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FERROCENYLTRITHIOCARBONATES

II *. SYNTHESIS AND X-RAY STRUCTURE DETERMINATION OF DIIRON HEXACARBONYL COMPLEXES

HENRI PATIN *, GÉRARD MIGNANI, CHRISTIAN MAHÉ,

Laboratoire de Chimie des Organométalliques, ERA CNRS No. 477, Université de Rennes, Campus de Beaulieu, 35042 Rennes Cedex (France)

JEAN-YVES LE MAROUILLE *, TIMOTHY G. SOUTHERN, ALAIN BENOIT et DANIEL GRANDJEAN

Laboratoire de Cristallochimie, LA CNRS No. 254, Université de Rennes, Campus de Beaulieu, 35042 Rennes Cedex (France)

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Summary

Ferrocenyltrithiocarbonates, I, react with $Fe_2(CO)_9$ to afford new types of binuclear complexes in which the diiron hexacarbonyl moiety is linked by two bridges resulting from the insertion of an iron atom into the carbon—sulfur single bond. The X-ray structure determination of μ-(thioferrocenylmethylmethane thiomethylene-C^1, S^2)-1,1,1,2,2,2-hexacarbonyl-μ-methylthioiron (*Fe—Fe*) has been refined to $R = 0.037$. Comparison of X-ray and ^{13}C data with those of the starting materials are in agreement with a metallocarbene structure.

Introduction

We have shown that versatile electron-rich *S*-alkyldithiocarbonate (or *S*-Alkylxanthate) ligands can be used to synthesize new types of diiron hexacarbonyl complexes [1] or to prepare a wide range of alkoxyalkylidine tricobalt nonacarbonyl clusters [2]. More recently we found that α-ferrocenylcarbinols can be transformed directly into trithiocarbonates via a S_Ni mechanism [3]. The facile synthesis of these compounds led us to study their behaviour towards diiron nonacarbonyl because (in principle) they can act as four- or six-electron ligands and furthermore there can be competition between the sulfur

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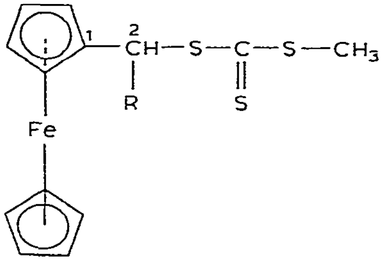
* For Part I see ref. 3.

atoms to give different types of complexes. In order to elucidate the unexpected structure of the diiron hexacarbonyl complexes obtained an X-ray structure determination was performed and this shows that we have obtained a new class of non-symetrically double-bridged compounds.

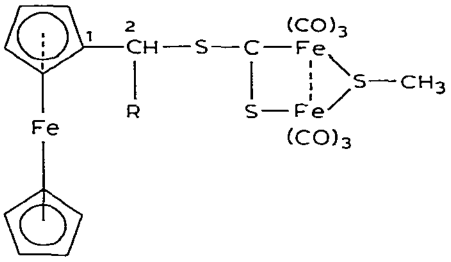
Results and discussion

Complexes of trithiocarbonates

When trithiocarbonate I (R = CH_3) was allowed to react with an excess of $Fe_2(CO)_9$ in acetone a single complex II was isolated after chromatography. Attempts at decomplexation by conventional oxidation procedures led to a complex mixture instead of the expected free ligand. Structure II was established by X-ray diffraction.

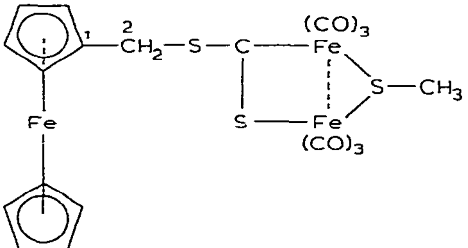


(I, R = CH_3;
III, R = H)

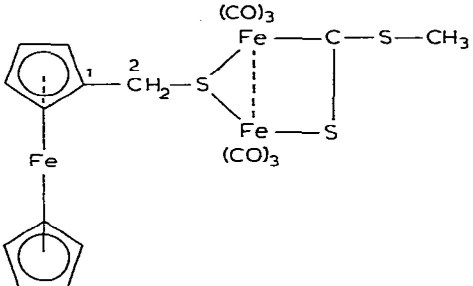


(II, R = CH_3)

In order to minimize the steric effects at carbon 2, trithiocarbonate III (R = H) was treated with $Fe_2(CO)_9$ in the same manner and afforded two compounds which were separated by TLC. Structures IV and V are attributed to these by comparison of their ^{1}H NMR and ^{13}C NMR data (Tables 1 and 2) with those of II.



