Journal of Organometallic Chemistry, 331 (1987) 247–262
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Carbonyl insertion into a C–S bond and complex dimerization during reaction of the dithioesters S=C(Me)SEt and S=C(Ph)SMe with iron carbonyl complexes

Gert J. Kruger, Antonie van A. Lombard and Helgard G. Raubenheimer *

Department of Chemistry, Rand Afrikaans University, P.O. Box 524, Johannesburg 2000 (South Africa)

(Received February 23th, 1987)

Abstract

Dithioesters react with pentacarbonyliron or nonacarbonyldiiron under UV irradiation to give three classes of compounds. In the metal–metal-bonded complexes $[Fe_2(CO)_6\{SC(R^1)SR^2\}]$ (R^1 = Me or Ph; R^2 = Et or Me) which belong to the first class, the iron atoms are doubly-bridged by a C–S unit and the original bicovalent sulphur atom of the intact dithioester unit. Similar metal links also exist in the complex $[Fe_2(CO)_6\{\mu\text{-}\eta^2\text{-}S\overline{CS(CH_2)_2S}\text{-}S,S'\}](Fe\text{-}Fe)$ (I), formed from a trithiocarbonate ($R^1R^2 = SCH_2CH_2$) and $[Fe(CO)_5]$, as confirmed by single-crystal X-ray diffraction. The nature of the bonding in the second class of compounds was established by determining the crystal structure of the dimeric compound $[Fe(CO)_3\{SC(Ph)SMe\}]_2$ (V) in which there is no metal–metal bond but each coordinated ligand forms a non-symmetrical dative sulphur–metal bond to the other iron atom. An X-ray crystal structure of a member of the third type of compound $[Fe_2(CO)_6\{SC(R^1)C(O)SR^2\}]$ (R^1 = Ph; R^2 = Me) (VI), shows that it is the result of carbonyl insertion into the C–SR^2 bond of the ligand.

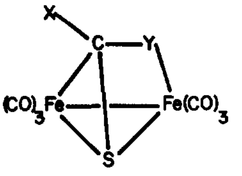
Introduction

Ultraviolet irradiation of heteroatom-containing thioketone derivatives S=C(X)Y with $[Fe_2(CO)_9]$ or $[Fe(CO)_5]$ has produced mainly two classes of dinuclear iron compounds, **A** and **B**, in which the C–S bond remains intact [1–3].

The formation of the dinuclear compound **C**, and trinuclear complex **D**, from $[Fe(CO)_5]$ and chromium coordinated $S{=}\overline{CS(CH_2)_2S}$, requires cleavage of the C–S bond [4].

The latter reaction also yields a product, I, for which a structure of type **A** (XY = $S(CH_2)_2S$) has been proposed. Differences in the fluxional behaviour of I and A_2 [4] cast some doubt on the proposed structure, but X-ray crystallography has now confirmed this structure and shown the influence of the ring system containing X and Y on the overall structure.

0022-328X/87/$03.50 © 1987 Elsevier Sequoia S.A.



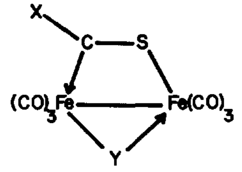
A

A_1 X = OR , Y = SMe

A_2 X = R , Y = SMe

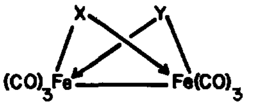
A_3 X = R , Y = OMe

A_4 X = NMe_2, Y = NMe_2



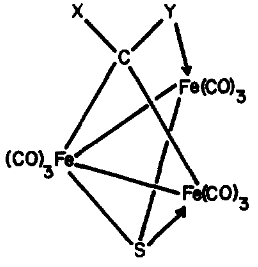
B

X = SR , Y = SMe



C

XY = $S(CH_2)_2S$



D

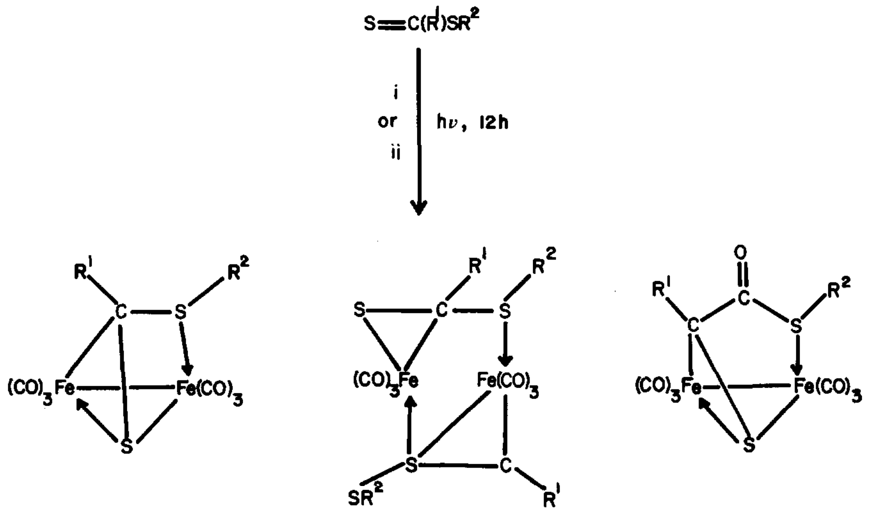
XY = $S(CH_2)_2S$

The formation of compound **D**, which contains a bridging carbene ligand, prompted the investigation of other desulphurization reactions of coordinated thiones with $[Fe(CO)_5]$ under ultraviolet irradiation. The dithioester complex $[(CO)_5Cr\{S{=}C(Me)SEt\}]$ yielded two products. One, as expected, was a member of class **A** [2], and the other was of an unknown type. Subsequent reactions in which uncoordinated ligands were used afforded the same products in higher yields. The results include the crystal structures of the new compounds formed (i) via an unusual carbonyl insertion into a carbon–sulphur bond, and (ii) via a novel dimerization of an iron complex. After completion of this work, Seyferth et al. [5] described an interesting structure of a compound, $[Fe_2(CO)_6\{HC(S)OEt\}_2]$, in which two iron atoms are bridged by *O*-ethyl thioformate groups. The results reported here are also relevant to the work of Alper et al. [6,7].

Results and discussion

(a) Reaction of dithioesters with $[Fe_2(CO)_5]$ or $[Fe_2(CO)_9]$

Irradiation of tetrahydrofuran (THF) solutions containing $S{=}C(Me)SEt$ and either $[Fe(CO)_5]$ or $[Fe_2(CO)_9]$ afforded, in somewhat different yields, the same two



red

II: R^1 = Me; R^2 = Et
i, 28%; ii, 20%

IV: R^1 = Ph; R^2 = Me
i, 19%; ii, 21%

brown

V: R^1 = Ph; R^2 = Me
i, 42%; ii, 16%

brown

III: R^1 = Me; R^2 = Et
i, 6%; ii, 3%

VI: R^1 = Ph; R^2 = Me
i, 13%; ii, 8%

Scheme 1. Reagents: (i) [$Fe(CO)_5$]; (ii) [$Fe_2(CO)_9$].

dinuclear iron compounds (II and III) after separation by column chromatography (Scheme 1).

