

SULPHUR-CONTAINING METAL COMPLEXES

X *. REACTIONS OF $[\text{Fe}(\text{CO})_5]$ WITH ETHYLENETRITHIOCARBONATE. STRUCTURE OF $[\text{Fe}_3(\text{CO})_9\{\overline{\text{CS}}(\text{CH}_2)_2\overline{\text{S}}\}]$ CONTAINING A μ -DITHIOCARBENE LIGAND

GERT J. KRUGER, LORNA LINFORD, HELGARD G. RAUBENHEIMER*,

Department of Chemistry, Rand Afrikaans University, Johannesburg 2000, (South Africa)

and ANTHONY A. CHALMERS

National Chemical Research Laboratory, Council for Scientific and Industrial Research, Pretoria 0001 (South Africa)

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Summary

Four different conversions were observed when a mixture of $[\text{Fe}(\text{CO})_5]$ and ethylenetrithiocarbonate was irradiated with ultraviolet light in tetrahydrofuran: (i) the thione bond in the ligand was broken and the sulphur atom was incorporated into a cluster to produce $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-S})_2]$, (I); (ii) cleavage of the two C–S single bonds occurred and the $\text{S}(\text{CH}_2)_2\text{S}$ moiety was used to stabilize the complex $[\text{Fe}_2(\text{CO})_6\{\mu\text{-S}(\text{CH}_2)_2\text{S}\}]$, (II); (iii) the ligand exhibited significant charge redistribution during coordination, in the compound $[\text{Fe}_2(\text{CO})_6\{\mu\text{-S}\overline{\text{CS}}(\text{CH}_2)_2\overline{\text{S}}\}]$, (III) and finally, (iv) the thione bond was cleaved and both fragments were used by the metalcarbonyl to yield the major product, $[\text{Fe}_3(\text{CO})_9\{\mu_3\text{-}\overline{\text{CS}}(\text{CH}_2)_2\overline{\text{S}}\}(\mu_3\text{-S})]$, (IV). A single crystal X-ray study of IV revealed that a dithiocarbene ligand caps an open iron triangle by forming a methylene bridge between two iron atoms and links up with the third iron atom via a sulphur atom.

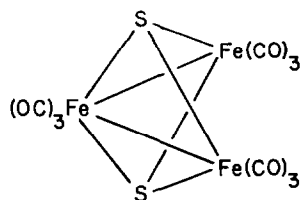
The recent preparation of a number of chromium complexes containing bivalent sulphur donor-atoms by formal S-insertion into metal–carbene bonds [2,3], prompted a study of formal S extrusion and desulphurization reactions. We describe here the isolation and characterization of four products, (I–IV), obtained from $[\text{Cr}(\text{CO})_5\{\text{SCS}(\text{CH}_2)_2\text{S}\}]$ and $[\text{Fe}(\text{CO})_5]$. The main product and title compound IV, is of special interest because (i) it is the first example of a Fe_3 system which contains

* For part IX see Ref. 1.

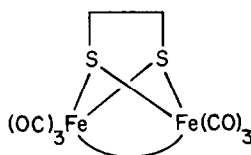
a bridging dithiocarbene ligand; (ii) its structure differs from the symmetrical one proposed for a tri-iron product obtained from the reactions of $[\text{Fe}(\text{CO})_5]$ and 1,3-dioxolane-2-ylids [4]; (iii) this type of product has not been isolated in elaborate studies of reactions between different thione derivatives and $[\text{Fe}_2(\text{CO})_9]$ [5]; (iv) μ -methylene complexes are of current interest in catalysis-related problems [6].