(IV)



(V)

The upfield shift for the S-methyl protons is equivalent in II and IV by comparison with the chemical shifts in the starting materials (I and III). On the other hand the upfield shift measured for the C^2 protons of II and IV (0.3 ppm) is lower than in compound V (0.9 ppm) where Fc—CH_2—S— bridges the two iron atoms. An analogous effect can be noticed in ^{13}C NMR where C^1 appears slightly shielded for complexes II and IV and significantly deshielded

TABLE 1

^{1}H NMR (δ ppm) DATA [a]

Compound	$C^2(H)$	Cp^1	Cp^2	$-S-CH_3$	CH_3
I	5.22 (q)	4.20 (9H)		2.76	1.80 (t)
II	4.88 (q)	4.22 (9H)		2.45	2.72 (t)
III	4.42 (s)	4.17 (5H)	4.17 (m)	2.73	—
IV	4.11 (s)	4.14 (5H)	4.13 (4H)	2.37	—
V	3.56 (s)	4.13 (5H)	4.22 (4H)	2.50	—

[a] Cp^1 and Cp^2 refer to π-C_5H_5 and π-C_5H_4, respectively. q = quartet; s = singlet, t = triplet, m = multiplet.

TABLE 2

^{13}C NMR (δ ppm) DATA [a]

Compound	C=S	CO	C^1	Cp^1	Cp^2	C^2	$S-CH_3$	CH_3
I	224.4	—	88.6	68.9	68.2 66.8	46.9	20.1	19.9
II	304.2	210	87.6	68.9	68.4 66.7	49.5	23.8	20.7
III	224.5	—	81.7	68.9	68.3	37.9	20.1	—
IV	303.9	210	80.4	69.0	68.6	41.6	23.9	—
V	306.2	210	86.3	68.9	68.6	40.9	24.1	—

[a] Cp^1 and Cp^2 refer to π-C_5H_5 and π-C_5H_4, respectively. q = quartet, s = singlet, t = triplet, m = multiplet.

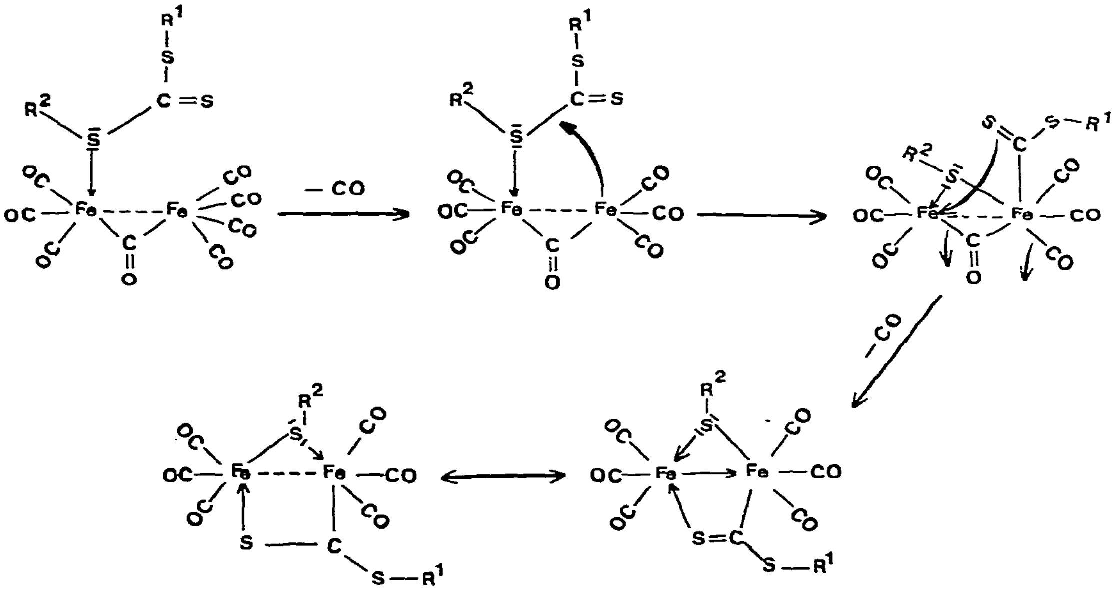


Fig. 1.

for complex V. Finally the downfield shift measured for C^2 is larger when it is attached to the sulfur atom which participates to the carbene stabilization (complexes II and IV) than when it is attached to the bridging sulfur (complex V). The considerable downfield shift for the carbon of the C—S bridge is in good agreement with the published values for transition metal stabilized carbenes [4].

The following mechanism (Fig. 1) accounts for the formation of the complexes and shows that the first coordination step is governed by the steric effects of the substituents attached to sulfur (coordination of $-S-R_2$ versus $-S-R_1$).

