

Reaction of $[(OC)_2(cp)FeC(S)SFe(cp)(CO)_2]$ ($cp = \eta^5-C_5H_5$) with Dicobalt Octacarbonyl; X-Ray Crystal Structure of $[Co_3Fe(cp)(CO)_9(CS)]^\dagger$ containing a Six-electron Donor Thiocarbonyl Group

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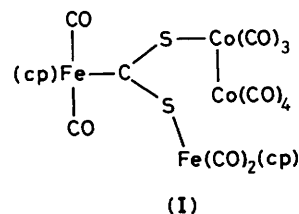
The reaction between $[(OC)_2(cp)FeC(S)SFe(cp)(CO)_2]$ ($cp = \eta^5-C_5H_5$) and $[Co_2(CO)_8]$ produces the novel mixed-metal cluster $[Co_3Fe(cp)(CO)_9(CS)]$ which contains a thiocarbonyl group, and the two known derivatives $[Co_4(CO)_{10}S_2]$ and $[CoFe(cp)(CO)_6]$. This product distribution, which accounts for the fragmentation and desulphurization of the starting dithioester complex, may be seen as occurring *via* an unstable dithiocarbene intermediate. The structure of $[Co_3Fe(cp)(CO)_9(CS)]$ has been determined by X-ray crystallography. The complex crystallizes in the orthorhombic space group *Pbca* (no. 61) with cell constants $a = 16.196(7)$, $b = 12.325(3)$, $c = 18.971(6)$ Å, and $Z = 8$. The structure has been solved from 1 292 reflections collected by counter methods, and refined by least-squares calculations to $R = 0.044$ ($R' = 0.040$). The molecule contains a triangle of Co atoms carrying an external $Fe(cp)(CO)_2$ fragment. The CS group, which lies parallel to the Co_3 triangle, contributes six electrons to the cluster orbitals. The carbon atom of this ligand bridges all metal atoms, while the sulphur atom is bonded only to two Co atoms. The bonding mode of the CS ligand is discussed in terms of σ and π interactions.

Reactions of metal clusters with elemental sulphur or sulphur-containing molecules have been widely studied. Among these significant work has been done on the reactions of dicobalt octacarbonyl (1) with H_2S , RSH , R_2S , CS_2 , $R'OC(S)SR''$, $R'C(S)NR''R'''$, and $R'C(S)SR''$ ($R, R', R'', R''' = H$, alkyl, aryl), which have afforded a number of organometallic complexes containing only sulphur, sulphur and the organic residue, or only the desulphurized starting material.¹⁻⁴

As a part of our research on the chemistry of electron-rich metal dithioesters derived from carbon disulphide⁵⁻⁷ it has been recently reported⁸ that $[Fe(cp)(CO)_2\{C(S)SMe\}]$ ($cp = \eta^5$ -cyclopentadienyl) reacts with $[Co_2(CO)_8]$ to form $[Co_3(CO)_9(CSMe)]$ in which the $MeSC$ fragment is bonded to a triangle of cobalt atoms. Since in analogous reactions organic dithioesters undergo complete desulphurization⁹ to form $[Co_3(CO)_9(CR')]$, we became interested in examining the reaction of $[(OC)_2(cp)FeC(S)SFe(cp)(CO)_2]$ (2) with $[Co_2(CO)_8]$. We now report the results of this investigation and describe the structural characterization of $[Co_3Fe(cp)(CO)_9(CS)]$ which contains a μ_4 -C, μ -S thiocarbonyl group acting as a six-electron donor.

Results and Discussion

Synthesis and Chemical Characterization.—The reaction of the complex $[(OC)_2(cp)FeC(S)SFe(cp)(CO)_2]$ (2) with a six-fold excess of $[Co_2(CO)_8]$ in Et_2O at room temperature yielded three main products after chromatography on an alumina column. Two of them, $[Co_4(CO)_{10}S_2]$ (3) and $[CoFe(cp)(CO)_6]$