A third product (brown), obtained in extremely low yield, was discarded. The detailed structure of the oily compound III could not be determined unequivocally by spectroscopy and elemental analysis. For the preparation of a crystalline analogue for single-crystal X-ray study, the reactions were repeated with S═C(Ph)SMe as ligand. In addition to compounds IV and VI (Scheme 1), which belong to the same classes as II and III, the non-symmetrical brown dimer, V, was then also isolated. All these compounds crystallized from pentane (−30 °C). The crystals are stable in an inert atmosphere, but the compounds decompose slowly in a solution in CH_2Cl_2.

The mass spectra (at 70 eV) of the new metal–metal-bonded coordination compounds showed the molecular ions. The highest peak for compound V at m/z 448 corresponds to the fragment ion formed by loss of six carbonyl ligands. All the compounds showed peaks for Fe_2S^+ and $Fe_2{}^+$. Compounds III and VI fragmented further by one-step CO extrusion from the ligands, and gave metastable peaks at m/z 207 and 255, respectively.

Complexes of the type [$Fe_2(CO)_6\{\mu\text{-}X_2\}$] have idealized C_{2v} symmetry which leads to five infrared-active vibration modes. In all the new compounds the ligands are asymmetrically bonded to the $Fe_2(CO)_6$ unit and six or more vibrations were observed in the carbonyl region of their infrared spectra (Table 1). The carbonyl ligands in compounds II, III, IV and VI are not greatly influenced by the change in

Table 1

Carbonyl frequencies for the new iron carbonyl complexes [a]

II	2072m	2025s	2005s	1982s	1971m	1963m	
III	2073m	2030s	2008s	1990s	1974m	1966(sh)	1677w
IV	2071m	2028s	2005s	1987s	1974m	1964m	
V	2060s	2038w	2019(sh)	2000(sh)	1992s	1985s	1974(sh)
VI	2072m	2033s	2006s	1994s	1979m	1967(sh)	1685w

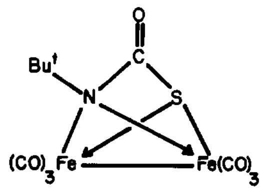
[a] Measured in hexane (cm^{-1}); m, medium; s, strong; sh, shoulder; w, weak.

the substituents in the dithioesters or by the carbonyl insertion, and they display a similar number of bands and intensity pattern at slightly changed frequencies. The bands at 1685 and 1677 cm^{-1} observed for compounds III and VI, respectively, were assigned to the carbonyl groups in the thioester ligand.

The proton chemical shifts for complexes II to VI are given in Table 2. The diastereotopic CH_2 protons of the SEt group and the δ 1.72 ppm signal from the SC(Me)S protons in II indicate the presence of a coordinated chiral sp^3 carbon atom. In keeping with the proposed structure, the δ 2.11 ppm chemical shift for the SMe group in IV and that of 2.6 ppm for SCH_2 in II correspond to values of δ 2.10 and 2.53 ppm in the thioester S(Me)Et [8], and not with the δ values of 2.68 and 3.31 ppm for the SMe and SCH_2 groups attached to an sp^2 carbon in S=C(Ph)Me or $[(CO)_5Cr\{SC(Me)SEt\}]$ [9] respectively. The spectra of III and VI are comparable to those of II and IV except that the SMe protons of VI appear as three peaks with relative intensities 3.5/1/1, indicating a diastereomeric mixture of the compound which contains three chiral atoms. The two singlets at δ 2.31 and 1.94 ppm in the spectra of V were assigned to the coordinated and uncoordinated SMe groups, respectively.

Proton decoupled ^{13}C NMR chemical shifts for IV and V (Table 2) correspond to their respective structures. The presence of two non-equivalent SC(Ph)SMe groups in V is indicated; the chiral carbons in IV and V have δ values between 73 and 95 ppm (which compare well with the δ 75.4 ppm value reported for I), and each complex shows six carbonyl resonances at 213 K. Compounds III and IV decomposed during data collection.

Insertions into C–S bonds are rare. We recently observed a complex rearrangement involving carbene insertion into a C–S single bond [10]. Meij et al. [11] reported a carbonyl insertion into an N–S bond in the formation of compound **E** from $Bu^tN=S=NBu^t$ and $[Fe_2(CO)_9]$.



E

We are still not in a position to discuss the sequence of reactions leading for example to IV, V and VI, but the nature of the substituents R^1 and R^2 in

Table 2

NMR data [a]

Coordinated ligand	^{1}H chemical shift (δ (ppm))
$SC(CH)_3SCH_2CH_3$ (II)	1.27 (t, 3H, CH_3CH_3), 1.72 (s, 3H, $SC(CH_3)S$), 2.0–3.2 (m, 2H, SCH_2)
$SC(CH_3)C(O)SCH_2CH_3$ (III)	1.27 (t, 3H, CH_2CH_3), 1.89 (s, 3H, $SC(CH_3)S$), 2.3–3.1 (m, 2H, SCH_2)
$SC(Ph)SCH_3$ (IV)	2.11 (s, 3H, CH_3), 7.26 (s, 5H, Ph)
2 × $SC(Ph)SCH_3$ (V)	1.94 (s, 3H, uncoord. SCH_3), 2.31 (s, 3H, coord. SCH_3) 7.0–7.7 (m, 10H, Ph)

Compound (temp.)	^{13}C chemical shifts (δ (ppm))								
	SCH_3	$C(sp^3)$	Ph(C(2)–C(6))			Ph(C(1))	C=O		
I (180 K) [b]		75.4					204.5	207.3	207.8
							209.2	213.0	215.3
IV (213 K)	32.5	72.7	122.0	126.8	128.7	146.3	204.7	207.1	208.0
							209.9	213.8	215.7
V (213 K)	19.9	82.5	125.9	126.5	126.9	146.1	202.7	203.9	204.7
	28.1	94.6	127.1	127.7	128.5	149.2	206.2	207.7	208.6
			128.8	129.4	129.6				

[a] Recorded in $CDCl_3$ rel. to int. $SiMe_4$. [b] Ref. 4.

dithioesters $S{=}C(R^1)SR^2$ clearly affect the formation and yield of compounds such as V.

