (μ-S$_2$)Fe$_2$(CO)$_6$) of red crystalline complex **2c**, m.p. 143–146°C. *Anal*. Found: C, 24.41; H, 1.32. Calc. for C$_{15}$H$_8$Fe$_4$O$_{12}$S$_2$Se: C, 24.13; H, 1.08%. ^{1}H NMR (CCl$_4$): δ (ppm) 1.50 (t, $J = 7$ Hz, 3H, Me), 2.16 (s, 3H, Me), 2.67 (q, $J = 7.5$ Hz, 2H, CH$_2$). IR: ν (cm^{-1}) 2083m, 2057s, 2035vs, 2006s, 1992s, 1969s (Fe–CO).

2.3. Preparation of (μ-PhSe)[μ-R^{2}C(O)S]-[Fe$_2$(CO)$_6$]$_2$(μ_4-S) (**3a**, R^2 = Me; **3b**, R^2 = Ph)

To a cooled solution of [Et$_3$NH][(μ-PhSe)(μ-CO)-Fe$_2$(CO)$_6$] generated from 0.82 g (1.61 mmol) of Fe$_3$(CO)$_{12}$, 0.18 ml (1.70 mmol) of PhSeH and 0.24 ml (1.71 mmol) of Et$_3$N in about 30 ml of THF was added 0.44 g (1.28 mmol) of (μ-S$_2$)Fe$_2$(CO)$_6$ with stirring for 30 min at -78°C. Subsequently 0.20 ml (1.82 mmol) of acetyl chloride was syringed. The mixture was warmed to room temperature and stirred overnight. Work-up as described in Section 2.1 gave 0.08 g (13% based on (μ-S$_2$)Fe$_2$(CO)$_6$) of (μ_3-S)$_2$Fe$_3$(CO)$_9$, 0.22 g (46% based on Fe$_3$(CO)$_{12}$) of (μ-PhSe)$_2$Fe$_2$(CO)$_6$ and 0.08 g (8% based on (μ-S$_2$)-Fe$_2$(CO)$_6$) of **3a** as red crystals, m.p. 130°C (dec.). *Anal*. Found: C, 29.38; H, 1.12. Calc. for C$_{20}$H$_8$Fe$_4$O$_{13}$S$_2$Se: C, 29.20; H, 0.98%. ^{1}H NMR (CCl$_4$): δ (ppm) 2.54 (s, 3H, Me), 7.20 (s, 5H, Ph). IR: ν (cm^{-1}) 2085m, 2054s, 2036vs, 1999s, 1988s, 1976s (Fe–CO); 1732w (MeCO).

A similar reaction, in which 0.16 ml (1.38 mmol) of benzoyl chloride was added to a cooled solution of anion **1** (prepared from 1.57 mmol of Fe$_3$(CO)$_{12}$, 1.61 mmol of PhSeH and 1.64 mmol of Et$_3$N and then 1.37 mmol of (μ-S$_2$)Fe$_2$(CO)$_6$), gave 0.11 g (16% based on (μ-S$_2$)Fe$_2$(CO)$_6$) of (μ_3-S)$_2$Fe$_3$(CO)$_9$, 0.08 g (17% based on Fe$_3$(CO)$_{12}$) of (μ-PhSe)$_2$Fe$_2$(CO)$_6$ and 0.26 g (21% based on (μ-S$_2$)Fe$_2$(CO)$_6$) of red crystals of **3b**, m.p. 140°C (dec.). *Anal*. Found: C, 34.06; H, 1.29. Calc. for C$_{25}$H$_{10}$Fe$_4$O$_{13}$S$_2$Se: C, 33.94; H, 1.14%. ^{1}H NMR (CDCl$_3$): δ (ppm) 7.18 (s, 5H, Ph), 7.34–7.46 (m, 3H, Ph), 7.97–8.09 (m, 2H, Ph). IR: ν (cm^{-1}) 2085m, 2052s, 2039vs, 2000s (Fe–CO); 1681m (PhCO).