Results and discussion

Irradiation of $[\text{Cr}(\text{CO})_5\{\overline{\text{SCS}(\text{CH}_2)_2\text{S}}\}]$ with an excess of $[\text{Fe}(\text{CO})_5]$ in thf (tetrahydrofuran) at room temperature for 7 h, afforded a series of compounds (tlc), four of which were obtained analytically pure by column chromatography (SiO_2) and crystallization (yields 4–14%). All the compounds are air-stable in the solid state and in solution. They are soluble in hexane, more so in polar solvents such as CHCl_3 and acetone. It has previously been reported, however, that the reaction between $[\text{Fe}(\text{CO})_5]$ and $[\text{W}(\text{CO})_5\{\overline{\text{SCS}(\text{CH}_2)_2\text{S}}\}]$ yielded no new products [7]. The formulation of the structures of the previously described compounds $[\text{Fe}_3(\text{CO})_9(\mu_3\text{S})_2]$, (I) [8], and $[\text{Fe}_2(\text{CO})_6\{\mu\text{-S}(\text{CH}_2)_2\text{S}\}]$, (II) [9], was based on their spectroscopic properties as well as on elemental analysis for II.

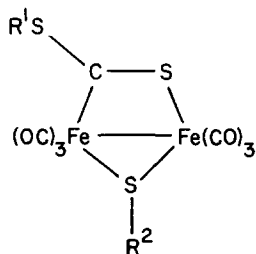


(I)



(II)

The composition of the third compound, (III), was established by elemental analysis and mass spectrometry to be $\text{Fe}_2\text{C}_9\text{H}_4\text{O}_6\text{S}_3$. The latter measurement also indicated the presence of six carbonyl ligands. These CO groups are terminally bound, with $\nu(\text{CO})$ frequencies between 1971 and 2070 cm^{-1} . During the reaction of open-chain trithiocarbonates and $[\text{Fe}_2(\text{CO})_9]$, a carbon-sulphur bond is broken and products of type **A** are formed [5a], but such a conversion is not feasible for the cyclic trithione $\overline{\text{SCS}(\text{CH}_2)_2\text{S}}$ under discussion.



(A)

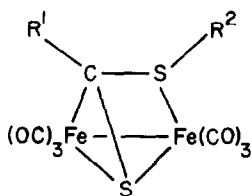
The limiting low-temperature ^{13}C -NMR spectrum of III at about 180 K has six sharp signals in the terminal carbonyl region (Table 1). As the temperature is raised,

TABLE 1
 ^{13}C AND ^1H NMR DATA FOR THE NEW COMPOUNDS III AND IV ^a

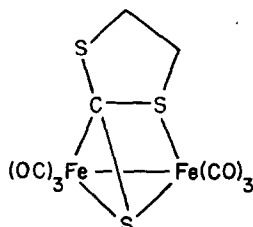
	Temperature (K)	III	IV
^{13}C NMR (CD_2Cl_2)	303	38.6 (CH_2), 50.1 (CH_2), 75.4 (CS), 208.9 br (3CO), 211.1 (3CO)	42.0 (CH_2), 45.9 (CH_2), 127.3 ($\mu\text{-C}$), 207.1 (6CO), 210.2 (3CO)
	180	$\delta(\text{CH}_2)$ and $\delta(\text{CS})$ unchanged, 204.5, 207.3, 207.8, 209.2, 230.0, 215.3 (6CO)	$\delta(\text{CH}_2)$ and $\delta(\mu\text{-C})$ unchanged, 201.7, 203.6, 207.0, 207.1, 207.4, 207.9 (6CO)
^1H NMR (CDCl_3)	303	2.3–2.8 m, 3.1–3.6 m (CH_2)	3.68–3.82 m (CH_2)

^a Chemical shifts (δ) in ppm, relative to SiMe_4 .

they coalesce and at 303 K one sharp and one broad signal remain. At this temperature, other carbon resonances are present at δ 75.4, 50.1 and 38.6 ppm (relative to internal SiMe_4). The latter two were assigned to the neighbouring sp^3 carbon atoms of the ligand, whereas the first resonance has to be due to the original thione carbon atom, suggesting appreciable rehybridization towards less s -character. This value corresponds well with the δ 70 ppm resonance obtained for the carbon atom in the compound-type B afforded by reaction of dithioesters, $\text{R}^1\text{C}(\text{S})\text{SR}^2$ and $[\text{Fe}_2(\text{CO})_9]$ [5b]. It is reasonable, therefore, to ascribe a similar structure C to III. This type of structure is consistent also with the other spectroscopic data mentioned above. In known compounds of type B, however, all the carbonyl ligands are