X-ray structure of complex II

The molecular structure is shown in Fig. 2. The three dimensional packing (Fig. 4) shows discrete molecules, the shortest intermolecular contact being 2.73 Å between H(19) and O(3).

The molecular structure of complex II contains a $Fe_2(CO)_6$ unit (Figs. 2 and 3) in which the Fe—Fe distance is equal to 2.621(0) Å, bridged by a thiomethyl group resulting from the insertion of Fe(1) into the carbon—sulfur single bond. The other bridge is derived from the coordination of the thiocarbonyl group on Fe(1) and Fe(2). This iron—iron distance is in the range observed for non

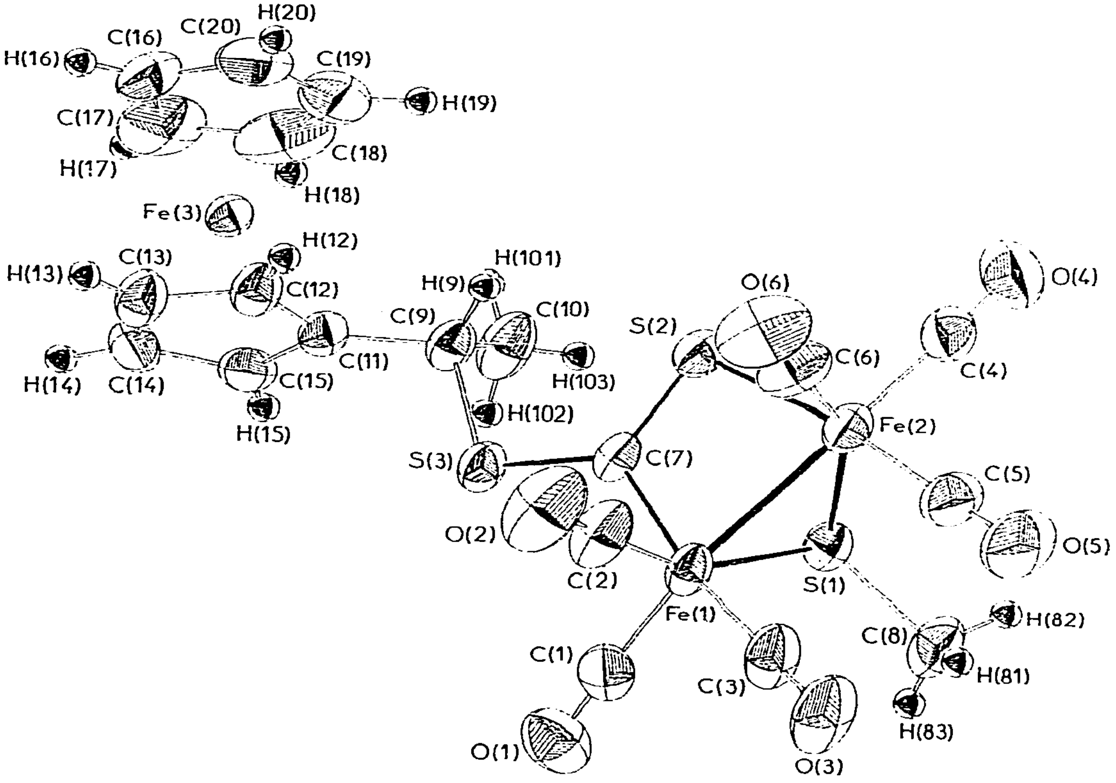


Fig. 2. Molecular structure of compound II.

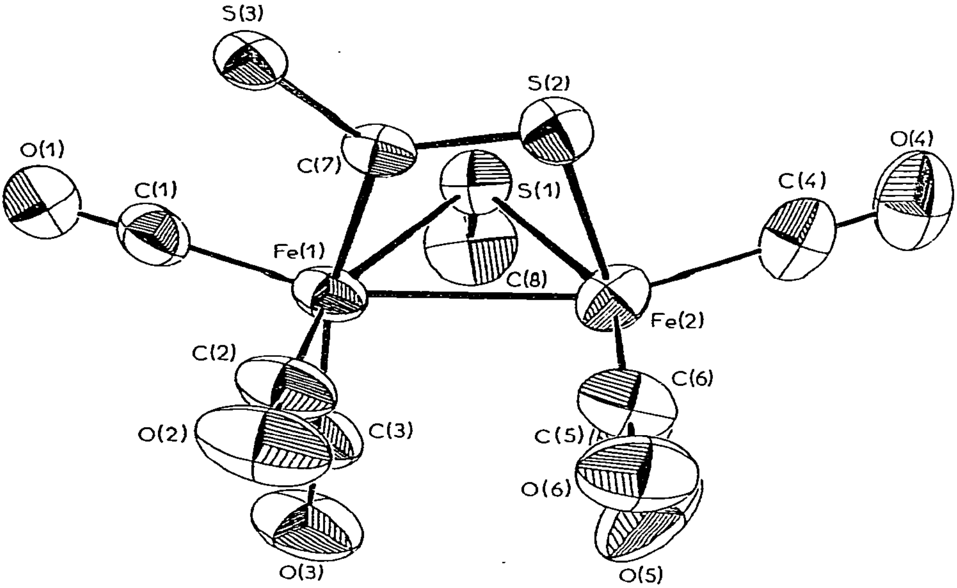


Fig. 3. Bimetallic skeleton of compound II.