2.4. Preparation of (μ-EtSe)[μ-Ph C(O)S]-[Fe$_2$(CO)$_6$]$_2$(μ_4-S) (**3c**)

The solution of [MgBr][(μ-EtSe)(μ-S){Fe$_2$(CO)$_6$}$_2$-(μ_4-S)] was prepared according to the same procedure and scale as described in Section 2.2. To the cooled solution was added 0.19 ml (1.64 mmol) of benzoyl chloride. The mixture was warmed to room temperature and stirred overnight. Work-up as described in Section 2.1 gave 0.07 g (9% based on (μ-S$_2$)Fe$_2$(CO)$_6$) of (μ_3-S)$_2$Fe$_3$(CO)$_9$ and 0.14 g (10% based on (μ-S$_2$)Fe$_2$(CO)$_6$) of red crystalline **3c**, m.p. 140°C (dec.). *Anal*. Found: C, 30.41; H, 1.38. Calc. for C$_{21}$H$_{10}$Fe$_4$O$_{13}$S$_2$Se: C, 30.14; H, 1.20%. ^{1}H NMR (CDCl$_3$): δ (ppm) 1.53 (t, $J = 7$ Hz, 3H, Me), 2.70 (q, $J = 7$ Hz, 2H, CH$_2$), 7.30–7.70 (m, 3H, Ph), 7.90–8.25 (m, 2H, Ph). IR: ν (cm^{-1}) 2085m, 2057s, 2036vs, 2000s, 1989vs (Fe–CO); 1681w (PhCO).

*2.5. Preparation of (μ-PhSe)(μ-PhS)[$Fe_2(CO)_6$]$_2$($μ_4$-S) (**4**)*

To a cooled solution of [Et_3NH][(μ-PhSe)(μ-CO)-$Fe_2(CO)_6$] generated from 0.78 g (1.53 mmol) of $Fe_3(CO)_{12}$, 0.17 ml (1.61 mmol) of PhSeH and 0.23 ml (1.64 mmol) of Et_3N in about 30 ml of THF was added 0.42 g (1.22 mmol) of (μ-S_2)$Fe_2(CO)_6$ and the mixture was stirred for 30 min at −78°C. Subsequently 0.24 g (1.25 mmol) of PhN_2BF_4 was added. The mixture was warmed to room temperature and stirred overnight. Work-up as described in Section 2.1 gave 0.08 g (14% based on (μ-S_2)$Fe_2(CO)_6$) of ($μ_3$-S)$_2Fe_3(CO)_9$, 0.23 g (50% based on $Fe_3(CO)_{12}$) of (μ-PhSe)$_2Fe_2(CO)_6$ and 0.07 g (7% based on (μ-S_2)$Fe_2(CO)_6$) of red crystals of **4**, m.p. 175°C (dec.). *Anal.* Found: C, 33.35; H, 1.35. Calc. for $C_{24}H_{10}Fe_4O_{12}S_2Se$: C, 33.64; H, 1.18%. ^{1}H NMR (CCl_4): δ (ppm) 7.22–7.62 (m, 10H, Ph). IR: ν (cm^{-1}) 2081m, 2057s, 2037vs, 1996s, 1976m (Fe–CO).

*2.6. Preparation of (μ-PhS)[μ-Cp(CO)$_2$FeS]-[$Fe_2(CO)_6$]$_2$($μ_4$-S) (**5a**) and ($μ_3$-S)$_2Fe_3(CO)_8$-[PhSeFe(CO)$_2$Cp] (**6**)*

To a cooled solution of [Et_3NH][(μ-PhSe)(μ-CO)-$Fe_2(CO)_6$] generated from 0.86 g (1.69 mmol) of $Fe_3(CO)_{12}$, 0.19 ml (1.80 mmol) of PhSeH and 0.25 ml (1.79 mmol) of Et_3N in 30 ml of THF was added 0.46 g (1.34 mmol) of (μ-S_2)$Fe_2(CO)_6$ and the mixture was stirred for 30 min at −78°C. Subsequently 0.41 g (1.35 mmol) of Cp(CO)$_2$FeI was added. The reaction mixture was warmed to room temperature and stirred overnight. Solvent was removed at reduced pressure and the residue extracted with CH_2Cl_2:petroleum ether (1:9 v/v). After removal of the solvent, the material remaining was subjected to filtration chromatography (silica gel). Petroleum ether eluted a purple band which gave 0.05 g (8% based on (μ-S_2)$Fe_2(CO)_6$) of ($μ_3$-S)$_2Fe_3(CO)_9$. The second band gave 0.05 g (10% based on $Fe_3(CO)_{12}$) of (μ-PhSe)$_2Fe_2(CO)_6$. Further elution with 2:8 v/v CH_2Cl_2:petroleum ether gave 0.19 g (15% based on (μ-S_2)$Fe_2(CO)_6$) of complex **5a** as black crystals and 0.10 g (9% based on (μ-S_2)$Fe_2(CO)_6$) of black crystalline complex **6**. **5a**: m.p. 150°C (dec.). *Anal.* Found: C, 31.38; H, 1.32. Calc. for $C_{25}H_{10}Fe_5O_{14}S_2Se$: C, 31.39; H, 1.05%. ^{1}H NMR ($CDCl_3$): δ (ppm) 5.08 (s, 5H, Cp), 7.20 (s, 5H, Ph). IR: ν (cm^{-1}) 2076m, 2051s, 2027vs, 1973s (Fe–CO). **6**: m.p. 87–88°C. *Anal.* Found: C, 31.63; H, 1.24. Calc. for $C_{21}H_{10}Fe_4O_{10}S_2Se$: C, 31.98; H, 1.28%. ^{1}H NMR ($CDCl_3$): δ (ppm) 4.90 (s, 5H, Cp), 7.20 (s, 5H, Ph). IR: ν (cm^{-1}) 2066s, 2039s, 2017vs, 1997vs, 1954m, 1947m (Fe–CO).