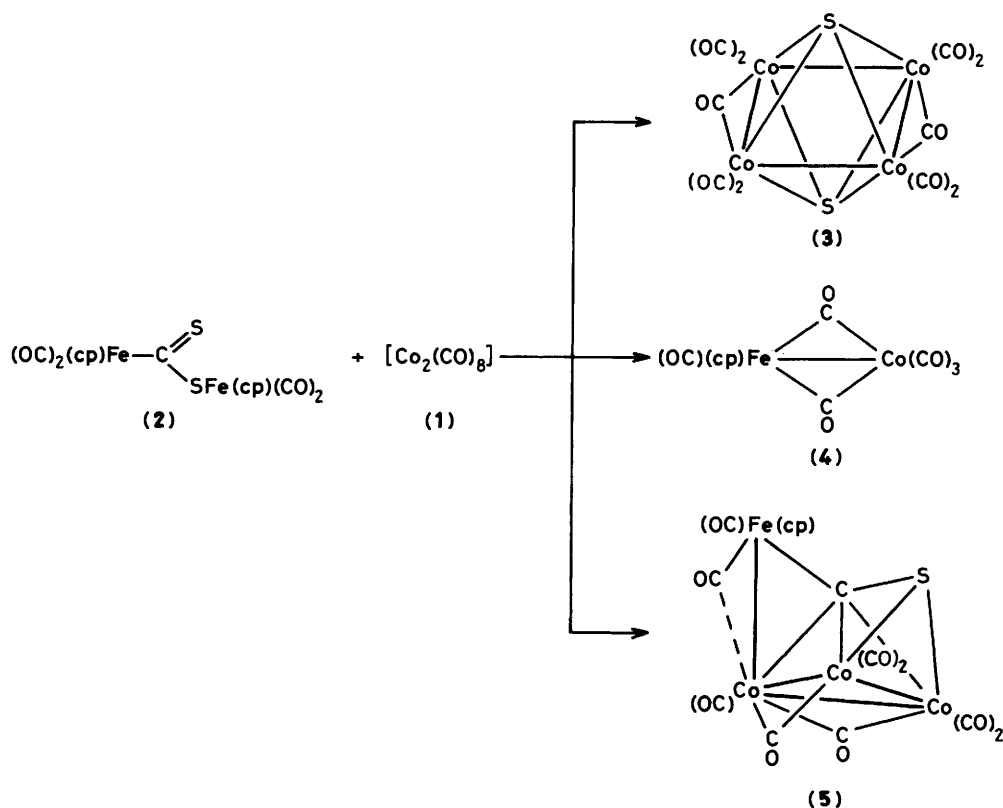


(4), had already been prepared by different routes,^{10,11} so that their nature was established by comparison with the spectral data and physical properties reported previously. Moreover the X-ray diffraction patterns of crystals of compound (3) showed them to be identical with those previously reported.¹⁰ The i.r. spectrum of the third product showed four strong absorptions in the terminal carbonyl region, two medium-weak intensity bands attributable to at least two different kinds of bridging carbonyl groups, and a strong absorption at 920 cm^{-1} which may be due to $\nu(CS)$ of a thiocarbonyl group. The 1H n.m.r. spectrum showed the presence of a C_5H_5 ring (δ 5.03). This, together with analytical data, is indicative of the incorporation of 1 mol of the fragment $Fe(cp)(CO)_2CS$ derived from the precursor (2) per mol of a cobalt-containing cluster. The present X-ray single-crystal diffraction study (see next section) has shown that the mixed-metal cluster $[Co_3Fe(cp)(CO)_9(CS)]$ (5) is formed. The nature and distribution of the products, which differ from those of the analogous reactions between $[Co_2(CO)_8]$ and $[Fe(cp)(CO)_2\{C(S)SMe\}]$ and $R'C(S)SR''$, are shown in Scheme 1.

It is worth pointing out that products (3)–(5) contain the S, $Fe(cp)(CO)_2$, and $Fe(cp)(CO)_2CS$ fragments respectively, of the precursor (2) which are trapped by multisite bonding within the cluster frameworks. This observation may provide an indication of the reaction mechanism. As suggested in the case of desulphurization of organic molecules by organometallic reagents,¹² the initial step of the reaction may involve formation

[†] 1,3 ; 2,3-Di- μ -carbonyl-1,1,2,2,3,4,4-heptacarbonyl-4- η -cyclopentadienyl- μ_4 -[thiocarbonyl-C(Co^{1-3} , Fe^4)S(Co^{1-2})]-tricobaltiron (3 Co - Co , Co^3 - Fe^4).

Supplementary data available (No. SUP 56559, 3 pp.): thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii–xx. Structure factors are available from the editorial office.