(b) Molecular structures of I, V and VI

The crystal structure shows that the structure proposed for I (A with YX = $S(CH_2)_2S$) is correct (Fig. 1). Ethylene trithiocarbonate doubly bridges the two iron atoms in a metal–metal-bonded $Fe_2(CO)_6$ unit while donating six electrons to the metal atoms. One bridge is formed by the original thiocarbonyl carbon atom and a neighbouring thioether sulphur, and the other by the original bicovalent sulphur atom. The arrangement of the atoms in the molecule is similar to that in the complex $[Fe_2(CO)_6[\mu\text{-}\eta^2\text{-}SC\{\overline{C(CH)_3S}\}SMe\text{-}S,S']$ (A_2), which has been described previously [2]. Notable differences exist, however, in the bond lengths of the two complexes. For I these values along with those of the bond angles are given in Table 3. The Fe–S(1) bonds (2.259(2) and 2.192(2) Å) in compound I are significantly shorter than the bond between Fe(1) and the thioether sulphur (2.301(2) Å). The shortest Fe–S distance is observed in the three-membered ring $\overline{Fe(2)\text{–}C(7)\text{–}S(1)}$. The Fe(1)–Fe(2) bond (2.671(1) Å) is longer by 0.052 Å than the corresponding distance in A_2, but still of the order expected for non-symmetric doubly-bridged complexes [12]. The carbonyl ligands coordinated to the two iron atoms are staggered at a torsion angle of 17.9°. There are no significant intermolecular interactions.

The molecular structure of complex V is illustrated in Fig. 2, and Table 4 contains selected bond lengths and angles. The complex does not contain a metal–metal bond (Fe(1)–Fe(2) 3.856(2) Å). Two five-coordinated iron complexes

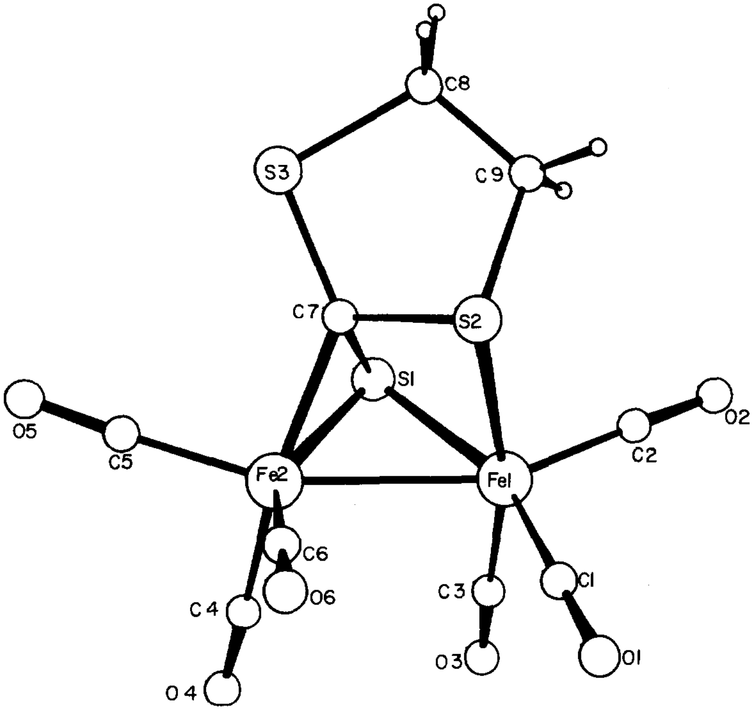


Fig. 1. The structure of compound I, $[\mathrm{Fe_2(CO)_6}\{\mathrm{S\overline{CS(CH_2)_2S}}\}]$.

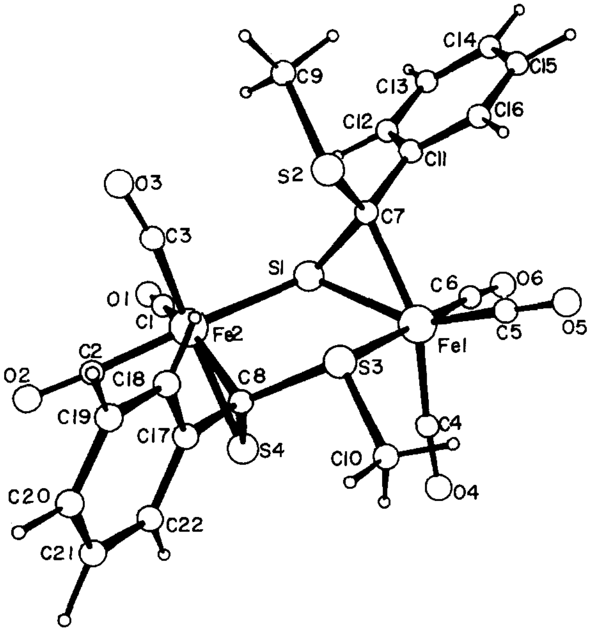


Fig. 2. The structure of compound V, $[\mathrm{Fe(CO)_3}\{\mathrm{SC(Ph)SMe}\}]_2$.

