

Preliminary communication

IRON CARBONYL COMPLEXATION OF DITHIOESTERS. FORMATION OF A CHIRAL CARBON CENTER σ -BONDED TO AN IRON ATOM

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Summary

Dithioesters react with diiron nonacarbonyl to afford binuclear complexes resulting from coordination of the carbon—sulfur double bond to the two iron atoms and donation of two electrons from the S-alkyl group to one iron center. This novel mode of complexation creates a carbon—iron single bond and a chiral center at the carbon atom bonded to the metal, as shown by the spectroscopic studies and by an X-ray structure determination,

During our investigation of the behaviour of sulfur containing ligands towards diiron nonacarbonyl we have shown that xanthates $[R^1OC(S)SR^2]$ (I), trithiocarbonates $[R^1SC(S)SR^2]$ (II) and dithiocarbonates $[R^1SC(O)SR^2]$ (III) give dinuclear complexes with structures depending on the relative positions of the sulfur atoms in the ligands. After fragmentation compounds I and II give $Fe_2(CO)_6$ complexes bridged by the SR^2 grouping and by the diatomic $\geq C-S$ fragment in which the carbon atom has the characteristics of a carbene bonded to one iron atom and stabilized by the participation of the external oxygen or sulfur atoms [1—3]. In contrast, compound III upon CO elimination yields mainly a complex consisting of a $Fe_2(CO)_6$ grouping doubly bridged by SR^1 and SR^2 [4]. The present study on the behaviour of dithioesters $[R^1C(S)SR^2]$ (IV) was undertaken to confirm their ability to give carbene species as a result of fragmentation. An additional feature of interest was the possibility of an *ortho*-metallation when R^1 is aromatic as observed in the case of thioesters $[R^1C(S)OR^2]$ [5].

Dithioesters are readily obtained by reaction of CS_2 on the Grignard reagents followed by quenching with an alkyl halide [6]. Compounds IV with $\text{R}^1 = i\text{-Pr}$, cyclohexyl, Ph, $p\text{-Ph-OMe}$, $p\text{-PhNMe}_2$, $p\text{-PhCH}_3$, $p\text{-PhBr}$, $p\text{-PhCH=CH}_2$, PhCH_2 , naphthyl, thiophenyl, and $\text{R}^2 = \text{methyl}$, were dissolved in toluene and treated at 55°C under nitrogen for 30 min with a slight excess of $\text{Fe}_2(\text{CO})_9$. After conventional treatment and chromatography on silica plates with elution by hexane, the major products were crystallized from pentane to give a 20–80% yield of the pure complexes V.

Complexes V were shown by elemental analysis, mass spectroscopy and IR spectroscopy, to contain a $\text{Fe}_2(\text{CO})_6$ grouping (with all terminal carbonyls) associated with the starting ligand. A ^{13}C NMR study revealed that the sp^2 carbon atom of the functional group was considerably shielded (δ 70 ppm for $\text{R}^1 = \text{aromatic}$, δ 85 ppm for $\text{R}^1 = \text{aliphatic}$ versus, δ 230 ppm in the free ligand) and that the carbonyls, which are all equivalent at room temperature show six well-separated peaks at -50°C . These results are in contrast with those for the xanthate complexes in which the iron-bonded carbon atom is found at very low field (293 ppm versus 213 ppm in the xanthate) [3] and where local scrambling of the carbonyls occurs at only one of the two $\text{Fe}(\text{CO})_3$ groupings [7]. The proton NMR study show that the S-methyl protons and the tertiary hydrogen α to the functional group ($\text{R}^1 = i\text{-Pr}$, cyclohexyl) are slightly shielded compared with those in the dithioesters. The most important finding is the diastereotopy of the methyls when $\text{R}^1 = i\text{-Pr}$, showing that a