(B)

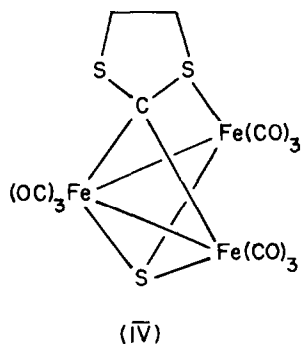


(C)

equivalent at room temperature, whereas no scrambling of the carbonyls between the two different metal atoms occurs in III and the ^{13}C NMR spectrum shows two resonances, each assignable to three carbonyl groups.

The complex ^1H NMR signals at δ 2.3–2.8 and 3.1–3.6 ppm (Table 1) were associated with the ring protons of the ligand. Stereoisomerism of the chiral sulphur atom bonded to only one iron atom in C, could explain the presence of these two clearly separated multiplets, because the structural alteration caused by inversion of the configuration completely changes the chemical environment of all the protons. Inversion of configuration at the chiral carbon atom, in solution, does not lead to such a dramatic change but could explain the finer splitting within each main signal. To obtain a clear picture of the bonding in III, an X-ray crystal-structure determination is intended.

Compound IV was isolated as crystalline material and partly characterized by elemental analysis (see Experimental) and spectroscopic methods. The detailed bonding pattern was finally revealed by X-ray crystallography (see below). The mass spectrum of compound IV showed the loss of nine carbonyl groups from the molecular ion ($m/z = 556$) as well as signals corresponding to Fe_3S_2^+ and Fe_2S^+ .



The ^{13}C NMR spectrum of IV at room temperature (Table 1) showed a single resonance for a μ -methylene carbon atom at δ 127.3 ppm [6]. Only two resonances, a sharp singlet at δ 210.2 and a broad one at δ 207.1 ppm were observed in the terminal CO region, indicating that the CO ligands were undergoing site exchange. The broad signal implies a slowing down, even at this temperature, of the fluxional process which presumably involves site exchange between the two outer $\text{Fe}(\text{CO})_3$ moieties of the iron triangle [10]. Similar broadening of the comparable peaks for $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-S})(\mu_3\text{-Te})]$ and $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-Te})_2]$ was observed at 294 and 288 K respectively [11]. The resonance at δ 210.2 ppm is assigned to the rotating seven-coordinated $\text{Fe}(\text{CO})_3$ group in the centre.

The dynamic behaviour is further restrained by a decrease in temperature (Fig. 1) and at about 233 K the original broad resonance is replaced by six sharp signals between δ 208.3 and 202.2 ppm. The peak at δ 210.2 ppm also broadens with decrease in temperature and, eventually, at about 180 K, collapses. Measurements at lower temperatures, where the two or three contributing resonances should appear, were not taken. Milone and coworkers [11] have shown that the same two-step restriction of carbonyl fluxionality in compounds of the types $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-X})(\mu_3\text{-Y})]$ ($\text{X} = \text{S}$, $\text{Y} = \text{Te}$) and $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-X})_2]$ ($\text{X} = \text{NMe}$, S , Se , Te), occurs at lower temperatures, indicating a lower energy barrier to carbonyl exchange for these complexes. In the ^1H NMR spectrum, the CH_2 protons of the ligand give rise to a finely-split multiplet at δ 3.68–3.82 ppm, indicating asymmetry within the molecule.