*2.7. Preparation of (μ-EtS)[μ-Cp(CO)$_2$FeS]-[$Fe_2(CO)_6$]$_2$($μ_4$-S) (**5b**)*

The solution of [MgBr][(μ-EtSe)(μ-S){$Fe_2(CO)_6$}$_2$-($μ_4$-S)] was prepared according to the same procedure and scale as described in Section 2.2. To the solution was added 0.50 g (1.64 mmol) of Cp(CO)$_2$FeI at −78°C with stirring. The mixture was warmed to room temperature and stirred overnight. Solvent was removed at reduced pressure and the residue extracted with CH_2Cl_2:petroleum ether (1:9 v/v). After removal of the solvent, the material remaining was subjected to filtration chromatography (silica gel). Petroleum ether eluted a purple band which gave 0.09 g (12% based on (μ-S_2)$Fe_2(CO)_6$) of ($μ_3$-S)$_2Fe_3(CO)_9$. Further elution with 2:8 v/v CH_2Cl_2:petroleum ether gave 0.13 g (9% based on (μ-S_2)$Fe_2(CO)_6$) of complex **5b** as black crystals, m.p. 142°C (dec.). *Anal.* Found: C, 28.27; H, 1.37. Calc. for $C_{21}H_{10}Fe_5O_{14}S_2Se$: C, 27.76; H, 1.11%. ^{1}H NMR ($CDCl_3$): δ (ppm) 1.50 (t, $J=7.5$ Hz, 3H, Me), 2.53 (q, $J=7.5$ Hz, 2H, CH_2), 5.10 (s, 5H, Ph). IR: ν (cm^{-1}) 2074m, 2050s, 2026vs, 1996s, 1982s, 1967vs (Fe–CO).

*2.8. Crystal data and structure determination of complex **6***

Black crystals of complex **6** were grown from a petroleum ether–CH_2Cl_2 solution at 0°C. Data were collected on a Siemens P4 four-circle diffractometer using graphite-monochromated Mo Kα radiation. Absorption correction was applied using SADABS. The structure was solved by the direct method and refined by full-matrix least-squares on F^2 with anisotropic thermal parameters for non-hydrogen atoms on a PC using SHELXS-86 and SHELXL-97 software packages, respectively [24,25]. A summary of crystal data and refinement parameters is given in Table 1. Selected bond distances and angles are listed in Table 2.

Table 1
Crystal data and refinement parameters for complex **6**

Formula	$C_{21}H_{10}Fe_4O_{10}S_2Se$
M	788.77
Crystal system	triclinic
Space group	$P\bar{1}$ (no. 2)
a (Å)	10.5626(10)
b (Å)	10.6168(10)
c (Å)	13.4368(12)
α (°)	75.686(2)
β (°)	70.409(2)
γ (°)	75.352(2)
U (Å^3)	1351.5(2)
Z	2
Crystal size (mm)	0.18×0.16×0.16
Radiation λ (Å)	0.71073
Temperature (K)	294(2)
Scan type	ω–2θ
$2\theta_{max}$ (°)	55.06
Total reflections	6109
Independent reflections	6106 ($R_{int}=0.0000$)
Reflections with $I>2\sigma(I)$	4884
Goodness-of-fit on F^2	0.679
Final R indices ($I>2\sigma(I)$)	
R_1 [a]	0.0282
wR_2 [b]	0.0814
Largest differences peak and hole (e Å^{-3})	0.441, −0.375