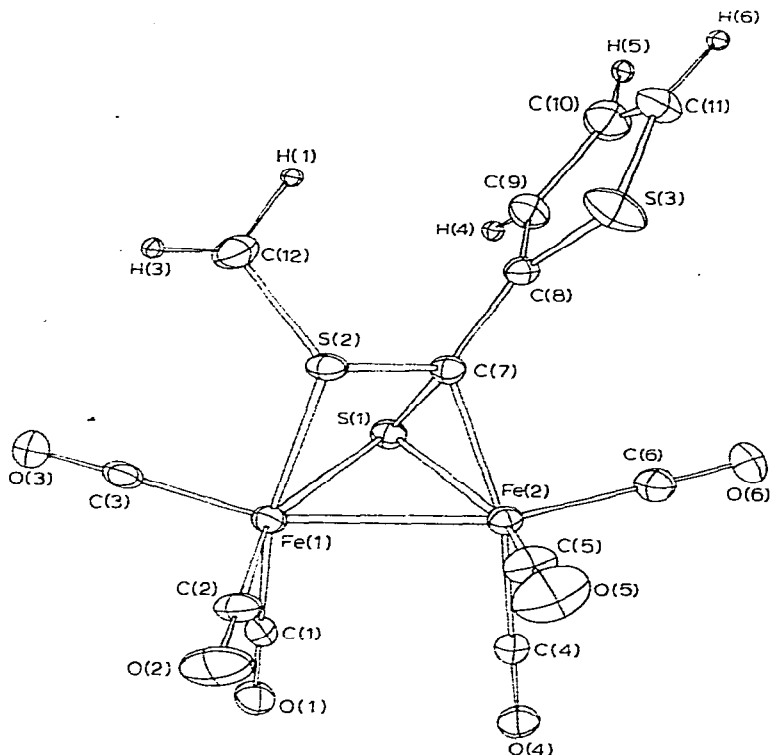


Fig. 1. ORTEP drawing showing the structure of complex 5.

chiral carbon atom is now present in the molecule. This result and the high field resonance in ^{13}C NMR demonstrate that the hybridization of the carbon atom of the functional group is no longer sp^2 but must be regarded as sp^3 . In order to confirm this assignment an X-ray structure determination was carried out on a single crystal of V ($R^1 = \text{thiophenyl}$, $R^2 = \text{methyl}$; m.p. 105–106°C) grown from hexane, from which 2244 independent diffracted intensities were observed with $I_0 > 2\sigma(I)$ from a set of 3073 independent reflexions measured using a θ – 2θ scan technique with graphite monochromatized Mo- K_α radiation on an Enraf–Nonius CAD4 diffractometer. The compound crystallizes with four molecules per unit cell in the space group $P2_1/C$ and the lattice constants are a 11.360(2); b 11.469(2); c 12.770(3) Å; β 94.80(6)°; V 1657.9 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 $R = 0.023$ and $R_w = 0.045$. All the structural calculations were performed on a PDP 11/60 computer with SDP package [8].

TABLE 1

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

Fe(1)—Fe(2)	2.618(1)	Fe(1)—S(1)—Fe(2)	71.90(3)
Fe(1)—S(1)	2.270(1)	Fe(1)—S(1)—C(7)	83.2(1)
Fe(1)—S(2)	2.282(1)	Fe(2)—S(1)—C(7)	59.8(1)
Fe(2)—S(1)	2.188(1)	Fe(2)—C(7)—S(1)	70.4(1)
Fe(2)—C(7)	2.007(3)	Fe(2)—C(7)—S(2)	105.0(1)
S(1)—C(7)	1.772(3)	Fe(2)—C(7)—C(8)	127.5(2)
S(2)—C(7)	1.781(3)	Fe(1)—S(2)—C(7)	82.6(1)
S(2)—C(12)	1.803(4)	S(1)—C(7)—S(2)	106.6(2)
C(7)—C(8)	1.465(4)	S(2)—C(7)—C(8)	117.1(2)
Fe(1)—C(1)	1.793(4)	S(1)—C(7)—C(8)	120.6(2)
Fe(1)—C(2)	1.791(4)	Fe(1)—S(2)—C(12)	110.2(1)
Fe(1)—C(3)	1.811(4)	C(7)—S(2)—C(12)	103.4(2)

