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Preliminary communication

STRUCTURE OF A CARBENIC PRECURSOR OF TETRATHIAFULVALENE COORDINATED TO A TRIIRON OCTACARBONYL CLUSTER COMPLEX

ALAIN BENOIT, JEAN-YVES LE MAROUILLE,
Laboratoire de Chimie du Solide et Inorganique Moléculaire, L.A. CNRS No. 254, Université de Rennes, Campus de Beaulieu, 35042 Rennes Cedex (France)
CHRISTIAN MAHÉ et HENRI PATIN*
Laboratoire de Chimie des Organométalliques, E.R.A. CNRS No. 477, Université de Rennes, Campus de Beaulieu, 35042 Rennes Cedex (France)

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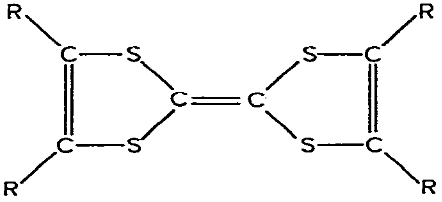
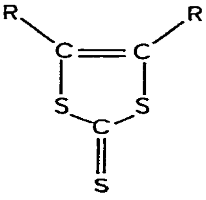
Summary

The reaction between 1,3-dithiole 2-thione and $Fe_2(CO)_9$ gives a 1,3-dithiole-2-ylidenetriiron octacarbonyl cluster complex, $(C_3H_2S_2)Fe_3(CO)_8S_2$, the structure of which has been determined by X-ray diffraction.

The recent structural determination of the complex $(C_3Ph_2)Fe_3S_2(CO)_8$ in which a carbene ligand formed by desulfurization of cyclopropenethione is coordinated to a tetragonal pyramidal Fe_3S_2 cluster [1], prompts us to report results obtained during the study of the reaction of 1,3-dithiole 2-thione with $Fe_2(CO)_9$. In recent years we have shown that sulfur-containing ligands such as xanthates, dithioesters, thioamides react with $Fe_2(CO)_9$ or $Co_2(CO)_8$ to afford polynuclear complexes resulting from fragmentation of the ligand [2] formation of metal—carbon bonds [3] or complete or partial desulfurization of the ligand [4—7]. We describe here the synthesis and structure of a new triiron cluster (III) in which half of a molecule of TTF (I, R = H) is coordinated to a metal center, showing that a carbenic species is formed during the desulfurization of 1,3-dithiole 2-thione (II, R = H).



(I)



(II)

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The discovery of highly conductive organic charge-transfer complexes which are formed from derivatives of tetrathiafulvalene (I) and acceptor molecules has raised interest in the discovery of new synthetic methods for TTF derivatives, and these have been recently reviewed [8]. Among them, some direct routes involving the coupling of 1,3-dithiole 2-thione (II) have been described, including, for example, electrochemical synthesis [9], photodesulfurization [10] or reaction with dicobalt octacarbonyl [11]. Although a reaction pathway involving the coupling of a carbenic intermediate has been postulated for the photochemical process [10], no evidence to support this has been obtained. We have found that thermal decomposition of cluster III affords TTF in high yield, which provides good evidence for the coupling of two carbenes. A solution of the thione II in toluene was treated with a fivefold excess of $Fe_2(CO)_9$ at 55°C under nitrogen for 0.5 h. After removal of the solvent the crude mixture was separated by chromatography on silica plates. Elution with hexane afforded small amounts of TTF (I) (5%, m.p. 119°C, litt. 119°C [8]) and of the known cluster IV $Fe_3(CO)_9S_2$ (8%) [12—14]. Then elution with a mixture of hexane and diethyl ether gave complex III (43%, m.p. 106—107°C) and finally elution with ether produced a more polar compound, as yet unidentified.

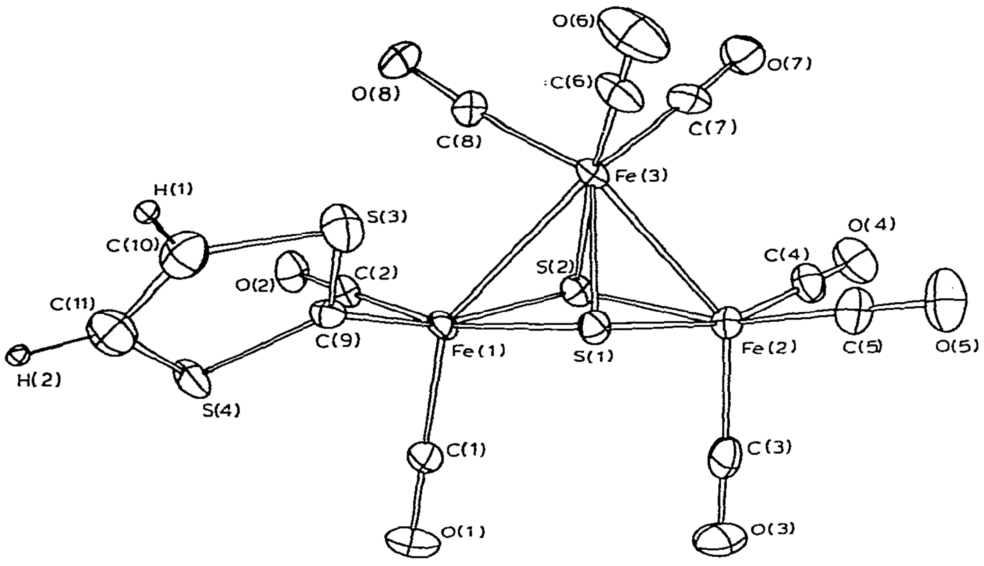
Compound III (M^{+} – CO,Calcd. 529.6731; Found 529.6717) gave satisfactory analytical data corresponding to $C_{11}H_2Fe_3O_8S_4$. The IR spectrum (Nujol) showed only terminal carbonyls and the proton NMR revealed one singlet at δ 8.5 ppm ($CDCl_3$, Me_4Si). The ^{13}C NMR spectrum (20 MHz, $CDCl_3$, Me_4Si) had signals at 114.4 ppm (two sp^2 carbon atoms of the 1,3-dithiole-2-ylidene ligand) at 205 and 210 ppm (carbonyl ligands) and 257.2 ppm in the range of chemical shifts reported for deshielded coordinated carbene carbon nuclei [15].

