

Preliminary communication

IRON CARBONYL COMPLEXES OF DITHIOCARBONATES. X-RAY CRYSTAL STRUCTURE OF $\text{Fe}_4(\text{CO})_{12}\text{S}(\text{SCH}_2\text{C}_5\text{H}_4\text{FeC}_5\text{H}_5)(\text{SCH}_3)$

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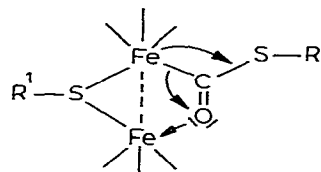
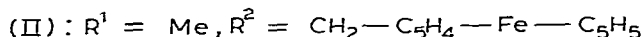
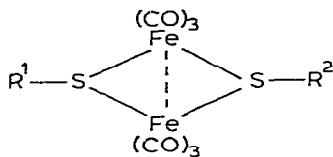
Summary

Reaction of *S*-ferrocenylmethyl-*S*-methylthiocarbonate (I) with diiron nonacarbonyl gives the dissymmetrically bridged complex $(\mu\text{-SCH}_2\text{C}_5\text{H}_4\text{FeC}_5\text{H}_5)(\mu\text{-SCH}_3)\text{Fe}_2(\text{CO})_6$, as a mixture of *syn* and *anti* isomers, along with the title compound, the structure of which has been determined by X-ray diffraction. This latter complex consists of two $\text{Fe}_2(\text{CO})_6$ units bridged by two *S*-alkyl ligands and by a central sulfur atom; its structure is compared with those of related molecules.

Fragmentation of *S*-alkyldithiocarbonates $[\text{R}^1\text{OC}(\text{S})\text{SR}^2]$ and trithiocarbonates $[\text{R}^1\text{SC}(\text{S})\text{SR}^2]$ occurs during their reaction with diiron nonacarbonyl to give good yields of dinuclear complexes resulting from insertion of an iron atom into a carbon sulfur single bond [1,2]. X-Ray structural determination shows that the two iron atoms are bridged by a three-electrons donor *S*-alkyl ligand and by a carbon-sulfur grouping possessing characteristics of a metallo-carbene [2,3]. Readily accessible dithiocarbonates $[\text{R}^1\text{SC}(\text{O})\text{SR}^2]$ [4] are also of interest because they can, in principle, yield similar binuclear complexes in which the two-atom bridge is formed by the carbon-oxygen grouping as in the complex $(\text{PhCO})_2\text{Fe}_2(\text{CO})_6$ [5]. We describe two complexes obtained from *S*-ferrocenylmethyl *S*-methylthiocarbonate (I); for one of them, the structure established by X-ray diffraction shows that it represents one of the few examples of a tetrahedral like sulfur atom linked to four iron atoms with which it shares all its valence electrons.

Reaction of I (5 mmol) with $\text{Fe}_2(\text{CO})_9$ (10 mmol) in acetone (40 ml) at

room temperature under N_2 gave two major complexes which were separated and purified by chromatography on silica plates (pentane). Complex II (18%, m.p. 99–100°C, $C_{18}H_{14}Fe_3O_6S_2$, $R_f = 0.61$) was shown by 1H NMR to be a mixture of *syn* and *anti* (45/55) μ -thioferrocenylmethyl μ -thiomethyl diiron hexacarbonyl (δ (ppm) ($CDCl_3$) CH_2 at 3.53 and 3.20, CH_3 at 2.20 and 1.60).



(IV)

By analogy to the complexation of dithiocarbonates and trithiocarbonates [2], formation of intermediate IV bridged by the carbon–oxygen grouping may be assumed. Insertion of iron into the other carbon–sulfur single bond, more strongly polarised by oxygen than by sulfur, will lead to complex II with loss of carbon monoxide.

Although several symmetrically bridged $(RS)_2Fe_2(CO)_6$ complexes have been obtained, no general route to dissymmetrical complexes such as II has been described. Our method provides a convenient synthesis of these compounds, which show a more complicated dynamic behaviour in solution as a result to the removal of the symmetry in the system.

Complex III (11%, m.p. 112–113°C, $C_{24}H_{14}Fe_5O_{12}S_3$, $R_f = 0.52$) gives a 1H spectrum with singlets for CH_2 (3.43 ppm) and CH_3 (2.10 ppm) and a mass spectrum showing, after loss of twelve molecules of CO, a fragment corresponding to $C_{12}H_{14}S_3Fe_5$ ($M_{calcd.} = 533.7004$, $M_{found} = 533.7009$). The X-ray structural determination was carried out on a single crystal grown from hexane, from which 3126 independent diffracted intensities were observed with $I_0 > 2\sigma(I)$ from a set of 3660 independent reflexions measured using a $\theta-2\theta$ scan technique with graphite monochromatized Mo- K_α radiation on an ENRAF-NONIUS CAD-4 diffractometer. The compound crystallizes with two molecules per unit cell in the space groups $P\bar{1}$ and the lattice constants are a 8.825(1); b 17.424(1); c 12.544(3) Å; α 121.84(5), β 94.51(4); γ 99.36(4)°; $V = 1585.3$ Å³. The structure was solved by direct methods with the MULTAN program; full matrix least squares refinement of atomic positional and thermal (anisotropic Fe, S, O, C, isotropic H) parameters converged to conventional values $R = 0.042$ and $R_w = 0.044$. All the structural calculations were performed on a PDP 11/60 computer with SDP package [6].