Table 3

Bond lengths (Å) and angles (°) in compound I

Fe(1)-Fe(2)	2.671(1)	Fe(1)-S(1)	2.259(2)
Fe(1)-S(2)	2.301(2)	Fe(1)-C(1)	1.793(8)
Fe(1)-C(2)	1.802(9)	Fe(1)-C(3)	1.795(8)
Fe(2)-S(1)	2.192(2)	Fe(2)-C(4)	1.796(8)
Fe(2)-C(5)	1.797(9)	Fe(2)-C(6)	1.781(8)
Fe(2)-C(7)	1.973(6)	S(1)-C(7)	1.795(7)
S(2)-C(7)	1.786(6)	S(2)-C(9)	1.822(8)
S(3)-C(7)	1.756(6)	S(3)-C(8)	1.846(9)
C(1)-O(1)	1.133(8)	C(2)-O(2)	1.137(8)
C(3)-O(3)	1.129(8)	C(4)-O(4)	1.152(8)
C(5)-O(5)	1.133(8)	C(6)-O(6)	1.139(8)
C(8)-C(9)	1.494(12)	C(8)-H(81)	0.80(11)
C(8)-H(82)	1.16(10)	C(9)-H(91)	0.93(7)
C(9)-H(92)	0.98(8)		
Fe(2)-Fe(1)-S(1)	52.0(1)	Fe(2)-Fe(1)-S(2)	74.8(1)
S(1)-Fe(1)-S(2)	78.2(1)	Fe(2)-Fe(1)-C(1)	101.3(3)
S(1)-Fe(1)-C(1)	153.0(3)	S(2)-Fe(1)-C(1)	92.3(2)
Fe(2)-Fe(1)-C(2)	156.7(2)	S(1)-Fe(1)-C(2)	105.5(2)
S(2)-Fe(1)-C(2)	96.2(2)	C(1)-Fe(1)-C(2)	100.5(3)
Fe(2)-Fe(1)-C(3)	91.5(2)	S(1)-Fe(1)-C(3)	93.0(2)
S(2)-Fe(1)-C(3)	166.3(2)	C(1)-Fe(1)-C(3)	91.0(3)
C(2)-Fe(1)-C(3)	96.3(3)	Fe(2)-Fe(1)-C(7)	43.0(1)
S(1)-Fe(1)-C(7)	41.2(1)	S(2)-Fe(1)-C(7)	40.8(1)
C(1)-Fe(1)-C(7)	118.7(3)	C(2)-Fe(1)-C(7)	117.4(3)
C(3)-Fe(1)-C(7)	126.9(3)	Fe(1)-Fe(2)-S(1)	54.3(1)
Fe(1)-Fe(2)-C(4)	98.9(2)	S(1)-Fe(2)-C(4)	105.3(2)
Fe(1)-Fe(2)-C(5)	161.9(2)	S(1)-Fe(2)-C(5)	110.0(2)
C(4)-Fe(2)-C(5)	94.0(3)	Fe(1)-Fe(2)-C(6)	91.3(2)
S(1)-Fe(2)-C(6)	140.3(2)	C(4)-Fe(2)-C(6)	98.6(3)
C(5)-Fe(2)-C(6)	99.3(3)	Fe(1)-Fe(2)-C(7)	69.4(2)
S(1)-Fe(2)-C(7)	50.7(2)	C(4)-Fe(2)-C(7)	156.0(3)
C(5)-Fe(2)-C(7)	93.8(3)	C(6)-Fe(2)-C(7)	102.4(3)
Fe(1)-S(1)-Fe(2)	73.7(1)	Fe(1)-S(1)-C(7)	82.9(2)
Fe(2)-S(1)-C(7)	58.3(2)	Fe(1)-S(2)-C(7)	81.8(2)
Fe(1)-S(2)-C(9)	115.4(3)	C(7)-S(2)-C(9)	92.5(3)
C(7)-S(3)-C(8)	96.3(4)	Fe(1)-C(1)-O(1)	176.5(7)
Fe(1)-C(2)-O(2)	177.8(7)	Fe(1)-C(3)-O(3)	178.0(7)
Fe(2)-C(4)-O(4)	178.0(7)	Fe(2)-C(5)-O(5)	176.6(7)
Fe(2)-C(6)-O(6)	179.5(6)	Fe(1)-C(7)-Fe(2)	67.6(2)
Fe(1)-C(7)-S(1)	56.0(2)	Fe(2)-C(7)-S(1)	71.0(2)
Fe(1)-C(7)-S(2)	57.3(2)	S(1)-C(7)-S(2)	106.8(3)
Fe(1)-C(7)-S(3)	157.3(3)	Fe(2)-C(7)-S(3)	135.0(4)
S(1)-C(7)-S(3)	121.7(4)	S(2)-C(7)-S(3)	108.4(3)
S(3)-C(8)-C(9)	111.3(6)	S(2)-C(9)-C(8)	108.2(6)

are held in dimers by unsymmetrical dative sulphur bonding. There is heavily distorted octahedral geometry about each iron atom, as may be seen from the angles S(1)-Fe(1)-C(5) 149.1(4)° and S(4)-Fe(2)-C(3) 152.3(4)°. The sulphur atom S(1) in the three-membered ring forms a weaker dative bond (Fe(2)-S(1) 2.340(3) Å) than the thioether sulphur, S(3) (Fe(1)-S(3) 2.304(3) Å).

The molecular structure of VI and the atom numbering scheme are shown in Fig.

(Continued on p. 258)

Table 4

Bond lengths (Å) and angles (°) in compound V

Fe(1)–S(1)	2.253(3)	Fe(1)–C(4)	1.834(12)
Fe(1)–C(5)	1.783(12)	Fe(1)–C(6)	1.805(12)
Fe(1)–C(7)	2.083(10)	Fe(1)–S(3)	2.304(3)
S(1)–C(7)	1.746(10)	S(1)–Fe(2)	2.340(3)
S(2)–C(7)	1.830(10)	S(2)–C(9)	1.817(12)
O(4)–C(4)	1.139(13)	O(5)–C(5)	1.150(12)
O(6)–C(6)	1.129(13)	C(7)–C(11)	1.505(13)
C(11)–C(12)	1.386(14)	C(11)–C(16)	1.400(14)
C(12)–C(13)	1.40(2)	C(13)–C(14)	1.39(2)
C(14)–C(15)	1.38(2)	C(15)–C(16)	1.38(2)
Fe(2)–S(4)	2.271(3)	Fe(2)–C(1)	1.838(13)
Fe(2)–C(2)	1.778(12)	Fe(2)–C(3)	1.808(12)
Fe(2)–C(8)	2.071(10)	S(3)–C(8)	1.818(10)
S(3)–C(10)	1.815(11)	S(4)–C(8)	1.745(10)
O(1)–C(1)	1.117(13)	O(2)–C(2)	1.148(12)
O(3)–C(3)	1.131(13)	C(8)–C(17)	1.52(2)
C(17)–C(18)	1.390(14)	C(17)–C(22)	1.38(2)
C(18)–C(19)	1.39(2)	C(19)–C(20)	1.37(2)
C(20)–C(21)	1.36(2)	C(21)–C(22)	1.39(2)