Scheme 1.

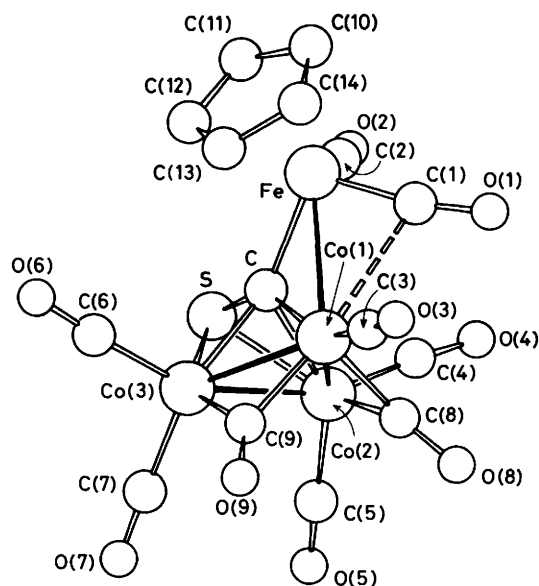


Figure. The structure of $[\text{Co}_3\text{Fe}(\text{cp})(\text{CO})_9(\text{CS})]$ showing the atom labelling

of the unstable complex (I). This dithiocarbene-type intermediate, in contrast with the behaviour of other μ_3 -CS₂ derivatives⁷ which undergo decarbonylation, promotes {in accord with the high thiophilicity of $[\text{Co}_2(\text{CO})_8]$, and with the ease of S-Fe cleavage⁵} fragmentation of the precursor (2) to yield 'S $\text{Co}(\text{CO})_3$ ', 'Fe(cp)(CO)₂', and 'Fe(cp)(CO)₂CS' fragments which react further to form the observed products (3)—(5), respectively.

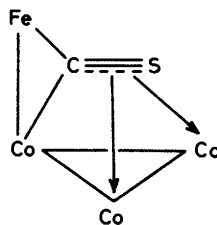
Structural Characterization of $[\text{Co}_3\text{Fe}(\text{cp})(\text{CO})_9(\text{CS})]$.—The molecule contains an open metal-atom polyhedron consisting of a triangle of cobalt atoms and an iron atom bonded to one cobalt atom along a direction nearly orthogonal to the Co₃ plane (Figure). Such an assemblage of metal atoms can be rationalized as a tetrahedron with two missing Co-Fe edges. Of the nine CO ligands, seven are terminal and two edge bridging two Co-Co bonds. The Co-Co bond not bridged by CO is bridged by the S atom. The Co atom linked to the Fe has only one terminal CO. The CS unit lies almost parallel to the Co₃ triangle with the C(CS) atom in the middle bonded to all metal atoms and the S atom externally bonded to Co(2) and Co(3). As most M₄ carbonyl clusters obey the noble-gas rule, their tetrahedra are characterized by 60 valence electrons. In our case the absence of two tetrahedral edges implies an electron count of 64 and the CS ligand is required to act as a six-electron donor.

The main feature of interest is the CS bonding interaction. The only other reported example of a thiocarbonyl-containing cluster in which the CS group behaves as a six-electron donor is in the pentanuclear $[\text{Fe}_5(\text{CO})_{13}(\text{CS})_2]$.¹³ In this case the CS system was almost parallel to a square of metal atoms with C(CS) connected to five and S(CS) connected to two metals. The present molecule shows a similar geometry, although based on a triangular framework. The C-S bond length of 1.69(1) Å (see Table 1) is almost equivalent to the values reported for both the six-electron donor of $[\text{Fe}_5(\text{CO})_{13}(\text{CS})_2][1.71(2) \text{ \AA}]$ ¹³ and for the four-electron donor of $[\text{Fe}_4(\text{CO})_{12}(\text{CS})\text{S}][1.695(5) \text{ \AA}]$.¹⁴ The absence of significant differences between CS acting as a six- or four-electron donor was taken to indicate that there is no multiple-bond interaction. Lack of specific donation from CS orbitals was also supported by the equivalence of all M-C(CS) bond distances, leading to the conclusion that the M-C(CS), M-S(CS), and C-S interactions are largely

Table 1. Selected bond distances (Å) and angles (°) for complex (5) with estimated standard deviations in parentheses