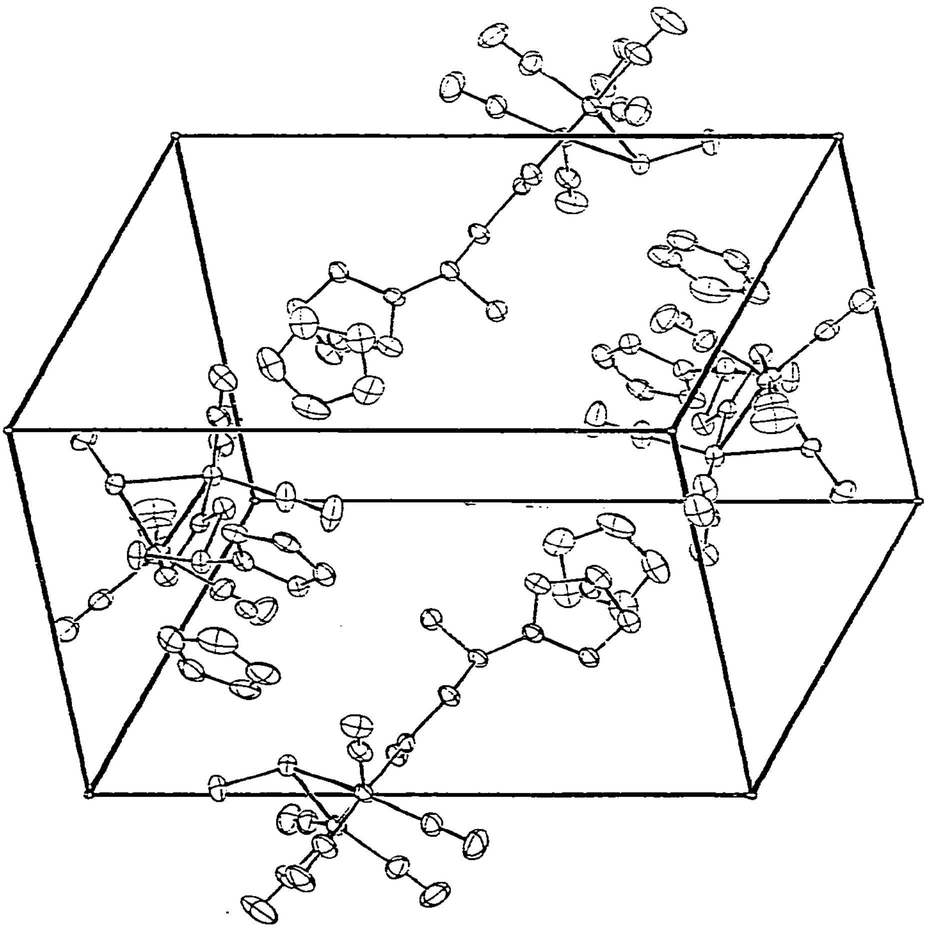


Fig. 4. Unit cell of II containing four molecules.

symmetrically double-bridged complexes [5] but is significantly longer than in complexes containing two identical thioalkyl or thioaryl bridges [6,7].

The three carbonyls of each $Fe(CO)_3$ group have the usual ternary symmetry around the iron atom. The Fe—C bond lengths are rather similar to those given by Dean [8] for a diiron complex bridged by a sulfur and a thiocarboxamide ligand. However the Fe—C bond lengths for the carbonyls located *trans* to the sulfur atoms are significantly longer (1.889(10) Å and 1.984(9) Å) than those we observed (1.793(5) Å and 1.782(5) Å). We also note that the Fe—C bonds for the carbonyls *trans* to a sulfur atom are noticeably shorter than the others.