In order to confirm the above deductions and to establish the mode of coordination when the $\text{CS}(\text{CH}_2)_2\text{S}$ ligand acts as a 4-electron donor, a single-crystal X-ray diffraction study of IV was carried out. This complex crystallizes as discrete molecules with no meaningful interatomic contacts. A perspective view of a single molecule, together with the atomic numbering scheme adopted, is given in Fig. 2 while Fig. 3 provides a stereoscopic view of the entire molecule. It is very similar to I [8], in which the four-electron donor is a sulphur atom instead of the more complicated thiocarbene ligand. The carbene carbon atom bridges two iron atoms, while a sulphur atom of the ligand donates two electrons to the third iron atom of the open triangle. The cluster belongs to the $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-X})(\mu_3\text{-Y})]$ class of

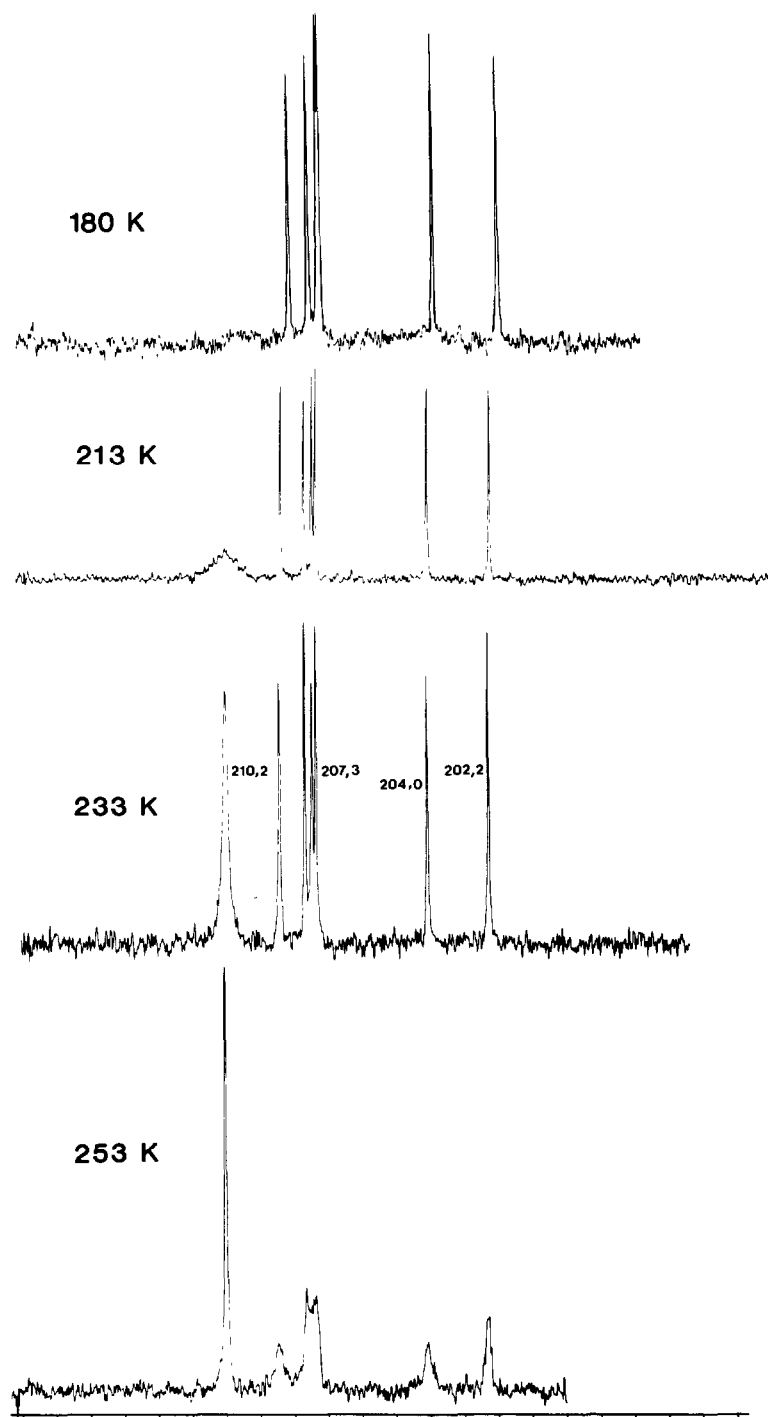


Fig. 1. ^{13}C -NMR spectra of $[\text{Fe}_3(\text{CO})_9(\text{CS}(\text{CH}_2)_2\text{S})]$ (IV), at different temperatures in the terminal CO region.