Fe—Co(1)	2.695(2)	Fe—C(1)	1.73(1)	Co(3)—C(9)	1.89(1)	Fe—C(10)	2.07(1)
Co(1)—Co(2)	2.483(2)	Fe—C(2)	1.74(1)	C(1)—O(1)	1.19(2)	Fe—C(11)	2.08(1)
Co(1)—Co(3)	2.476(2)	Co(1)—C(3)	1.71(1)	C(2)—O(2)	1.14(2)	Fe—C(12)	2.09(2)
Co(2)—Co(3)	2.544(2)	Co(1)—C(8)	1.84(1)	C(3)—O(3)	1.17(2)	Fe—C(13)	2.11(1)
Co(2)—S	2.248(3)	Co(1)—C(9)	1.88(1)	C(4)—O(4)	1.16(1)	Fe—C(14)	2.07(2)
Co(3)—S	2.235(3)	Co(2)—C(4)	1.75(1)	C(5)—O(5)	1.14(1)	C(10)—C(11)	1.36(2)
Fe—C	2.03(1)	Co(2)—C(5)	1.78(1)	C(6)—O(6)	1.15(1)	C(10)—C(14)	1.41(2)
Co(1)—C	1.90(1)	Co(2)—C(8)	1.97(1)	C(7)—O(7)	1.13(2)	C(11)—C(12)	1.37(2)
Co(2)—C	2.01(1)	Co(3)—C(6)	1.77(1)	C(8)—O(8)	1.18(1)	C(12)—C(13)	1.35(2)
Co(3)—C	2.03(1)	Co(3)—C(7)	1.78(1)	C(9)—O(9)	1.19(1)	C(13)—C(14)	1.39(2)
S—C	1.69(1)						
Fe—Co(1)—Co(3)	96.1(1)	Co(2)—S—Co(3)	69.2(1)	Co(2)—S—C	59.5(3)	Co(3)—C(6)—O(6)	175(1)
Fe—Co(1)—Co(2)	91.2(1)	Co(1)—Co(2)—S	92.3(1)	Fe—C(1)—O(1)	171(1)	Co(3)—C(7)—O(7)	178(1)
Co(2)—Co(1)—Co(3)	61.7(1)	Co(3)—Co(2)—S	55.2(1)	Fe—C(2)—O(2)	174(1)	Co(2)—C(8)—O(8)	135(1)
Co(1)—Co(3)—Co(2)	59.3(1)	Co(2)—Co(3)—S	55.7(1)	Co(1)—C(3)—O(3)	176(1)	Co(1)—C(8)—O(8)	144(1)
Co(1)—Co(2)—Co(3)	59.0(1)	Co(1)—Co(3)—S	92.8(1)	Co(2)—C(4)—O(4)	176(1)	Co(3)—C(9)—O(9)	140(1)
Fe—C—S	129.9(6)	Co(3)—S—C	60.3(3)	Co(2)—C(5)—O(5)	175(1)	Co(1)—C(9)—O(9)	138(1)
Co(1)—C—S	144(1)						

independent.¹⁵ However, in the present case, M—C(CS) interactions are far from being equivalent, the distance to Co(1) [1.90(1) Å] being shorter than those to the other two Co atoms [mean 2.02(1) Å]. A different situation could be envisaged by considering the thiocarbonyl group as bridging the Co—Fe bond and undergoing an η^2 interaction with the other two Co atoms. The S—C—Fe angle [129.9(6)°] is in agreement with a sp^2 -hybridized C(CS) carbon atom and longer Co—C distances would be expected for a π -type interaction. A similar bonding



mode can be found in some alkyne and acetylide derivatives such as $[\text{Fe}_3(\text{CO})_9(\text{C}_2\text{Ph}_2)]$ ¹⁶ and $[\text{Ru}_3\text{H}(\text{CO})_9(\text{C}_2\text{Bu}^t)]$ ¹⁷ where both the C_2Ph_2 and the C_2Bu^t bond in a μ_3 - η^2 fashion to three metal centres by formally contributing six and five electrons, respectively. Finally it is interesting that, while the Fe atom is electron rich, formally receiving 11 electrons from the ligands, Co(1) has 17 electrons. Such an uneven charge distribution is partially alleviated by sharing C(1)—O(1) with Co(1) through semi-bridging [Co(1)—C(1) 2.669(3) Å; Fe—C(1)—O(1) 171(1)°, mean M—C—O (M = Fe or Co) 176(1)°].