The carbon C(7) of the S(3)—C(7)—S(2) bridge possesses a carbene character with a Fe(1)—C(7) bond equal to 1.970(3) Å which is of the same magnitude as other iron-carbene stabilized compounds 1.980 Å [9], 1.969 Å [10]. This carbene character for C(7) is confirmed by its low field resonance in ^{13}C NMR (304 ppm). The planarity of the system Fe(1)—Fe(2)—S(3)—C(7)—S(2) shows that the two sulfur atoms also contribute to the stabilization of the carbene. We have found C(7)—S(2) and C(7)—S(3) bond lengths, equal to 1.658(4) Å and 1.698(4) Å, respectively, both shorter than a single carbon—sulfur bond,

TABLE 3a

FINAL ATOMIC COORDINATES OF NON-HYDROGEN ATOMS (× 10^4), ANISOTROPIC THERMAL PARAMETERS β_{ij} AND THEIR E.S.D.'S (× 10^4) DEFINED BY: $\Sigma_{ij}\beta_{ij}h_ih_j$

Atom	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe(1)	2368(1)	7076(0)	4836(0)	96(1)	49(0)	28(0)	—14(0)	8(0)	2(0)
Fe(2)	861(1)	7873(1)	5644(0)	68(1)	81(1)	38(0)	1(0)	7(0)	17(0)
Fe(3)	3305(1)	12859(0)	2764(0)	79(1)	44(0)	34(0)	1(0)	16(0)	4(0)
S(1)	2626(1)	7692(1)	6113(1)	72(1)	77(1)	27(0)	1(1)	2(0)	6(0)
S(2)	1494(1)	9453(1)	5045(1)	91(1)	63(1)	38(0)	3(1)	11(1)	10(1)
S(3)	3250(1)	9281(1)	4001(1)	101(1)	53(1)	34(0)	—8(1)	17(1)	6(0)
C(1)	3741(5)	6773(4)	4653(3)	110(5)	60(4)	43(2)	—9(3)	21(3)	—8(2)
C(2)	1633(5)	6919(4)	3862(3)	160(7)	79(4)	34(2)	—31(4)	—6(3)	—2(2)
C(3)	2106(5)	5620(4)	5099(3)	156(6)	63(4)	41(2)	—22(4)	22(3)	—3(2)
C(4)	254(4)	8737(5)	6360(3)	69(4)	139(6)	38(2)	12(4)	4(2)	17(3)
C(5)	500(4)	6556(5)	6055(4)	77(5)	120(6)	78(3)	7(4)	25(3)	40(4)
C(6)	—209(5)	7775(4)	4822(3)	114(5)	85(5)	52(2)	2(4)	—20(3)	3(3)
C(7)	2398(3)	8720(3)	4610(2)	78(4)	52(3)	25(2)	—10(3)	0(2)	6(2)
C(8)	2939(5)	6558(6)	6841(3)	105(6)	137(7)	39(2)	13(5)	0(3)	32(3)
C(9)	3033(4)	10838(3)	3984(2)	82(4)	54(3)	30(2)	—13(3)	4(2)	4(2)
C(10)	3638(6)	11374(5)	4733(3)	152(6)	82(4)	31(2)	—32(5)	—3(3)	1(2)
C(11)	3375(3)	11250(3)	3210(2)	73(4)	46(3)	34(2)	—7(3)	11(2)	1(2)
C(12)	2718(4)	11287(4)	2459(3)	88(4)	60(3)	35(2)	—12(3)	9(2)	3(2)
C(13)	3364(5)	11691(4)	1890(3)	131(6)	68(4)	32(2)	—5(4)	15(3)	—1(2)
C(14)	4403(5)	11901(4)	2266(3)	103(5)	81(4)	52(2)	9(4)	40(3)	4(3)
C(15)	4432(4)	11627(4)	3092(3)	63(4)	69(4)	51(2)	8(3)	13(2)	5(2)
C(16)	2754(8)	14339(5)	2227(5)	201(10)	85(5)	62(3)	56(6)	36(5)	29(4)
C(17)	3744(7)	14515(5)	2722(7)	164(10)	50(4)	130(6)	—8(5)	39(7)	16(4)
C(18)	3523(8)	14195(5)	3524(5)	178(10)	54(4)	87(5)	13(5)	—3(5)	—30(4)
C(19)	2462(7)	13847(6)	3449(4)	173(9)	93(6)	59(3)	47(6)	29(4)	—12(3)
C(20)	1998(6)	13928(6)	2678(5)	135(7)	120(7)	72(4)	60(6)	17(5)	3(4)
O(1)	4603(4)	6537(3)	4544(2)	117(4)	108(4)	70(2)	—10(3)	32(2)	—19(2)
O(2)	1166(4)	6862(4)	3244(2)	235(7)	153(5)	46(2)	—44(4)	—36(3)	—7(2)
O(3)	1950(4)	4693(3)	5255(2)	242(6)	69(3)	64(2)	—41(4)	35(3)	7(2)
O(4)	—127(3)	9284(4)	6806(2)	101(4)	201(6)	45(2)	26(4)	13(2)	0(3)
O(5)	266(4)	5719(4)	6324(3)	127(5)	155(5)	134(4)	0(4)	59(3)	77(4)
O(6)	—902(4)	7692(4)	4314(3)	130(4)	148(5)	82(3)	—18(4)	—42(3)	—4(3)