S(1)–Fe(1)–C(4)	109.4(3)	S(1)–Fe(1)–C(5)	149.1(4)
C(4)–Fe(1)–C(5)	101.4(5)	S(1)–Fe(1)–C(6)	90.4(4)
C(4)–Fe(1)–C(6)	89.8(5)	C(5)–Fe(1)–C(6)	91.1(5)
S(1)–Fe(1)–C(7)	47.3(3)	C(4)–Fe(1)–C(7)	156.7(4)
C(5)–Fe(1)–C(7)	101.9(4)	C(6)–Fe(1)–C(7)	89.2(5)
S(1)–Fe(1)–S(3)	88.3(1)	C(4)–Fe(1)–S(3)	90.4(4)
C(5)–Fe(1)–S(3)	90.1(4)	C(6)–Fe(1)–S(3)	178.7(4)
C(7)–Fe(1)–S(3)	90.1(3)	Fe(1)–S(1)–C(7)	61.2(3)
Fe(1)–S(1)–Fe(2)	114.2(1)	C(7)–S(1)–Fe(2)	121.2(3)
C(7)–S(2)–C(9)	101.2(5)	Fe(1)–C(4)–O(4)	175.4(10)
Fe(1)–C(5)–O(5)	178.7(11)	Fe(1)–C(6)–O(6)	176.6(11)
Fe(1)–C(7)–S(1)	71.5(3)	Fe(1)–C(7)–S(2)	115.8(5)
S(1)–C(7)–S(2)	119.2(5)	Fe(1)–C(7)–C(11)	117.2(7)
S(1)–C(7)–C(11)	118.6(8)	S(2)–C(7)–C(11)	110.0(7)
C(7)–C(11)–C(12)	120.5(10)	C(7)–C(11)–C(16)	119.5(10)
C(12)–C(11)–C(16)	120.0(10)	C(11)–C(12)–C(13)	119.6(12)
C(12)–C(13)–C(14)	120.6(12)	C(13)–C(14)–C(15)	119.0(11)
C(14)–C(15)–C(16)	121.8(12)	C(11)–C(16)–C(15)	119.0(12)
S(1)–Fe(2)–S(4)	89.2(1)	S(1)–Fe(2)–C(1)	82.9(3)
S(4)–Fe(2)–C(1)	105.4(4)	S(1)–Fe(2)–C(2)	172.5(4)
S(4)–Fe(2)–C(2)	88.6(4)	C(1)–Fe(2)–C(2)	90.9(5)
S(1)–Fe(2)–C(3)	96.4(3)	S(4)–Fe(2)–C(3)	152.3(4)
C(1)–Fe(2)–C(3)	102.2(5)	C(2)–Fe(2)–C(3)	88.8(5)
S(1)–Fe(2)–C(8)	93.4(3)	S(4)–Fe(2)–C(8)	47.1(3)
C(1)–Fe(2)–C(8)	152.5(5)	C(2)–Fe(2)–C(8)	90.3(5)
C(3)–Fe(2)–C(8)	105.4(4)	Fe(1)–S(3)–C(8)	109.8(4)
Fe(1)–S(3)–C(10)	109.2(4)	C(8)–S(3)–C(10)	100.8(5)
Fe(2)–S(4)–C(8)	60.4(3)	Fe(2)–C(1)–O(1)	179.3(11)
Fe(2)–C(2)–O(2)	176.7(11)	Fe(2)–C(3)–O(3)	171.2(10)
Fe(2)–C(8)–S(3)	113.8(5)	Fe(2)–C(8)–S(4)	72.5(4)
S(3)–C(8)–S(4)	119.1(6)	Fe(2)–C(8)–C(17)	118.2(7)
S(3)–C(8)–C(17)	108.2(7)	S(4)–C(8)–C(17)	121.2(8)
C(8)–C(17)–C(18)	120.8(10)	C(8)–C(17)–C(22)	119.3(10)
C(18)–C(17)–C(22)	120.0(11)	C(17)–C(18)–C(19)	119.2(11)
C(18)–C(19)–C(20)	120.8(11)	C(19)–C(20)–C(21)	119.2(12)
C(20)–C(21)–C(22)	121.9(11)	C(17)–C(22)–C(21)	118.8(10)

Table 5

Bond lengths (Å) and angles (°) in compound VI

Fe(1)-Fe(2)	2.705(1)	Fe(1)-S(2)	2.181(1)
Fe(1)-C(1)	1.782(6)	Fe(1)-C(2)	1.811(5)
Fe(1)-C(3)	1.795(6)	Fe(1)-C(7)	2.110(4)
Fe(2)-S(1)	2.260(1)	Fe(2)-S(2)	2.250(1)
Fe(2)-C(4)	1.792(6)	Fe(2)-C(5)	1.793(6)
Fe(2)-C(6)	1.821(6)	S(1)-C(8)	1.841(5)
S(1)-C(15)	1.807(6)	S(2)-C(7)	1.765(4)
O(1)-C(1)	1.150(5)	O(2)-C(2)	1.132(5)
O(3)-C(3)	1.139(5)	O(4)-C(4)	1.144(6)
O(5)-C(5)	1.142(5)	O(6)-C(6)	1.129(6)
O(7)-C(8)	1.211(5)	C(7)-C(8)	1.450(6)
C(7)-C(9)	1.503(6)	C(9)-C(10)	1.389(7)
C(9)-C(14)	1.382(7)	C(10)-C(11)	1.380(7)
C(11)-C(12)	1.373(9)	C(12)-C(13)	1.356(9)
C(13)-C(14)	1.383(8)		
Fe(2)-Fe(1)-S(2)	53.6(0)	Fe(2)-Fe(1)-C(1)	90.9(2)
S(2)-Fe(1)-C(1)	111.3(2)	Fe(2)-Fe(1)-C(2)	163.1(2)
S(2)-Fe(1)-C(2)	110.3(2)	C(1)-Fe(1)-C(2)	91.1(2)
Fe(2)-Fe(1)-C(3)	96.6(2)	S(2)-Fe(1)-C(3)	138.6(2)
C(1)-Fe(1)-C(3)	95.2(2)	C(2)-Fe(1)-C(3)	100.0(2)
Fe(2)-Fe(1)-C(7)	80.4(1)	S(2)-Fe(1)-C(7)	48.5(1)
C(1)-Fe(1)-C(7)	159.1(2)	C(2)-Fe(1)-C(7)	92.0(2)
C(3)-Fe(1)-C(7)	104.6(2)	Fe(1)-Fe(2)-S(1)	89.1(0)
Fe(1)-Fe(2)-S(2)	51.2(0)	S(1)-Fe(2)-S(2)	85.1(1)
Fe(1)-Fe(2)-C(4)	98.0(2)	S(1)-Fe(2)-C(4)	93.2(2)
S(2)-Fe(2)-C(4)	149.2(2)	Fe(1)-Fe(2)-C(5)	89.6(2)
S(1)-Fe(2)-C(5)	174.5(2)	S(2)-Fe(2)-C(5)	89.9(2)
C(4)-Fe(2)-C(5)	92.3(2)	Fe(1)-Fe(2)-C(6)	159.4(2)
S(1)-Fe(2)-C(6)	89.1(2)	S(2)-Fe(2)-C(6)	108.2(2)
C(4)-Fe(2)-C(6)	102.5(2)	C(5)-Fe(2)-C(6)	90.2(2)
Fe(2)-S(1)-C(8)	102.8(2)	Fe(2)-S(1)-C(15)	115.8(2)
C(8)-S(1)-C(15)	100.2(3)	Fe(1)-S(2)-Fe(2)	75.2(0)
Fe(1)-S(2)-C(7)	63.6(1)	Fe(2)-S(2)-C(7)	102.2(2)
Fe(1)-C(1)-O(1)	175.9(5)	Fe(1)-C(2)-O(2)	178.6(5)
Fe(1)-C(3)-O(3)	177.3(5)	Fe(2)-C(4)-O(4)	177.5(5)
Fe(2)-C(5)-O(5)	177.7(5)	Fe(2)-C(6)-O(6)	176.4(5)
Fe(1)-C(7)-S(2)	67.8(2)	Fe(1)-C(7)-C(8)	104.7(3)
S(2)-C(7)-C(8)	120.0(3)	Fe(1)-C(7)-C(9)	119.6(3)
S(2)-C(7)-C(9)	116.5(3)	C(8)-C(7)-C(9)	117.5(4)
S(1)-C(8)-O(7)	118.2(4)	S(1)-C(8)-C(7)	112.7(4)
O(7)-C(8)-C(7)	129.1(5)	C(7)-C(9)-C(10)	120.2(4)
C(7)-C(9)-C(14)	121.7(5)	C(10)-C(9)-C(14)	118.1(5)
C(9)-C(10)-C(11)	120.8(6)	C(10)-C(11)-C(12)	119.8(6)
C(11)-C(12)-C(13)	120.3(6)	C(12)-C(13)-C(14)	120.3(6)
C(9)-C(14)-C(13)	120.7(6)		
C(10)-H(10)	1.01(4)	C(11)-H(11)	0.94(4)
C(12)-H(12)	0.86(5)	C(13)-H(13)	0.91(4)
C(14)-H(14)	0.99(4)	C(15)-H(151)	0.94(5)
C(15)-H(152)	0.96(5)	C(15)-H(153)	0.93(5)