All remaining M—C(CO) and C—O interactions are within the range of other values for neutral carbonyl clusters of Co and Fe.

Experimental

The reactions were carried out by using standard Schlenk techniques under a nitrogen atmosphere. Solvents were distilled under N_2 over an appropriate drying agent immediately prior to use. The complex $[\text{Co}_2(\text{CO})_8]$ was used without further purification and $[(\text{OC})_2(\text{cp})\text{Fe}(\text{S})\text{SFe}(\text{cp})(\text{CO})_2]$ was prepared as reported previously.⁵ Infrared spectra were recorded on a Perkin-Elmer 983G spectrophotometer, ¹H n.m.r. on a Varian XL 100 instrument using SiMe_4 as internal standard, and mass spectra on a JEOL JMS-D100 spectrometer working

at 75 eV (*ca.* 1.20×10^{-17} J). Microanalyses were by Pascher Microanalytical Laboratorium (Bonn, Germany).

Syntheses of the Complexes.—Complex (2) (0.250 g, 0.58 mmol) was dissolved in Et_2O (30 cm^3) and a diethyl ether solution containing $[\text{Co}_2(\text{CO})_8]$ (1) (1.190 g, 3.48 mmol) was added by use of a syringe. The reaction mixture was allowed to stir for 1 h at room temperature until the initial gas evolution (CO) had stopped. The mixture was evaporated to dryness under high vacuum for a few hours to eliminate the unreacted $[\text{Co}_2(\text{CO})_8]$. Chromatography of the residue on an alumina column eluting with CH_2Cl_2 –light petroleum (b.p. 40–70 °C) (1:8) afforded a broad violet-red band which yielded about 12% (0.040 g) of $[\text{Co}_4(\text{CO})_{10}\text{S}_2]$ (3), purified by crystallization from CH_2Cl_2 at –20 °C and identified by its i.r. spectra: $\nu_{\text{max.}}(\text{CO})$ (n-heptane): 2 053vs, 2 042m, 2 028s, 1 990vw, and 1 895m cm^{-1} (Found: C, 20.2; S, 11.5. Calc. for $\text{C}_{10}\text{Co}_4\text{O}_{10}\text{S}_2$: C, 20.7; S, 11.05%). Further elution with CH_2Cl_2 –light petroleum (1:4) gave the most abundant deep red fraction from which $[\text{CoFe}(\text{cp})(\text{CO})_6]$ (4) was collected, purified by sublimation (36 °C; 0.2 mmHg, *ca.* 27 Pa), and subsequent crystallization from pentane solutions at –20 °C (0.042 g, 21%; m.p. 52–53 °C; $\nu_{\text{max.}}(\text{CO})$ (cyclohexane): 2 061s, 2 006s, 1 987m, 1 971s, 1 949w, and 1 821w cm^{-1} ; $\delta(\text{CDCl}_3)$ 4.93 (5 H, s, C_5H_5) (Found: C, 38.2; H, 2.15. Calc. for $\text{C}_{11}\text{H}_5\text{CoFeO}_6$: C, 37.95; H, 1.45%; m/z 348 (M^+). Finally elution with CH_2Cl_2 –light petroleum (1:1) gave a dark fraction of $[\text{Co}_3\text{Fe}(\text{cp})(\text{CO})_9(\text{CS})]$ (5) which was evaporated to dryness and crystallized from CH_2Cl_2 –light petroleum at 0 °C, affording dark red crystals suitable for X-ray crystallographic determination (0.062 g, 18%; m.p. 122–125 °C (decomp.); $\nu_{\text{max.}}(\text{CO})$ (CH_2Cl_2): 2 067s, 2 035vs, 2 021(sh), 2 003s, 1 843m, and 1 817mw cm^{-1} ; $\nu_{\text{max.}}(\text{CS})$ (KBr) 910ms cm^{-1} ; $\delta(\text{CDCl}_3)$ 5.03 (5 H, s, C_5H_5) (Found: C, 30.6; H, 1.20; S, 5.35. Calc. for $\text{C}_{15}\text{H}_5\text{Co}_3\text{FeO}_9\text{S}$: C, 30.35; H, 0.85; S, 5.40%). At the top of the column much decomposition occurred, partly during the reaction, partly due to the instability of the second and third fractions; in addition, traces of the first fraction, because of its low solubility, were retained on the column and could be eluted with acetone.