TABLE 3b

FINAL ATOMIC COORDINATES OF HYDROGEN ATOMS (X 10^4) ISOTROPIC THERMAL PARAMETERS (Å^2) AND E.S.D.'s (X 10^4)

Atom	x	y	z	B
H (81)	2465 (51)	5929 (52)	6725 (37)	6.0
H (82)	2708 (51)	6833 (49)	7337 (38)	6.0
H (83)	3697 (52)	6389 (55)	6875 (35)	6.0
H (9)	2230 (42)	10987 (32)	3961 (28)	3.83
H (101)	3530 (49)	12159 (51)	4705 (35)	5.57
H (102)	4458 (50)	11110 (49)	4830 (34)	5.57
H (103)	3454 (49)	11082 (50)	5151 (35)	5.57
H (12)	2024 (43)	11144 (46)	2388 (30)	4.13
H (13)	3107 (14)	11775 (46)	1379 (35)	4.98
H (14)	5015 (48)	12234 (46)	1998 (34)	5.32
H (15)	5065 (44)	11658 (44)	3465 (31)	4.32
H (16)	2616 (56)	14418 (58)	1667 (43)	7.96
H (17)	4269 (69)	14667 (74)	2676 (56)	8.54
H (18)	4136 (63)	14248 (65)	3783 (46)	7.92
H (19)	2064 (55)	13477 (60)	3887 (40)	7.28
H (20)	1279 (58)	13633 (63)	2514 (43)	7.56

1.740 Å [3], and longer than a carbon—sulfur double bound, 1.634 Å [3]. This proves the participation of S(2) and S(3) in the stabilization of the carbene. In addition all the bond angles around C(7): 125.1(1), 121.8(2) and 113.1(1)° are close to the theoretical value for a *sp*^{2} hybridized carbon atom.

TABLE 4

PRINCIPAL BOND LENGTHS AND E.S.D.'s (Å)

Atoms	Distance	Atoms	Distance
Fe (1) — Fe (2)	2.621 (0)	S(3) — C (7)	1.698 (4)
Fe (1) — S (1)	2.256 (1)	S (3) — C (9)	1.850 (4)
Fe (2) — S (1)	2.237 (1)	C (1) — O (1)	1.140 (7)
Fe (1) — C (1)	1.803 (6)	C (2) — O (2)	1.127 (6)
Fe (1) — C (2)	1.782 (5)	C (3) — O (3)	1.143 (6)
Fe (1) — C (3)	1.807 (4)	C (4) — O (4)	1.138 (7)
Fe (1) — C (7)	1.970 (3)	C (5) — O (5)	1.136 (7)
Fe (2) — S (2)	2.299 (1)	C (6) — O (6)	1.136 (7)
Fe (2) — C (4)	1.815 (5)	C (9) — C (10)	1.521 (6)
Fe (2) — C (5)	1.777 (6)	C (9) — C (11)	1.504 (6)
Fe (2) — C (6)	1.793 (5)	C (11) — C (12)	1.416 (5)
Fe (3) — C (11)	2.033 (3)	C (12) — C (13)	1.409 (7)
Fe (3) — C (12)	2.027 (4)	C (13) — C (14)	1.380 (8)
Fe (3) — C (13)	2.024 (5)	C (14) — C (15)	1.427 (7)
Fe (3) — C (14)	2.030 (5)	C (15) — C (11)	1.420 (6)
Fe (3) — C (15)	2.036 (4)	C (16) — C (17)	1.407 (13)
Fe (3) — C (16)	2.038 (6)	C (17) — C (18)	1.465 (15)
Fe (3) — C (17)	2.025 (6)	C (18) — C (19)	1.366 (13)
Fe (3) — C (18)	2.022 (7)	C (19) — C (20)	1.356 (10)
Fe (3) — C (19)	2.022 (8)	C (20) — C (16)	1.368 (12)
Fe (3) — C (20)	2.039 (7)	A — S (1)	2.762 (3) [a]
S (1) — C (8)	1.819 (6)	A — Fe (1)	2.419 (3) [a]
S (2) — C (7)	1.658 (4)	A — Fe (2)	2.493 (3) [a]

[a] With A the mid point of S (2) — C (7) bond.

TABLE 5

SELECTED NON HYDROGEN BOND ANGLES (°).