Table 6

Crystallographic data for the compounds [$Fe_2(CO)_6\{SCS(CH_2)_2S\}$] (I), [$Fe(CO)_3\{SC(Ph)SMe\}]_2$ (V) and [$Fe_2(CO)_6\{Sc(Ph)C(O)SMe\}$] (VI) and structure determination details

	I	V	VI
Crystal data			
Formula	$C_9H_4O_6S_3Fe_2$	$C_{22}H_{16}O_6S_4Fe_2$	$C_{15}H_8O_7S_2Fe_2$
Crystal habit	red needles	brown prisms	brown needles
Crystal size (mm)	0.20×0.20×0.15	0.30×0.20×0.20	0.15×0.20×0.15
Crystal symmetry	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/c$	$Pna2_1$	$C2/c$
Unit cell determination:			
least-squares fit to	25 reflections, θ(Mo) < 13°	25 reflections, θ(Mo) < 12°	25 reflections, θ(Mo) < 12°
Unit cell dimensions			
a (Å)	10.327(1)	18.304(2)	31.576(3)
b (Å)	7.571(1)	7.373(1)	7.025(2)
c (Å)	18.276(1)	18.579(2)	21.483(2)
β (°)	95.1(1)		131.6(1)
Packing: V (Å^3), Z	1423,4	2507,4	3561,8
$F(000)$	824	1248	1903
D_{calc} (g cm^{-3}), M	1.89, 416.01	1.63, 616.30	1.78, 476.04
Experimental data			
Diffractometer	Philips PW1100	Philips PW1100	Philips PW1100
Radiation	Mo-K_α (0.71073 Å)	Mo-K_α (0.71073 Å)	Mo-K_α (0.71073 Å)
Monochromator	Graphite	Graphite	Graphite
Collection mode	$\omega-2\theta$ scans, θ range: 3–23°	$\omega-2\theta$ scans, θ range: 3–23°	$\omega-2\theta$ scans, θ range: 3–23°
scan width	1.1°θ	1.1°θ	1.26°θ
scan speed	0.044°θ s^{-1}	0.044°θ s^{-1}	0.051° s^{-1}
Reflections measured	2167	2037	4942 (triclinic set)
Observable reflections	1600 with $\|F\| > 3\sigma(F)$	1627 with $\|F\| > 3\sigma(F)$	1904 with $\|F\| > 3\sigma(F)$
Stability	3 reflections every 60 min, no variation	3 reflections every 60 min, no variation	3 reflections every 60 min, no variation
Corrections	Lp	Lp	Lp
μ (cm^{-1})	23.8	14.4	18.0

Solution and refinement			
Solution	Direct methods, SHELX76 [16]	Direct methods, SHELX76 [16]	Direct methods, SHELX76 [16]
Refinement	Least-squares, full matrix	Least-squares, full matrix	Least-squares, full matrix
Temperature factors	non-H: anisotropic H: isotropic	non-H: anisotropic H: two common isotropic factors one each for methyl and phenyl hydrogens	non-H: anisotropic H: two common isotropic factors one each for methyl and phenyl hydrogens
H positions	From Δ maps, individually refined	calculated in ideal portions refined as riding on attached atoms at 1.08 Å	From Δ maps, individually refined
Number of variables	197	314	261
Reflections used	1600 observed with $\lvert F \rvert > 3\sigma(F)$	1627 observed with $\lvert F \rvert > 3\sigma(F)$	1904 observed with $\lvert F \rvert > 3\sigma(F)$
Weighting scheme	$w = (\sigma(F))^{-2}$	$w = (\sigma(F))^{-2}$	$w = (\sigma(F))^{-2}$
Final Δ peaks	0.7 eÅ^{-3}	0.3 eÅ^{-3}	0.3 eÅ^{-3}
Final R, R_w	0.045, 0.044	0.036, 0.042	0.042, 0.029

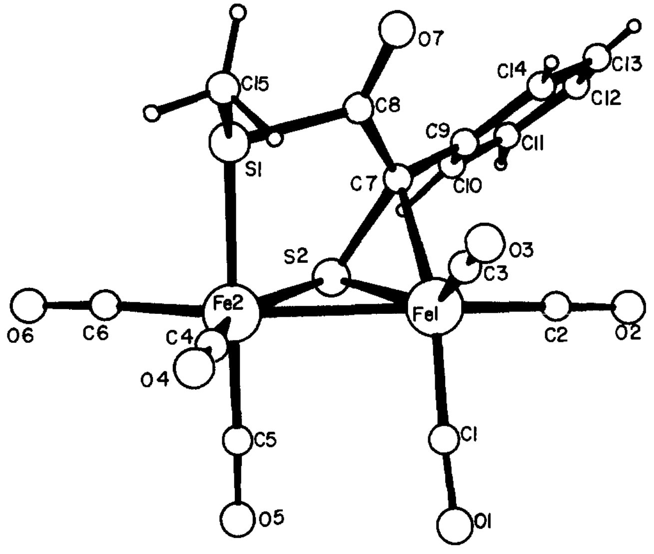


Fig. 3. The structure of compound VI, $[Fe_2(CO)_6\{SC(Ph)C(O)SMe\}]$.

3. Table 5 contains relevant interatomic distances and angles. Carbonyl insertion into a C–S bond has led to the formation of a five-membered ring system containing the two metal atoms, rather than the four-membered metal-containing ring in A-type complexes. Nevertheless, the geometries about the two irons and the sp^3 hybridized C(7) atom, are comparable with those in I. The metal–metal separation of 2.705(1) Å is the same, but the longer Fe(1)–C(7) bond length of 2.110(4) Å agrees better with the expected 2.10 Å value for a Fe–C(sp^3) distance [13]. In VI the metal–carbonyl bonds that are approximately aligned with the metal–metal bond are longer than the others, in accord with the results of Benoit et al. [2] for a complex of type A (Fe(2)–Fe(1)–C(2), 163.1(2)°; Fe(2)–Fe(1)–C(6), 159.4(2)°; Fe(1)–C(2), 1.811(5) Å; Fe(2)–C(6) 1.821(6) Å). The S(1)–CO distance (1.841(5) Å) is greater than the 1.749(3) Å of the MeS–CO bond in the compound MeSCH=C(OMe)C(O)C(O)SMe [14]. This lengthening is probably the result of the S(1)–metal bond formation, since the comparable distance in $[(\eta^5\text{-}C_5H_5)(CO)Mo\{\overline{C(O)C(CF_3)=C(CF_3)C(O)S}Me\}]$ is also relatively long (1.852(4) Å) [15].