Crystallography.—The complex $[\text{Co}_3\text{Fe}(\text{cp})(\text{CO})_9(\text{CS})]$ crystallizes in two polymorphic modifications (A) and (B).

Crystal data. (A), monoclinic, $a = 8.837(2)$, $b = 9.548(1)$, $c = 23.259(4)$ Å, $\beta = 103.68(2)^\circ$, $U = 1 906.7$ Å³, $Z = 4$, $D_c = 2.07$ g cm^{-3} , space group $P2_1/c$ (no. 14), Mo- K_α radiation, $\lambda = 0.710 69$ Å, $\mu(\text{Mo}-K_\alpha) = 34.59$ cm^{-1} , $F(000) = 1 160$.

Table 2. Fractional atomic co-ordinates for complex (5)

Atom	x	y	z	Atom	x	y	z
Fe	0.372 54(11)	0.299 13(13)	0.483 69(8)	O(5)	0.359 5(5)	0.514 5(7)	0.165 8(5)
Co(1)	0.378 75(10)	0.226 41(12)	0.349 80(7)	C(6)	0.160 1(8)	0.253 9(10)	0.355 1(6)
Co(2)	0.381 73(10)	0.414 97(12)	0.303 85(7)	O(6)	0.104 4(6)	0.223 0(7)	0.386 8(5)
Co(3)	0.247 00(10)	0.309 54(12)	0.311 53(7)	C(7)	0.203 1(8)	0.344 4(10)	0.228 3(7)
S	0.272 4(2)	0.463 8(2)	0.369 6(1)	O(7)	0.176 2(6)	0.364 3(7)	0.174 6(4)
C	0.326 8(6)	0.350 5(8)	0.389 5(5)	C(8)	0.448 5(7)	0.285 0(10)	0.283 6(6)
C(1)	0.471 0(8)	0.262 6(11)	0.457 4(6)	O(8)	0.503 5(6)	0.265 4(7)	0.245 1(5)
O(1)	0.541 8(6)	0.240 5(8)	0.448 8(5)	C(9)	0.301 2(7)	0.181 3(9)	0.282 2(6)
C(2)	0.398 8(8)	0.435 4(11)	0.494 9(6)	O(9)	0.295 2(5)	0.112 5(7)	0.238 7(4)
O(2)	0.408 7(5)	0.526 5(7)	0.501 8(5)	C(10)	0.372 6(9)	0.243 0(11)	0.586 6(7)
C(3)	0.421 9(8)	0.099 7(12)	0.355 1(7)	C(11)	0.306 3(9)	0.309 8(12)	0.577 4(7)
O(3)	0.449 2(7)	0.012 3(9)	0.362 3(5)	C(12)	0.255 7(10)	0.267 7(12)	0.526 2(7)
C(4)	0.467 6(7)	0.490 6(10)	0.330 6(6)	C(13)	0.288 5(9)	0.172 8(12)	0.504 8(7)
O(4)	0.526 8(6)	0.538 1(8)	0.345 6(5)	C(14)	0.362 8(10)	0.155 3(13)	0.539 8(7)
C(5)	0.368 1(8)	0.471 6(10)	0.218 6(6)				

(B), orthorhombic, $a = 16.196(7)$, $b = 12.325(3)$, $c = 18.971(6)$ Å, $U = 3 786.9$ Å³, $Z = 8$, $D_c = 2.085$ g cm⁻³, space group $Pbca$ (no. 61), Mo- K_α radiation, $\lambda = 0.710 69$ Å, $\mu(\text{Mo-}K_\alpha) = 34.86$ cm⁻¹, $F(000) = 2 320$.