Atoms	Angle	Atoms	Angle
S (1) — Fe (1) — Fe (2)	54.0 (1)	S (2) — C (7) — S (3)	125.1 (1)
S (1) — Fe (1) — C (7)	82.4 (1)	Fe (1) — C (7) — S (2)	113.1 (1)
Fe (2) — Fe (1) — C (7)	77.5 (1)	Fe (1) — S (1) — Fe (2)	71.4 (6)
C (1) — Fe (1) — C (2)	101.6 (2)	C (7) — S (3) — C (9)	107.5 (3)
C (1) — Fe (1) — C (3)	93.4 (2)	Fe (1) — Fe (2) — S (1)	54.7 (1)
C (1) — Fe (1) — C (7)	96.8 (2)	Fe (1) — Fe (2) — S (2)	75.8 (1)
C (2) — Fe (1) — C (3)	92.4 (2)	S (1) — Fe (2) — S (2)	81.9 (1)
C (2) — Fe (1) — C (7)	86.8 (2)	Fe (2) — S (1) — C (8)	115.0 (2)
C (3) — Fe (1) — C (7)	169.8 (2)	S (3) — C (9) — C (10)	109.9 (4)
Fe (1) — S (1) — C (8)	113.7 (2)	S (3) — C (9) — C (11)	106.0 (2)
Fe (2) — S (2) — C (7)	93.6 (1)	Fe (1) — A — Fe (2) [a]	64.5 (1)

[a] A is the mid point of S (2) — C (7).

The dihedral angle between the plane of the thiomethyl bridge and the C(7)—S(2)—Fe(2)—Fe(1) plane is equal to 91° and the S(1)—Fe(2) bond (2.237(1) Å) is slightly shorter than the S(1)—Fe(1) bond (2.256(1) Å). These bonds are significantly shorter than those in other complexes bridged by —SR groups, namely, 2.265 Å to 2.284 Å [5] and 2.267 to 2.278 Å [6], where the sulfur atom is almost equidistant from the two iron atoms. On the other hand, it is important to note that the S(2)—Fe(2) bond is much longer (2.299(1) Å) than the other iron—sulfur bonds.

The two cyclopentadienyl rings are planar and nearly parallel (dihedral angle 1.74°), with the iron atom located at the same distance from both rings

TABLE 6

LEAST SQUARES PLANES AND ATOMIC DISPLACEMENTS THEREFROM (Å)

a) Equation of the C (9), C (11), C (12), C (13), C (14), C (15) plane $0.2930\,X - 0.9376\,Y - 0.1873\,Z + 12.4051 = 0$ [a]

$X^2 = 31.9$

Atom distances from the plane (Å)

C (9)	0.012	C (14)	0.007	H (13)	0.021
C (11)	−0.016	C (15)	−0.002	H (14)	−0.031
C (12)	−0.003	Fe (3)	−1.641	H (15)	0.049
C (13)	0.009	H (12)	−0.069		

b) Equation of the C (16), C (17), C (18), C (19), C (20) plane $0.3086\,X - 0.9374\,Y - 0.1613\,Z + 15.5147 = 0$ [a]

$X^2 = 2.0$

Atom distances from the plane (Å)

C (16)	−0.005	C (20)	0.003	H (18)	0.082
C (17)	0.007	Fe (3)	1.649	H (19)	0.104
C (18)	−0.003	H (16)	0.050	H (20)	0.109
C (19)	0.000	H (17)	0.056		

c) Equation of the Fe (1), Fe (2), S (2), S (3), C (7) plane $-0.6001\,X - 0.1409\,Y - 0.7874\,Z + 8.8479 = 0$ [a]

$X^2 = 20.2$

Atom distances from the plane (Å)

Fe (1)	0.000	Fe (2)	0.000	S (2)	0.000
S (3)	0.001	C (7)	−0.018	C (9)	−0.074

[a] X, Y and Z are atomic coordinates (in Å) in the orthogonal axis system a,c *; a,c *

(1.64 Å, Table 4). As usual the non-substituted ring has the largest thermal vibration and e.s.d. [3].

Conclusion

All the data, including the X-ray structure determination, show that the trithiocarbonates behave as six electron ligands coordinated to the diiron hexacarbonyl moiety by two bridges resulting from the insertion of one iron atom into a carbon—sulfur single bond. This insertion which leads to a thio-alkyl bridge depends markedly on the steric effect of the substituents located α to the sulfur atom. The novelty of these new compounds extends also to the C—S bridge, where the carbene carbon atom is stabilized by the metal and by electron delocalisation with the neighbouring heteroatoms.