The ORTEP drawing presented in Fig. 1 illustrates that complex V is a binuclear iron carbonyl complex in which the dithioester function behaves as a six electron donor. It is also apparent that C(7), bonded to Fe(2), S(1) and S(2)—CH₃, is chiral, although the geometrical constraints impose angle values quite different from the ideal tetrahedron (Table 1). Another interesting feature is that the carbonyl ligands are not eclipsed as in most of the Fe₂(CO)₆ complexes, the torsion angle C(2)—Fe(1)—Fe(2)—C(5) having a value of 19.7°. The alternative valence bond formulations represented on Fig. 2 clearly show that the two π -electrons of the carbon-sulfur double bond have been used to form the carbon-iron bond and one of the two sulfur-iron bonds.

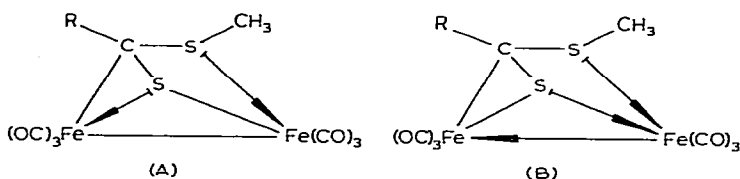


Fig. 2. Alternative valence bond formulations of complexes of type V.

Considerations based primarily on bond lengths favor formula B because the C(7)—S(2) and C(7)—S(1) bond lengths (respectively 1.781(3) and 1.772(3) Å) are nearly equal, in the range for single rather than double carbon—sulfur bonds (compare 1.630 Å for C=S and 1.724 and 1.788 for C—S in the *para*-*t*-butylphenyl-*S*-methyl dithioester [9]). On the other hand, the S(1)—Fe(2) bond length (2.188(1) Å) is significantly shorter than those of S(1)—Fe(1) and S(2)—Fe(1) which are, respectively, 2.270(1) and 2.282(1) Å. It is also striking that among the metal—carbonyl distances the longest by far is Fe(1)—C(3), and it can be predicted that the monosubstitution product obtained by replacement of one carbonyl by trimethylphosphite in complex V corresponds to the removal of CO(3) [10].

Finally the metal—metal distance of 2.618(1) Å is very close to that in the trithiocarbonate or the xanthate complexes (2.620(0) Å) [2,3]; this is not surprising, because in the present case we again have a biatomic bridge C(7)—S(2) and a monoatomic bridge S(1). The main difference lies in the existence of the C(7)—S(1) bond, which imposes a different geometry of complex V, producing the distortion already noticed in the molecule. The two sulfur atoms almost retain their positions (the dihedral angle between the planes Fe(2)—Fe(1)—S(2) and Fe(2)—Fe(1)—S(1) has a value of 85° versus 90° for the Fe₂(CO)₆ complexes of xanthates and trithiocarbonates [2,3]) but C(7) is no longer coplanar with Fe(1), Fe(2), and S(2), the dihedral angle between this plane and S(2)—C(7)—Fe(2) having a value of 31°. This modification of the geometry is responsible for the staggered conformation of the carbonyl ligands. There is little doubt about the covalent character of the Fe(2)—C(7) bond if we take into account the geometry of the complex and the high field resonance observed for C(7). The value of the Fe(2)—C(7) bond length in our compound: 2.007(3) Å is less than that regarded as nominal for a Fe—C(*sp*³) single bond, viz. 2.0977(23) Å [11]. This shortening may be the result of the electron-withdrawing capacity of the sulfur atoms bonded to C(7). We are currently investigating the possibility of resolving compounds V into enantiomers.

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