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

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

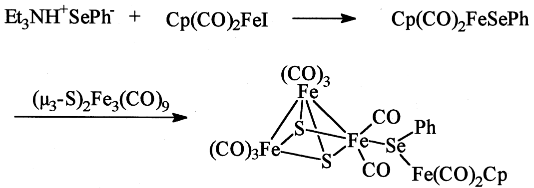
Table 2
Selected bond distances (Å) and angles (°) for complex **6**

Se(1)–C(16)	1.9415(19)	Fe(2)–S(2)	2.2545(6)
Se(1)–Fe(4)	2.4134(4)	Fe(2)–S(1)	2.2569(6)
Se(1)–Fe(1)	2.4433(3)	Fe(2)–Fe(3)	2.5728(5)
Fe(1)–S(1)	2.2080(6)	Fe(3)–S(1)	2.2416(6)
Fe(1)–S(2)	2.2351(5)	Fe(3)–S(2)	2.2516(5)
Fe(1)–Fe(2)	2.6291(4)	Fe(4)–Cent [a]	1.714
C(16)–Se(1)–Fe(4)	99.76(6)	S(2)–Fe(2)–S(1)	78.91(2)
C(16)–Se(1)–Fe(1)	112.89(6)	S(2)–Fe(2)–Fe(3)	55.130(15)
Fe(4)–Se(1)–Fe(1)	114.556(13)	Fe(3)–Fe(2)–Fe(1)	81.516(14)
S(1)–Fe(1)–S(2)	80.36(2)	S(1)–Fe(3)–S(2)	79.29(2)
S(1)–Fe(1)–Se(1)	158.195(18)	S(1)–Fe(3)–Fe(2)	55.396(17)
S(2)–Fe(1)–Se(1)	85.752(15)	S(2)–Fe(3)–Fe(2)	55.236(16)
S(1)–Fe(1)–Fe(2)	54.792(16)	Fe(1)–S(1)–Fe(3)	99.51(2)
S(2)–Fe(1)–Fe(2)	54.499(15)	Fe(1)–S(1)–Fe(2)	72.138(17)
S(1)–Fe(2)–Fe(3)	54.836(18)	Fe(3)–S(1)–Fe(2)	69.768(17)
S(2)–Fe(2)–Fe(1)	53.812(14)	Fe(1)–S(2)–Fe(3)	98.40(2)
S(1)–Fe(2)–Fe(1)	53.070(15)	Fe(1)–S(2)–Fe(2)	71.689(18)
Se(1)–Fe(1)–Fe(2)	103.412(13)	Fe(3)–S(2)–Fe(2)	69.634(18)

[a] Cent is the centroid of the Cp ring composed of carbon atoms C(11)–C(15).

3. Results and discussion

The synthesis and reactions of [(μ-RSe)(μ-S)-$\{Fe_2(CO)_6\}_2$(μ_4-S)]$^-$ are summarized in Scheme 1. Both [Et_3NH][(μ-PhSe)(μ-CO)$Fe_2(CO)_6$] and [MgBr][(μ-EtSe)(μ-CO)$Fe_2(CO)_6$] were prepared by reported methods [12,14] and reacted readily with (μ-S_2)$Fe_2(CO)_6$ at −78°C, as indicated by gas evolution. Treatment of the reaction mixture with electrophiles such as alkyl halides, acid chlorides and PhN_2BF_4 gave neutral complexes of the type (μ-RSe)(μ-R′S)[$Fe_2(CO)_6$]$_2$(μ_4-S) (R′ = alkyl, acyl or phenyl). Thus the expected anions **1** were formed. Similarly to the reaction between [(μ-RS)(μ-CO)$Fe_2(CO)_6$]$^-$ and (μ-S_2)$Fe_2(CO)_6$, the sulfur–sulfur bond of (μ-S_2)-$Fe_2(CO)_6$ is cleaved by the iron-centered anions and the μ-CO ligand of [(μ-RSe)(μ-CO)$Fe_2(CO)_6$]$^-$ is replaced by one of the sulfur atoms of (μ-S_2)$Fe_2(CO)_6$. It is noteworthy that the yields of (μ-RSe)(μ-R′S)[$Fe_2(CO)_6$]$_2$-(μ_4-S) were low and, for R = Ph, the oxidation product (μ-PhSe)$_2Fe_2(CO)_6$ was formed in low to moderate yield. In addition, (μ_3-S)$_2Fe_3(CO)_9$ was also obtained in each reaction. Treatment of the reaction mixture of [(μ-RSe)(μ-CO)$Fe_2(CO)_6$]$^-$ and (μ-S_2)$Fe_2(CO)_6$ with Cp(CO)$_2$FeI afforded pentanuclear complexes **5a** and **5b**. For R = Ph, an unexpected product, (μ_3-S)$_2Fe_3(CO)_8$[Se(Ph)Fe-(CO)$_2$Cp] (**6**), was also isolated. The formation of complex **6** may arise from the reaction of (μ_3-S)$_2Fe_3(CO)_9$ with PhSeFe(CO)$_2$Cp produced from Cp(CO)$_2$FeI and excess $Et_3NH^+SePh^-$ (Scheme 2).