Experimental

All reactions were performed by Schlenk techniques under nitrogen. Solvents were freshly distilled under nitrogen from drying agents. For column chromatography at −10 °C, Merck Kieselgel 60 (0.063–0.200 mm) was dried under vacuum and saturated with nitrogen. A Philips 93136 E mercury vapour lamp, enclosed in a watercooled quartz jacket during irradiation, was used for photochemical reactions. Melting points (Kofler) are uncorrected. Elemental analyses were performed at the microanalytical laboratory Pascher and Pascher in Bonn. Mass spectral data were obtained on a Hitachi Perkin–Elmer RMU-6H apparatus, infrared data on a Perkin–Elmer 297, ^1H NMR spectra on a Varian T60 or Bruker WP-80 and ^{13}C

NMR spectra on a Bruker 500 MHz spectrometer. Yields are based on the limiting reactant.

Preparation of the $Fe_2(CO)_6$ complexes II–VI

In a typical experiment 5.9 g (30 mmol) [Fe(CO)$_5$] and 1.7 g (10 mmol) S=C(Ph)SMe were irradiated with UV light for 12 h in 100 ml THF. After concentration of the dark mixture it was stripped of solvent under reduced pressure and the residue then chromatographed with hexane/CH_2Cl_2 (1/10–1/1) as eluant. First a red fraction, then a red-brown zone, and finally another red fraction, were collected, and each was concentrated under vacuum. Recrystallization of the resulting powders from pentane at −30 °C afforded the analytically pure compounds IV, V and VI. Compounds II and III were prepared similarly from [Fe(CO)$_5$] and S=C(Me)SEt. The same compounds were obtained when 15 mmol [Fe$_2$(CO)$_9$] was used in place of the 30 mmol of [Fe(CO)$_5$]. The products are listed below in the order in which they were eluted from the columns.

[Fe$_2$(CO)$_6${μ-η^2-SC(Me)SEt-S,S'}](Fe–Fe) (II). Red needles. Yield: [Fe(CO)$_5$], 28%; [Fe$_2$(CO)$_9$], 20%. M.p. 51–52 °C. Anal. Found: C, 30.16; H, 2.10; S, 15.6. $Fe_2C_{10}H_8O_6S_2$ calc: C, 30.03; H, 2.02; S, 16.03%.

[Fe$_2$(CO)$_6${μ-η^2-SC(Me)C(O)SEt-S,S'}](Fe–Fe) (III). Red oil. Yield: [Fe(CO)$_5$], 6%; [Fe$_2$(CO)$_9$], 3%. Anal. Found: C, 29.23; H, 2.23; O, 27.0; S, 14.4. $Fe_2C_{11}H_8O_7S_2$ calc: C, 30.87; H, 1.88; O, 26.17; S, 14.98%.

[Fe$_2$(CO)$_6$(μ-η^2-SC(Ph)SMe-S,S'}](Fe–Fe) (IV). Red needles. Yield: [Fe(CO)$_5$], 19%; [Fe$_2$(CO)$_9$], 21%. M.p. 102–103 °C. Anal. Found: C, 37.57; H, 1.90; S, 13.9. $Fe_2C_{14}H_8O_6S_2$ calc: C, 37.53; H, 1.80; S, 14.31%.

Table 7

Fractional coordinates (×10^4, ×10^5 for Fe and S) and equivalent isotropic temperature factors (Å^2, ×10^3, ×10^4 for Fe) for the non-H atoms of compound I

Atom	x/a	y/b	z/c	U_{eq}
Fe(1)	82298(8)	75504(14)	13035(5)	382(5)
Fe(2)	71274(9)	46412(13)	7011(5)	353(5)
S(1)	61218(16)	67275(26)	12601(9)	40(1)
S(2)	82680(16)	55259(26)	22440(9)	38(1)
S(3)	58902(19)	36000(30)	23370(10)	53(1)
C(1)	9908(8)	7172(11)	1173(4)	52(5)
C(2)	8363(7)	9484(11)	1881(4)	50(5)
C(3)	8000(7)	8715(11)	447(4)	50(5)
C(4)	7034(7)	5295(10)	−247(4)	44(4)
C(5)	6070(8)	2774(11)	531(4)	47(5)
C(6)	8655(8)	3536(10)	751(4)	47(4)
C(7)	6792(6)	4828(9)	1744(3)	36(4)
C(8)	6481(9)	4779(16)	3186(5)	58(5)
C(9)	7428(9)	6196(13)	3034(4)	50(5)
O(1)	10967(5)	7010(9)	1071(3)	76(4)
O(2)	8489(6)	10703(8)	2243(3)	76(4)
O(3)	7889(6)	9470(9)	−88(3)	67(4)
O(4)	6940(5)	5688(8)	−858(3)	69(4)
O(5)	5421(6)	1568(8)	459(3)	68(4)
O(6)	9628(5)	2818(8)	781(3)	68(4)

Table 8

Fractional coordinates ($\times 10^4$, $\times 10^5$ for Fe and S) and equivalent isotropic temperature factors (Å^2, $\times 10^3$, $\times 10^4$ for Fe) for the non-H atoms of compound V

Atom	x/a	y/b	z/c	U_{eq}
Fe(1)	−5390(7)	−4260(20)	−50000	366(8)
S(1)	−17672(12)	−5873(35)	−49479(17)	34(1)
S(2)	−12419(15)	−45547(40)	−48466(16)	40(2)
O(4)	−60(4)	2823(11)	−5820(5)	55(5)
O(5)	894(5)	−1971(13)	−4650(5)	71(6)
O(6)	−485(5)	1796(12)	−3692(5)	57(5)
C(4)	−271(6)	1580(17)	−5521(6)	45(7)
C(5)	329(7)	−1385(15)	−4788(6)	44(7)
C(6)	−525(6)	915(16)	−4187(7)	43(7)
C(7)	−1252(6)	−2232(13)	−4500(5)	29(5)
C(9)	−1958(7)	−5595(16)	−4309(7)	51(8)
C(11)	−1258(6)	−2252(15)	−3691(6)	36(6)
C(12)	−1826(6)	−1454(16)	−3312(6)	42(6)
C(13)	−1808(7)	−1428(17)	−2561(6)	49(7)
C(14)	−1237(7)	−2232(15)	−2190(6)	43(7)
C(15)	−681(7)	−3034(18)	−2575(7)	55(8)
C(16)	−676(6)	−3051(16)	−3319(6)	45(7)
Fe(2)	−23266(7)	−12065(19)	−60532(12)	355(8)
S(3)	−5847(13)	−21289(34)	−60390(17)	37(1)
S(4)	−15971(16)	9050(36)	−65775(17)	41(2)
O(1)	−3548(5)	865(15)	−5417(5)	67(6)
O(2)	−3131(5)	−1603(12)	−7405(5)	60(5)
O(3)	−2793(5)	−4953(11)	−5795(5)	64(6)
C(1)	−3086(7)	75(19)	−5654(6)	50(7)
C(2)	−2808(6)	−1398(16)	−6881(6)	45(7)
C(3)	−2576(6)	−3523(17)	−5851(5)	48(7)
C(8)	−1342(5)	−1374(13)	−6597(6)	28(6)
C(10)	186(6)	−1537(18)	−6607(7)	53(8)
C(17)	−1320(6)	−2430(16)	−7300(6)	36(6)
C(18)	−1339(6)	−1536(16)	−7958(6)	44(7)
C(19)	−1321(7)	−2549(20)	−8591(6)	49(8)
C(20)	−1283(7)	−4407(19)	−8570(6)	54(7)
C(21)	−1253(6)	−5256(17)	−7924(7)	52(7)
C(22)	−1276(6)	−4303(16)	−7279(6)	38(7)