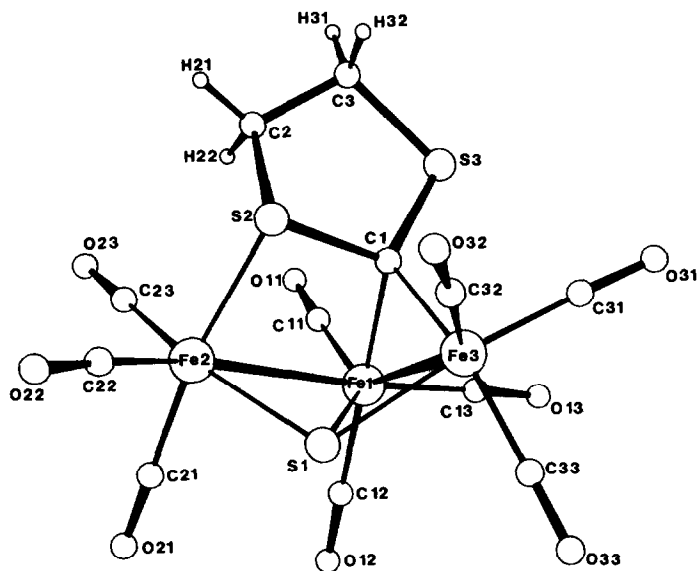


Fig. 2. Labelling of all atoms within the $[\text{Fe}_3(\text{CO})_9\{\overline{\text{CS}(\text{CH}_2)_2\text{S}}\}]$ complex.

compounds, but differs from previous examples in that X is a two-atom donor ligand. Bond distances and angles are given in Tables 2 and 3.

The feature that most clearly manifests the diatomic nature of the μ_3 -bridge is the widening of the Fe(3)–Fe(1)–Fe(2) angle to a relatively large $91.4(1)^\circ$. In other $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-X})(\mu_3\text{-Y})]$ clusters, the angle ranges from $78.3(2)^\circ$ for X = S, Y = $\text{NC}_6\text{H}_4\text{Me-}p$ [12] to $82.8(1)^\circ$ for X = S, Y = PPh [13]. Noteworthy is the difference in bond lengths between the iron atoms {2.681(1) Å for Fe(1)–Fe(2) and 2.572(1) Å

TABLE 2
BOND DISTANCES (Å)

Fe(1)–Fe(2)	2.681(1)	S(2)–C(2)	1.825(5)
Fe(1)–Fe(3)	2.572(1)	S(3)–C(1)	1.784(4)
Fe(1)–S(1)	2.228(1)	S(3)–C(3)	1.805(5)
Fe(1)–C(1)	2.080(4)	C(2)–C(3)	1.487(8)
Fe(1)–C(11)	1.795(5)	C(11)–O(11)	1.139(6)
Fe(1)–C(12)	1.811(5)	C(12)–O(12)	1.142(6)
Fe(1)–C(13)	1.784(5)	C(13)–O(13)	1.135(6)
Fe(2)–S(1)	2.244(1)	C(21)–O(21)	1.134(6)
Fe(2)–S(2)	2.275(1)	C(22)–O(22)	1.127(6)
Fe(2)–C(21)	1.800(5)	C(23)–O(23)	1.131(6)
Fe(2)–C(22)	1.813(5)	C(31)–O(31)	1.135(6)
Fe(2)–C(23)	1.801(5)	C(32)–O(32)	1.139(6)
Fe(2)–S(1)	2.228(1)	C(33)–O(33)	1.127(6)
Fe(3)–C(1)	1.965(4)	C(2)–H(21)	0.98(4)
Fe(2)–C(31)	1.805(5)	C(2)–H(22)	1.00(5)
Fe(3)–C(32)	1.768(5)	C(3)–H(31)	0.99(5)
Fe(3)–C(33)	1.841(4)	C(3)–H(32)	0.83(6)
S(2)–C(1)	1.793(4)		

for Fe(1)–Fe(3)}. Both the Fe–Fe and Fe–C bond lengths in the methylene-containing metallocycle are comparable with those observed for similar bonding units [6].