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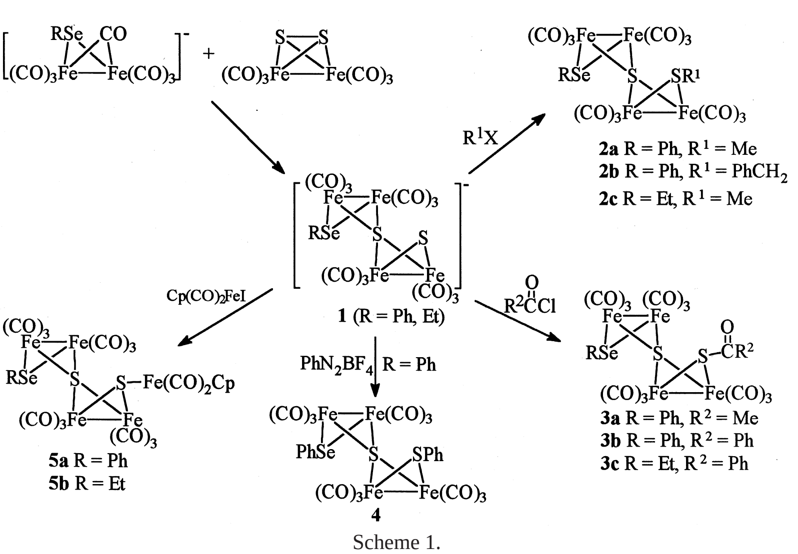
Scheme 2.

Both complexes (μ_3-S)$_2Fe_3(CO)_9$ and (μ-PhSe)$_2Fe_2$-(CO)$_6$ are known and were identified by elemental analyses and by comparison of their melting points, IR and ^{1}H NMR (for the latter) spectra with those of authentic samples [26,27].

Complexes **2**–**4** are red solids and **5a** and **5b** are black solids. They are air stable in the solid state, but slightly air sensitive in solution. The new complexes **2**–**5** were characterized by elemental analyses, IR and ^{1}H NMR spectra. Their IR spectra showed four to six terminal carbonyl absorption bands in the range 2085–1969 cm^{-1}. For complexes **3a**–**3c** the absorption bands of thiocarboxylato groups were also observed. Their ^{1}H NMR spectra all exhibited respective organic group resonance signals. It is worthy of note that complexes **2**–**5** can exist as only one isomer in which the two substituents are bonded to the bridged Se and S atoms with an equatorial type of bond. This is because the μ_4-S atom of **2**–**5** utilizes two axial bonds to attach both (μ-RSe)-



Scheme 1.