The ORTEP drawing presented in Fig. 1 shows that the molecule consists of two doubly bridged $Fe_2(CO)_6$ units sharing a common central sulfur atom ligand, with one unit also bridged by a thioferrocenylmethyl group and the other unit by a thiomethyl group. The molecular geometry closely resembles those of the three previously reported complexes of this type, namely the symmetric $[CH_3SF_2(CO)_6]_2S$ (V) [7] and the dissymmetric $Fe_4(CO)_{12}S(C_5H_4N)-(C_5H_4NS)$ (VI) [8] and $Fe_4(CO)_{12}S(CSNMe_2)(CNMe_2)$ (VII) [9]. From the

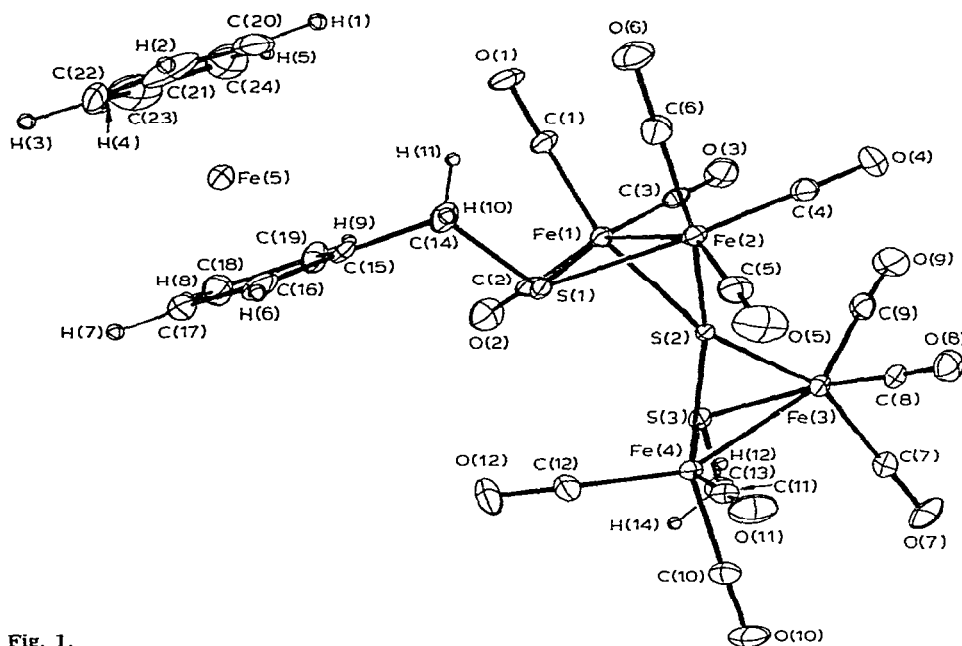


Fig. 1.

TABLE 1

MORE RELEVANT BOND LENGTHS (Å) AND ANGLES (°) WITH THEIR e.s.d's

| | | | |
|-------------|----------|------------------|-----------|
| Fe(1)—Fe(2) | 2.532(1) | S(1)—Fe(1)—S(2) | 76.98(6) |
| Fe(3)—Fe(4) | 2.520(1) | S(1)—Fe(2)—S(2) | 77.48(6) |
| Fe(1)—S(1) | 2.275(2) | S(2)—Fe(3)—S(3) | 76.85(6) |
| Fe(2)—S(1) | 2.258(2) | S(2)—Fe(4)—S(3) | 76.85(7) |
| Fe(1)—S(2) | 2.244(2) | Fe(1)—S(1)—Fe(2) | 67.90(6) |
| Fe(2)—S(2) | 2.236(2) | Fe(1)—S(2)—Fe(2) | 68.83(6) |
| Fe(3)—S(2) | 2.238(2) | Fe(3)—S(2)—Fe(4) | 68.47(6) |
| Fe(4)—S(2) | 2.242(2) | Fe(3)—S(3)—Fe(4) | 67.48(6) |
| Fe(3)—S(3) | 2.271(2) | Fe(1)—S(2)—Fe(3) | 135.25(9) |
| Fe(4)—S(3) | 2.267(2) | Fe(1)—S(2)—Fe(4) | 127.51(8) |
| S(1)—C(14) | 1.837(8) | Fe(2)—S(2)—Fe(3) | 133.44(8) |
| S(3)—C(13) | 1.831(9) | Fe(2)—S(2)—Fe(4) | 135.80(8) |
| | | Fe(1)—S(1)—C(14) | 114.0(3) |
| | | Fe(3)—S(3)—C(13) | 115.8(4) |

data listed in Table 1 we conclude that the $\text{Fe}_4(\text{CO})_{12}\text{S}_3$ framework is very similar to that in compound V. The significantly different Fe—Fe, Fe—S(2) and Fe—S(Alkyl) distances in complexes VI and VII can be attributed to the presence of one two-atom bridge and one mono-atom bridge in the latter compounds.

Coordination about the sulfur atom is tetrahedral, so that the two $\text{Fe}_2(\text{CO})_6$ units are oriented at right angles to one another. In this situation the S(2) atom shares three electrons with each bimetallic group, so that all the metal atoms can attain the closed-shell electronic configuration with all the valence electrons engaged in bonding orbitals. As has been previously noted [7], such a situation bears a resemblance to that in simple metal sulfides possessing the blende and wurtzite structures, but is uncommon in organometallic chemistry.

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