Experimental

Melting points were determined on a Kofler hot stage apparatus and are uncorrected. ^{1}H NMR spectra were recorded using a Varian A 60 and ^{13}C NMR using a Bruker WP 80, with TMS as an internal standard and $CDCl_3$ as solvent. Petroleum ether refers to the fraction with B.P. 40—60°C. TLC was carried out on Merck Kieselgel plates. Organic solutions were dried over $MgSO_4$. Satisfactory elemental analyses were obtained for all new compounds. Mass spectra were recorded using a Varian MAT 311. The syntheses of trithiocarbonates have been described previously [3].

Complex II

To a solution of trithiocarbonate I (60 mmol) in dry acetone (50 ml), 6 g of $Fe_2(CO)_9$ were added all at once. The mixture was stirred under N_2 at room temperature in a dark room for 24 h. After concentration of the solution under vacuum the black suspension was spread on silica plates eluted with petroleum ether. The red strip (Rf = 0.53) was separated and extracted with dry ether. Distillation of solvent to dryness and crystallization from hexane gave 1.7 g (45%) of red crystals, m.p.: 138°C, M^+ 616, ν(CO): 2095, 2060, 2010 cm^{-1} (Nujol).

Complexes IV and V

Compound III (40 mmol) was reacted as described above with 4 g of $Fe_2(CO)_9$ · TLC with petroleum ether as solvent to give complex IV (Rf = 0.43) and complex V (Rf = 0.52). IV: 32%, m.p.: 117°C, mass spectrum (m/e): 602 (M^+), 518 ($M^+ - 3$ CO), 490 ($M^+ - 4$ CO), 434 ($M^+ - 6$ CO), 246, 199 (Fc—CH_2, 100%); ν(CO) (Nujol): 1990, 2050, 2040, 1995, 1980 cm^{-1}. V: 29%, m.p.: 152°C (decomp.), 602 (M^+); ν(CO) (Nujol): 2090, 2060, 2040, 1990, 1980, 1970 cm^{-1}.

X-Ray data collection and refinement

Crystals of complex II were grown from hexane; mol.wt. = 616; they are monoclinic, space group $P2_1/c$, with 4 formula units per unit cell. a = 12.382(1) Å; b = 11.752(2) Å; c = 16.877(2) Å; β = 97.44(2)°; V = 2435 Å^3;

$d_{calc.} = 1.67$ g cm^{-3}; $d_{obs.} = 1.68$ g cm^{-3}; $Z = 4$.

The unit cell parameters were refined by a least squares method using 25 accurately centered diffractometer reflexions with Mo-K_α graphite monochromated radiation ($\lambda = 0.70926$ Å). With a crystal of 0.180 × 0.090 × 0.260 mm the intensities of 2838 reflections were collected at room temperature up to $\theta \leqslant 27°$ on a Nonius CAD-4 automatic diffractometer with the following conditions: $\omega/2\theta$ scan technique, scan angle $S = (1.0 + 0.35 \tan\theta)°$, detector aperture width of $(2 + 0.35 \tan\theta)$ mm, maximum scan time 80 s. Three standard reflections were monitored every 200 min of exposure and showed no significant variation. All non zero reflexions were then considered and corrected for Lorentz and polarisation effects by the program MAXE [11].

A large number of atoms were located in the first run of the program MULTAN [12] and the few remaining atoms were found on a three dimensional electron density difference map. After several cycles of full matrix least squares refinement [13] of positional and isotropic thermal parameters, the hydrogen atoms were located with the aid of electron density difference maps using the reflections below $\sin\theta/\lambda \leqslant 0.3$ Å^{-1}. Least squares refinements of all the positional parameters and the anisotropic thermal parameters of the non-hydrogen atoms and the isotropic thermal parameters for the hydrogen atoms (taken equal to the isotropic equivalent B's of the bearing atom) converged to $R = \Sigma|\Delta F/\Sigma|F_0| = 0.037$ and $R_w = [\Sigma w|\Delta F|^2/\Sigma w|F_0|^2]^{1/2} = 0.045$ where $\Delta F = |F_0| - |F_c|$ and

$$1/\omega = \sigma_F^2 = \frac{\sigma_I^2 + (0.06I)^2}{4I} \quad [14] .$$

The standard deviation of an observation of unit weight was equal to 1.089; no shift greater than 0.2 σ was observed in the last refinement cycle for the non hydrogen atoms and 0.5 σ for the hydrogen atoms. Atomic scattering factors were taken from Moore [15] and anomalous dispersion factors $\Delta f'$ and $\Delta f''$ for Fe and S atoms were taken from the International Tables of Crystallography [16].

Tables of observed and calculated structure factors are available from the authors on request. Final coordinates and thermal parameters are given in Table 3a for the non hydrogen atoms and in table 3b for the hydrogen atoms. The atomic numbering scheme used can be seen on the ORTEP plot [17], Fig. 2. Interatomic distances and relevant bond angles are shown in Tables 4 and 5.

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