The configurations of the carbonyl ligands about Fe(2) and Fe(3) are approximately octahedral, but the remaining ligands completely distort this symmetry. Neither the Fe–S(1) bond distances nor the Fe(1)–S(1)–Fe(2) and Fe(1)–S(1)–Fe(3) angles differ markedly from observed values in other $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-X})(\mu_3\text{-Y})]$ com-

TABLE 3
BOND ANGLES (degrees)

<i>Angles around Fe(1)</i>						
	Fe(2)	Fe(3)	S(1)	C(1)	C(11)	C(12)
Fe(3)	91.4(0)					
S(1)	53.4(0)	54.8(0)				
C(1)	77.5(1)	48.5(1)	82.2(1)			
C(11)	86.5(1)	136.1(1)	139.9(1)	88.5(2)		
C(12)	97.5(1)	124.6(1)	88.6(1)	170.8(2)	99.1(2)	
C(13)	170.7(2)	79.8(1)	121.7(1)	94.2(2)	97.8(2)	90.0(2)
<i>Angles around Fe(2)</i>						
	Fe(1)	S(1)	S(2)	C(21)	C(22)	
S(1)	52.9(0)					
S(2)	78.2(0)	87.2(0)				
C(21)	93.0(1)	85.9(1)	171.0(1)			
C(22)	151.1(1)	99.2(1)	94.8(1)	91.9(2)		
C(23)	106.7(1)	159.2(1)	92.1(2)	92.4(2)	101.5(2)	
<i>Angles around Fe(3)</i>						
	Fe(1)	S(1)	C(1)	C(31)	C(32)	
S(1)	54.7(0)					
C(1)	52.5(1)	84.8(1)				
C(31)	114.7(1)	166.9(1)	94.0(2)			
C(32)	138.5(1)	99.1(1)	98.6(2)	94.0(2)		
C(33)	108.7(1)	85.9(1)	160.9(2)	91.3(2)	99.3(2)	
<i>Angles around C(1)</i>						
	Fe(1)	Fe(3)	S(2)			
Fe(3)	78.9(1)					
S(2)	108.2(2)	113.3(2)				
S(3)	123.1(2)	122.9(2)	107.7(2)			
<i>Other angles</i>						
Fe(2)–S(1)–Fe(1)		73.7(0)	O(11)–C(11)–Fe(1)			177.2(4)
Fe(3)–S(1)–Fe(1)		70.5(0)	O(12)–C(12)–Fe(1)			178.0(4)
Fe(3)–S(1)–Fe(2)		114.4(0)	O(13)–C(13)–Fe(1)			173.6(4)
C(1)–S(2)–Fe(2)		95.0(1)	O(21)–C(21)–Fe(2)			178.7(5)
C(2)–S(2)–Fe(2)		115.6(2)	O(22)–C(22)–Fe(2)			175.9(4)
C(2)–S(2)–C(1)		97.1(2)	O(23)–C(23)–Fe(2)			179.4(4)
C(3)–S(3)–C(1)		99.9(2)	O(31)–C(31)–Fe(3)			175.6(4)
C(3)–C(2)–S(2)		105.7(4)	O(32)–C(32)–Fe(3)			176.6(4)
C(2)–C(3)–S(3)		109.6(4)	O(33)–C(33)–Fe(3)			179.0(4)

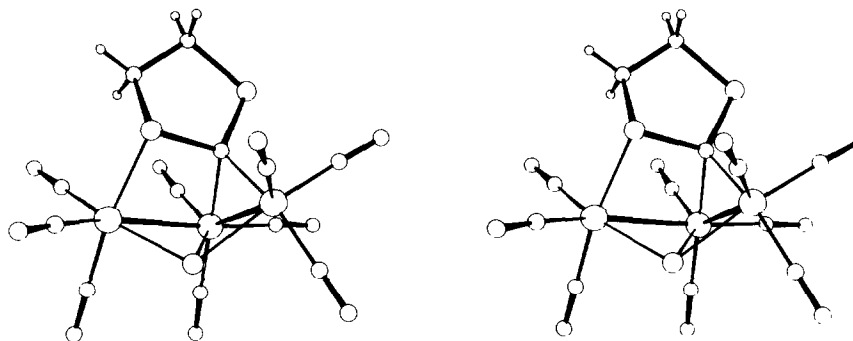


Fig. 3. Stereoscopic view of the tri-iron cluster, $[\text{Fe}_3(\text{CO})_9(\overline{\text{CS}(\text{CH}_2)_2\text{S}})\text{S}]$.