[$Fe_2(CO)_6${μ-η^2-SC(Ph)SMe-S}{μ-η^2-SC(Ph)SMe-S'}] (V). Brown prisms. Yield: [$Fe(CO)_5$], 42%; [$Fe_2(CO)_9$], 16%. M.p. 108–110 °C. Anal. Found: C, 42.78; H, 2.71; O, 16.2; S, 20.4. $Fe_2C_{22}H_{16}O_6S_4$ calc: C, 42.88; H, 2.62; O, 15.58; S, 20.81%.

[$Fe_2(CO)_6${μ-η^2-SC(Ph)C(O)SMe-S,S'}](Fe–Fe) (VI). Brown needles. Yield: [$Fe(CO)_5$], 13%; [$Fe_2(CO)_9$], 8%. M.p. 99–100 °C. Anal. Found: C, 37.70; H, 2.17; O, 23.3; S, 12.8. $Fe_2C_{15}H_8O_7S_2$ calc: C, 37.85; H, 1.69; O, 23.53; S, 13.47%.

X-ray structure determinations

Crystal data for compounds I, V and VI and details of their crystal structure determinations are given in Table 6. Atomic coordinates are given in Tables 7 to 9, the atom-numbering schemes being illustrated in Figs. 1 to 3.

Table 9

Fractional coordinates ($\times 10^4$, $\times 10^5$ for Fe and S) and equivalent isotropic temperature factors (Å^2, $\times 10^3$, $\times 10^4$ for Fe and S) for the non-H atoms of compound VI

Atom	x/a	y/b	z/c	U_{eq}
Fe(1)	16502(3)	−1395(10)	7821(4)	304(4)
Fe(2)	6695(3)	6163(10)	−7790(4)	335(4)
S(1)	2070(5)	−12425(18)	−5385(8)	357(7)
S(2)	10350(5)	20559(17)	4232(8)	332(7)
O(1)	2331(2)	849(6)	352(2)	54(3)
O(2)	2665(2)	211(6)	2561(2)	55(3)
O(3)	1677(2)	−4224(5)	525(3)	57(3)
O(4)	715(2)	−2438(6)	−1667(3)	65(3)
O(5)	1259(2)	3345(5)	−1010(2)	53(3)
O(6)	−402(2)	2516(6)	−2159(3)	61(3)
O(7)	703(2)	−2886(5)	907(2)	47(2)
C(1)	2051(2)	515(7)	503(3)	39(3)
C(2)	2272(2)	58(8)	1879(3)	39(3)
C(3)	1662(2)	−2648(8)	635(3)	36(3)
C(4)	710(2)	−1240(8)	−1311(4)	45(4)
C(5)	1040(2)	2262(8)	−909(3)	39(3)
C(6)	0(3)	1769(8)	−1622(3)	43(4)
C(7)	1102(2)	145(7)	1017(3)	30(3)
C(8)	723(2)	−1474(7)	604(3)	33(3)
C(9)	1344(2)	611(8)	1882(3)	33(3)
C(10)	1339(2)	2474(8)	2094(3)	37(3)
C(11)	1568(3)	2926(10)	2890(4)	51(4)
C(12)	1802(3)	1520(13)	3480(4)	55(5)
C(13)	1808(3)	−310(11)	3285(4)	53(5)
C(14)	1578(2)	−776(8)	2488(4)	45(4)
C(15)	126(3)	−3713(9)	−835(4)	49(4)

Supplementary material available

Tables of anisotropic thermal parameters, hydrogen positions, and observed and calculated structure factors for compounds I, V and VI are available from the authors.

Acknowledgement

We thank the Foundation for Research Development for financial assistance, and the NPRL of the S.A. Council for Scientific and Industrial Research for collecting the diffractometer data.

References

1 E.K. Lladi, H. Patin and A. Darchen, Organometallics, 4 (1984) 1128.
2 A. Benoit, J.Y. Le Marouille, C. Mahe and H. Patin, J. Organomet. Chem., 218 (1981) C67.
3 H. Patin, G. Mignani, A. Benoit, J.Y. Le Marouille and D. Grandjean, Inorg. Chem., 20 (1981) 4351.
4 G.J. Kruger, L. Linford, H.G. Raubenheimer and A.A. Chalmers, J. Organomet. Chem., 262 (1984) 69.
5 D. Seyferth, G.B. Womack, M. Cowie and B.W. Hames, Organometallics, 3 (1984) 1891.
6 H. Alper and C.K. Foo, Inorg. Chem., 14 (1975) 2928.
7 H. Alper, F.W.B. Einstein, F.W. Hartstock and A.C. Willis, J. Am. Chem. Soc., 107 (1985) 173.

8 N.S. Bhaca, D.P. Hollis, L.F. Johnson, E.A. Pier and J.N. Shoolery, High Resolution NMR Spectra Catalog, Varian Associates, New York, 1962.

9 H.G. Raubenheimer, G.J. Kruger and A. van A. Lombard, unpublished results.

10 H.G. Raubenheimer, G.J. Kruger and H.W. Viljoen, J. Organomet. Chem., 319 (1987) 361.

11 R. Meij, J. van der Helm, D.J. Stufkens and K. Vrieze, J. Chem. Soc., Chem. Commun., (1978) 506.

12 C. Krüger, B.L. Barnett and D. Brauer in E.A.K. Von Gustorf, F.W. Grevels and I. Tischler (Eds.), The Organic Chemistry of Iron, Vol. I, Academic Press, London, 1978, p. 1.

13 M.R. Churchill and S.W.Y. Ni Chiang, J. Am. Chem. Soc., 95 (1973) 5931.

14 C.H. Eugster, M. Balmer, R. Prewo, J.H. Bieri, Helv. Chim. Acta, 64 (1981) 2636.

15 J.E. Guerchais, F. Le Floch-Perennou, F.Y. Petillon, A.N. Keith, L. Manojlović-Muir, K.W. Muir and D.W. Sharp, J. Chem. Soc., Chem. Commun., (1979) 410.

16 G.M. Sheldrick in H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld and G.C. Bassi (Eds.), Computing in Crystallography, Delft, University Press, 1978.