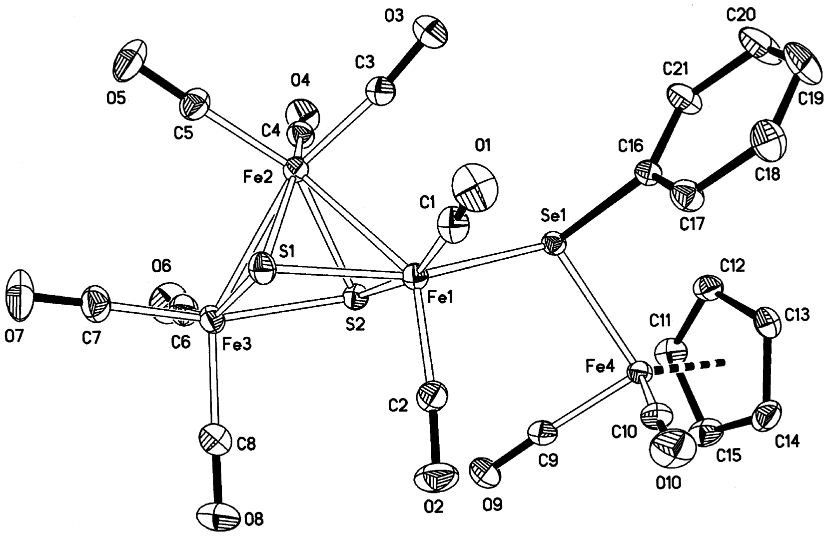


Fig. 1. ORTEP representation of the molecular structure of complex **6**. The thermal ellipsoids are drawn at the 20% probability level.

$Fe_2(CO)_6$ and (μ-R′S)$Fe_2(CO)_6$ units, respectively, and because there are larger non-bonded repulsions between the axial R (or R′) group and axial $Fe(CO)_3$ group [28]. This deduction can be verified by some of the ^1H NMR spectra. For example, the ^1H NMR spectrum of **2c** showed one quartet at δ 2.67 ppm for $SeCH_2$ [29] and one singlet at δ 2.16 ppm for SCH_3 [28]; the $CH_3C(O)$ group of **3a** showed one singlet at δ 2.54 ppm [30] and the CH_2Se group of **3c** showed one quartet at δ 2.70 ppm [29].

Complex **6** was isolated as a black solid. Its IR spectrum exhibited terminal carbonyl absorption bands and the ^1H NMR spectrum showed the presence of phenyl and cyclopentadienyl groups. The C/H analytical data agree closely with the calculated values for complex **5**. From these analytical results it seems as if complex **6** was an isomer of complex **5**. However, the chemical shift of the ^1H NMR spectrum for the Cp group (δ 4.90 ppm) was close to that of an axial $Fe(CO)_2Cp$ [31]. This would involve considerable non-bonded repulsion between two axial groups. For this reason, a single-crystal X-ray diffraction study was undertaken. The result showed that complex **6** is a mono-substituted product of (μ_3-S)$_2Fe_3(CO)_9$ by Se(Ph)$Fe(CO)_2Cp$ (Fig. 1). The skeletal structure is very similar to that of (μ_3-S)$_2Fe_3(CO)_9$ [32], i.e. it consists of an open triangle of iron atoms (Fe(1)Fe(2)Fe(3)) capped on each side by the two sulfur ligands, and S_2Fe_3 is a distorted square pyramid.

Se(Ph)$Fe(CO)_2Cp$ replaces the carbonyl at the basal position and the orientation of Se(Ph)$Fe(CO)_2Cp$ is axial. This is consistent with (μ_3-S)$_2Fe_3(CO)_8$[P(OMe)$_3$] [33] and (μ_3-S)$_2Fe_3(CO)_8$[P(SPh)$_3$] [34]. The bond lengths Fe–Fe and Fe–S are comparable with the corresponding values in (μ_3-S)$_2Fe_3(CO)_8$[P(OMe)$_3$] [33] and (μ_3-S)$_2Fe_3(CO)_8$[P(SPh)$_3$] [34]. The Se–Fe bond length (2.4433(3) and 2.4134(4) Å, respectively) is close to those found in $Fe_4(CO)_{10}$(μ-CO)(μ_4-Se) (average 2.428 Å) [35], but a little longer than those in (μ-PhSe)(μ-$PhCH_2SC{=}S$)-$Fe_2(CO)_6$ (average 2.374 Å) [8] and (μ-Se_2)$Fe_2(CO)_6$ (average 2.364 Å) [36].

Supplementary data

Supplementary data are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk) on request, quoting the deposition number CCDC 134795.