The first data set was collected on a dark red crystal of approximate dimensions $0.1 \times 0.05 \times 0.2$ mm in the monoclinic space group $P2_1/c$ [see (A)] on an Enraf-Nonius CAD4 diffractometer. Fast decay under X-ray exposure was detected and the data collection had to be terminated. Nonetheless, positional parameters for the metal atoms, the CS ligand, part of the CO ligands, and for a poorly defined image of the C₅H₅ ligand could be obtained. Refinement to $R = 0.13$ was carried out on 629 reflections [$F_o > 5 \sigma(F_o)$]. A new attempt to collect a more reliable data set was subsequently made on a fresh crystal of dimensions $0.2 \times 0.05 \times 0.3$ mm and the crystal system was found to be orthorhombic. The space group $Pbca$ (no. 61) was chosen on the basis of systematic absences and confirmed by successful refinement of the structure. Because of the identity of the two structure models, the first was abandoned and all molecular features discussed herein are based only on the second, far better, data set. For the latter, 2 821 reflection intensities were collected on the same diffractometer, in the range $2.5 < \theta < 28^\circ$ by the ω - 2θ scan method. The scan angle was $0.6 + 0.35\text{tg}\theta^\circ$ and a prescan acceptance parameter was set equal to $\sigma(I)/I = 0.5$; the final required $\sigma(I)/I$ was set equal to 0.01 in a maximum time of 120 s. The structure was solved by direct methods, which revealed the position of the metal atoms. Subsequent Fourier difference maps afforded positions for all light atoms. Refinement was carried out on 1 292 independent reflections [$F_o > 4\sigma(F_o)$] by the full-matrix least-squares method. The Co, Fe, and S atoms were allowed to vibrate anisotropically, all other atoms isotropically. Hydrogen atoms of the C₅H₅ ligand were added in calculated positions and not refined. The refinement converged to $R = 0.044$ and $R' = 0.040$. The weighting scheme employed was $w = k/[\sigma^2(F) + |g|F^2]$ where both k and g were refined (2.35 and 0.000 17, respectively). For all calculations the SHELX¹⁸ package of crystallographic programs was used. Final positional parameters are reported in Table 2.

Acknowledgements

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References

- 1 L. Marko', G. Bor, E. Klumpp, B. Marko', and G. Almasy, *Chem. Ber.*, 1963, **96**, 955.
- 2 D. L. Stevenson, V. R. Magnuson, and L. F. Dahl, *J. Am. Chem. Soc.*, 1967, **89**, 3727 and refs. therein.
- 3 L. Stanghellini, G. Gervasio, R. Rossetti, and G. Bor, *J. Organomet. Chem.*, 1980, **187**, C37.
- 4 A. Benoit, A. Darchen, J. Y. Le Marouille, C. Mahe', and H. Patin, *Organometallics*, 1983, **2**, 555 and refs. therein.
- 5 L. Busetto, A. Palazzi, and M. Monari, *J. Chem. Soc., Dalton Trans.*, 1982, 1631.
- 6 L. Busetto, A. Palazzi, and M. Monari, *J. Organomet. Chem.*, 1982, **228**, C19.
- 7 L. Busetto, M. Monari, A. Palazzi, V. G. Albano, and F. Demartin, *J. Chem. Soc., Dalton Trans.*, 1983, 1849.
- 8 H. Stolzenberg, W. P. Fehlhammer, L. Busetto, M. Monari, and V. Zanotti, *J. Organomet. Chem.*, 1984, **272**, 73.
- 9 H. Patin, G. Mignani, and M. T. Van Hulle, *Tetrahedron Lett.*, 1979, 2441.
- 10 C. H. Wei and L. F. Dahl, *Cryst. Struct. Commun.*, 1975, **4**, 583.
- 11 A. R. Manning, *J. Chem. Soc. A*, 1971, 2321.
- 12 H. Alper and H. N. Paik, *J. Org. Chem.*, 1977, **42**, 3520.
- 13 P. V. Broadhurst, B. F. G. Johnson, J. Lewis, and P. R. Raithby, *J. Am. Chem. Soc.*, 1981, **103**, 3198.
- 14 P. V. Broadhurst, B. F. G. Johnson, J. Lewis, and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1980, 812.
- 15 P. V. Broadhurst, B. F. G. Johnson, J. Lewis, and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1982, 1641.
- 16 J. F. Blount, L. F. Dahl, C. Hoogzand, and W. Hubel, *J. Am. Chem. Soc.*, 1966, **88**, 292.
- 17 M. Catti, G. Gervasio, and S. A. Mason, *J. Chem. Soc., Dalton Trans.*, 1977, 2260.
- 18 SHELX 76 System of Computer Programs, G. M. Sheldrick, Cambridge, 1976.

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