plexes [12,13]. The S–C–S angle of the heterocyclic ring in IV $\{197.7(1)^\circ\}$ is slightly smaller than the corresponding angle of other methylene bridges [6], and differs considerably from the original $114.7(2)^\circ$ in the thione compound, $\overline{\text{SCS}(\text{CH}_2)_2\text{S}}$ [14]. Although the C(1)–S bonds of IV are somewhat longer than in the free ligand, the other bond distances remain essentially unchanged.

Experimental

All solvents were dried and freshly distilled before use and all manipulations carried out under nitrogen, using Schlenk-tube techniques. Commercial $[\text{Fe}(\text{CO})_5]$ (Merck) was used without purification. $[\text{Cr}(\text{CO})_5\{\overline{\text{SCS}(\text{CH}_2)_2\text{S}}\}]$ was prepared by a literature method [7]. Yield 44.7% red plates, m.p. 115°C (dec.). ^1H NMR (CDCl_3): δ (ppm) 3.98 (s, $(\text{CH}_2)_2$), IR (hexane) $\nu(\text{CO})$ (cm^{-1}): 2070w, 1950s, 1934m. MS: m/z 328 M^+ . Analysis, Found: Cr, 16.0; C, 29.02; H, 1.28. $\text{CrC}_8\text{H}_4\text{O}_5\text{S}_3$ calcd.: Cr, 15.84; C, 29.27; H, 1.28%.

Mass spectra were recorded on a Hitachi Perkin–Elmer RMU-6H spectrometer (70 eV), ^1H NMR spectra on a Bruker WP-80, infrared spectra on a Perkin–Elmer 237 and ^{13}C NMR spectra on a Bruker WP 20. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. Elemental analyses were carried out by the Mikroanalytisches Labor, Bonn. An Engelhard-Hanovia mercury vapour lamp, enclosed in a watercooled quartz jacket during irradiation, was used for photochemical reactions.

Preparation of compounds I–IV

Irradiation of $[\text{Cr}(\text{CO})_5\{\overline{\text{SCS}(\text{CH}_2)_2\text{S}}\}]$ (0.98 g, 3 mmol) and $[\text{Fe}(\text{CO})_5]$ (2.35 g, 12 mmol) in thf solution for 7 h yielded a mixture of products which were separated by column chromatography (SiO_2 , -20°C , CH_2Cl_2 /hexane, 1/7) and crystallized from CH_2Cl_2 /pentane (-30°C). The yields, melting points and analytical data for the compounds thus isolated in pure form, are given in Table 4. IR (hexane) $\nu(\text{CO})$ (cm^{-1}): III, 2070m, 2037s, 2003s, 1988s, 1978m, 1971m; IV, 2073w, 2053s, 2030vs, 2007s, 1993m, 1978w, 1973w(sh).

Structure determination

A crystal with dimensions $0.23\text{ mm} \times 0.28\text{ mm} \times 0.35\text{ mm}$ was selected for X-ray