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References

[1] D. Seyferth, G.B. Womack, J.C. Dewan, Organometallics 4 (1985) 508.
[2] D. Seyferth, J.B. Hoke, J.C. Dewan, Organometallics 6 (1987) 895.
[3] D. Seyferth, L.L. Anderson, W.M. Davis, J. Organomet. Chem. 459 (1993) 271.
[4] D. Seyferth, D.P. Ruschke, W.M. Davis, M. Cowie, A.D. Hunter, Organometallics 13 (1994) 3834.
[5] D. Seyferth, L.L. Anderson, F. Villafane, M. Cowie, R.W. Hilts, Organometallics 11 (1992) 3262.
[6] L.-C. Song, Q.-M. Hu, J. Organomet. Chem. 414 (1991) 219.
[7] L.-C. Song, Chem. J. Chin. Univ. 17 (1996) 575.
[8] L.-C. Song, C.-G. Yan, Q.-M. Hu, R.-J. Wang, T.C.W. Mak, Organometallics 14 (1995) 5513.
[9] L.-C. Song, C.-G. Yan, Q.-M. Hu, X.-Y. Huang, J. Organomet. Chem. 505 (1995) 119.
[10] D. Seyferth, J.B. Hoke, D.R. Wheele, J. Organomet. Chem. 341 (1988) 421.
[11] L.-C. Song, C.-G. Yan, Q.-M. Hu, R.-J. Wang, T.C.W. Mak, X.-Y. Huang, Organometallics 15 (1996) 1535.

[12] D. Seyferth, G.B. Womack, C.M. Archer, J.C. Dewan, Organometallics 8 (1989) 430.

[13] L.-C. Song, C.-G. Yan, Q.-M. Hu, B.-M. Wu, T.C.W. Mak, Organometallics 16 (1997) 632.

[14] L.-C. Song, G.-L. Lu, Q.-M. Hu, X.-D. Qin, C.-X. Sun, J. Yang, J. Sun, J. Organomet. Chem. 571 (1998) 55.

[15] E. Delgado, E. Hernández, O. Rossell, M. Seco, E.G. Puebla, C. Ruiz, J. Organomet. Chem. 455 (1993) 177.

[16] J. Chen, C.L. Day, R.A. Jacobson, R.J. Angelici, J. Organomet. Chem. 522 (1996) 21.

[17] Z. Qin, J. Sun, J. Chen, Organometallics 17 (1998) 600.

[18] Z.-X. Wang, C.-S. Jia, Z.-Y. Zhou, X.-G. Zhou, J. Organomet. Chem. 580 (1999) 201.

[19] D.G. Foster, Organic Synthesis, Coll. vol. 3, Wiley, New York, 1955, p. 771.

[20] D.T. Flood, Organic Synthesis, Coll. vol. 2, Wiley, New York, 1955, p. 295.

[21] R.B. King, Organometallic Synthesis, vol. 1, Academic Press, New York, 1965, p. 95.

[22] R.B. King, Organometallic Synthesis, vol. 1, Academic Press, New York, 1965, p. 175.

[23] L.E. Bogan Jr., D.A. Lesch, T.B. Ranchfuss, J. Organomet. Chem. 250 (1983) 429.

[24] G.M. Sheldrick, SHELXS-86, Program for X-ray Crystal Structure Determination, University of Göttingen, Germany, 1986.

[25] G.M. Sheldrick, SHELXL-97, Program for X-ray Crystal Structure Refinement, University of Göttingen, Germany, 1986.

[26] R. Havlin, G.R. Knox, J. Organomet. Chem. 4 (1965) 247.

[27] E.D. Schermer, W.H. Baddley, J. Organomet. Chem. 30 (1971) 67.

[28] D. Seyferth, R.S. Henderson, L.-C. Song, Organometallics 1 (1982) 125.

[29] L.-C. Song, R.-J. Wang, Y. Li, H.-G. Wang, J.-T. Wang, Acta Chim. Sinica 48 (1990) 867.

[30] L.-C. Song, Z.-Y. Zhao, J.-T. Wang, Youji Huaxue 2 (1987) 119.

[31] L.-C. Song, R.-G. Liu, J.-T. Wang, Acta Chim. Sinica 45 (1987) 1138.

[32] C.H. Wei, L.F. Dahl, Inorg. Chem. 4 (1965) 493.

[33] T.M. Bockman, J.K. Kochi, J. Am. Chem. Soc. 109 (1987) 7725.

[34] Q.-W. Liu, B.-F. Wu, X. Hu, S.-T. Liu, X.-Y. Yan, J.-Q. Shi, Acta Chim. Sinica 50 (1992) 778.

[35] P. Mathur, Md.M. Hossain, R.S. Rashid, J. Organomet. Chem. 467 (1994) 254.

[36] C.F. Campana, F.Y.-K. Lo, L.F. Dahl, Inorg. Chem. 18 (1979) 3060.