In order to confirm the presence of the carbenic ligand $C_3H_2S_2$ on the $Fe_3S_2(CO)_8$ cluster an X-ray structure determination was carried out on a single crystal of III obtained from a hexane solution cooled to −10°C. 2155 independent diffracted intensities were observed with $I_0 > 2\sigma(I)$ from a set of 2780 independent reflections 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 $P2_1/n$ and the lattice constants are a 9.181(8), b 11.059(2), c 18.543(9) Å;

TABLE 1

SOME RELEVANT BOND LENGTHS (Å) AND ANGLES (0°) WITH THEIR e.s.d.

Fe(1)—Fe(3)	2.620(1)		
Fe(2)—Fe(3)	2.577(1)		
Fe(1)—S(1)	2.224(1)		
Fe(1)—S(2)	2.241(1)		
Fe(2)—S(1)	2.235(1)		
Fe(2)—S(2)	2.253(1)		
Fe(3)—S(1)	2.249(1)		
Fe(3)—S(2)	2.262(1)	S(1)—Fe(1)—S(2)	80.06(3)
Fe(1)—C(9)	1.948(3)	S(1)—Fe(2)—S(2)	79.58(3)
C(9)—S(3)	1.675(3)	Fe(1)—S(1)—Fe(2)	99.53(3)
C(9)—S(4)	1.683(3)	Fe(1)—S(2)—Fe(2)	98.48(3)
C(10)—S(3)	1.723(3)	Fe(1)—Fe(2)—Fe(3)	81.80(3)
C(11)—S(4)	1.720(4)	S(1)—Fe(3)—S(2)	79.09(3)
C(11)—C(10)	1.317(5)	C(9)—Fe(1)—Fe(3)	106.08(8)



β 103.25(6)°; V 1832.6 Å^3. 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 $R = 0.022$ and $R_\omega = 0.034$. All the structural calculations were performed on a PDP 11/60 computer with SDP package [16].

The ORTEP drawing presented in Fig. 1 shows that the complex consists of discrete molecules (shortest intermolecular contacts O(3)—H(1) 2.843(3) Å) containing the Fe_3S_2 core already described as Hieber's compound [14,17]. Complex III can be considered as a $Fe(CO)_3$ grouping bonded to the Fe(1), Fe(2), S(1) and S(2) atoms. These four atoms are nearly coplanar the iron and sulfur being respectively displaced by +0.11 and −0.11 Å from the plane. The 1,3-dithiole 2-ylidene ligand is bonded to Fe(1) in the apical position and acts as a two electron donor. The plane of the three iron atoms contains the C(1)O(1) and C(3)O(3) ligands and is orthogonal (90.1°) to the plane defined by Fe(3), S(1) and S(2). The Fe(2)—C(9) bond eclipses the Fe(2)—C(4) bond. The carbenic character of C(9) deduced from the ^{13}C NMR data is also shown by the Fe(1)—C(9) bond length of 1.948(3) Å, in the range of other carbenes bonded to iron atoms [2,18]. The C_3H_2S ligand which represents half of the molecule of TTF (I, R = H) has retained strong aromatic character (δ(H(1) and H(2)) = 8.5 ppm vs. 7.32 ppm in II) despite minor changes in the interatomic distances compared to those found for TTF [19].

Replacement of one carbonyl in the symmetrical cluster IV by the carbenic ligand results in significant modifications of the metal—metal and metal—sulfur bond lengths. We note (Table 1) the lengthening of the Fe(1)—S(2) and Fe(2)—S(2) bonds compared to Fe(1)—S(1) and Fe(2)—S(1). A lengthening is also observed for the Fe(1)—Fe(3) bond, while Fe(3)—Fe(2) is shortened (compared with 2.598(0) and 2.590(0) Å in IV [14]). These modifications are in agreement with the electronic character of the carbenes, which are stronger σ-donor and weaker π-acceptors than the carbonyls [20].

Our results support the view that upon desulfurization of II cluster IV is formed and that the intermediate carbene can be trapped by the cluster. The small amount of TTF produced during the synthesis of III may originate from the coupling of two carbenes but can also be derived by partial decomposition of III. We have shown that thermal degradation of III at 160°C in decalin affords a good yield of TTF. Generalisation of these findings for the synthesis of TTF is currently under investigation.

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