TABLE 4
YIELDS, MELTING POINTS AND ANALYTICAL DATA OF COMPOUNDS I-IV

Compound	Yield (%)	M.p. (°C)	Analysis (Found (calcd.) (%))			
			Fe	C	H	S
I	8.3, red needles	113–114				
II	4.2, orange needles	74–76	30.9 (30.03)	25.86 (25.83)	1.22 (1.08)	16.9 (17.24)
III	7.5, red prisms	101–102	26.5 (26.85)	25.96 (25.98)	1.02 (0.97)	22.6 (23.12)
IV	13.5, black prisms	120(dec.)		26.09 (25.93)	0.87 (0.73)	

analysis. Crystal data and details of the data collection are given in Table 5. The crystal structure was determined by direct methods and refined by least-squares techniques using the computer program SHELX-76 [15]. All non-hydrogen atoms were refined anisotropically. All four hydrogens could be placed from difference maps and were refined with individual isotropic thermal parameters. ($1/\sigma_p^2$) weights were used during refinement which converged with $R = 0.039$ and $R_w = 0.031$. A final difference map contained no residual electron density higher than $0.3 \text{ e}\text{\AA}^{-3}$. Final atomic coordinates are listed in Table 6. Tables of observed and calculated structure factors and anisotropic thermal parameters are available upon request from the authors (GJK).

TABLE 5
EXPERIMENTAL DETAILS FOR X-RAY ANALYSIS

Crystal data

Cell: a 16.549(8) Å Crystal system: monoclinic
 b 11.301(6) Å Space group $P2_1/n$
 c 9.919(5) Å $Z = 4$
 β 94.66(9)°

Molecular formula $\text{Fe}_3\text{C}_{12}\text{H}_4\text{O}_9\text{S}_3$

Molecular mass 555.9

Calculated density 1.98 g cm^{-3}

Data collection

Four circle diffractometer: PW 1100

Radiation: graphite monochromated Mo- K_α

Wavelength 0.7107 Å

Scan mode $\omega - 2\theta$

Scan width 1.2°

Scan speed $0.04^\circ \text{ s}^{-1}$

Angular range $\theta = 3\text{--}23^\circ$

Number of reflections:

Total = 2614

Unobserved ($I > 2\sigma$) = 603

TABLE 6
ATOMIC COORDINATES

Atom	x	y	z
Fe(1)	0.27708(3)	0.23964(5)	0.62031(6)
Fe(2)	0.41144(3)	0.33662(5)	0.74316(6)
Fe(3)	0.26292(3)	0.40979(5)	0.44775(6)
S(1)	0.29694(6)	0.43048(9)	0.6685(1)
S(2)	0.44257(6)	0.3300(1)	0.5241(1)
S(3)	0.35674(7)	0.1831(1)	0.3215(1)
C(1)	0.3438(2)	0.2822(3)	0.4582(4)
C(2)	0.4980(3)	0.1988(5)	0.4764(5)
C(3)	0.4658(3)	0.1703(6)	0.3358(6)
C(11)	0.3302(2)	0.1012(4)	0.6343(4)
O(11)	0.3627(2)	0.0123(3)	0.6380(4)
C(12)	0.2199(3)	0.2278(4)	0.7679(5)
O(12)	0.1823(2)	0.2227(3)	0.8593(4)
C(13)	0.1908(3)	0.1901(4)	0.5159(5)
O(13)	0.1352(2)	0.1506(4)	0.4581(4)
C(21)	0.3708(3)	0.3372(4)	0.9061(5)
O(21)	0.3454(2)	0.3398(4)	1.0089(4)
C(22)	0.4748(3)	0.4640(4)	0.7869(4)
O(22)	0.5104(2)	0.5460(3)	0.8180(4)
C(23)	0.4795(3)	0.2165(4)	0.7900(5)
O(23)	0.5216(2)	0.1404(3)	0.8196(4)
C(31)	0.2199(3)	0.3675(4)	0.2816(5)
O(31)	0.1917(2)	0.3485(3)	0.1758(3)
C(32)	0.3234(3)	0.5236(4)	0.3863(4)
O(32)	0.3650(2)	0.5962(3)	0.3523(4)
C(33)	0.1720(3)	0.4966(4)	0.4781(4)
O(33)	0.1170(2)	0.5507(3)	0.4979(4)
H(21)	0.554(3)	0.226(4)	0.480(4)
H(22)	0.486(3)	0.130(4)	0.535(4)
H(31)	0.481(3)	0.092(4)	0.302(4)
H(32)	0.485(3)	0.209(5)	0.274(6)

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