

Journal of Organometallic Chemistry, 401 (1991) 65–73
Elsevier Sequoia S.A., Lausanne
JOM 21061

Synthesis and crystal structure of the fourth isomeric product of the reaction of norbornadiene with sulfur and dodecacarbonyltriiron

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(Received May 14th, 1990)

Abstract

The fourth isomeric complex of the composition $\text{Fe}_2(\text{CO})_6(\text{S}_2\text{C}_7\text{H}_8)$ (IV), namely μ -(*S,S'*-bicyclo[2.2.1]hept-5-ene-2,2-ylenedithiolato)hexacarbonyldiiron, has been isolated from the reaction products of norbornadiene with S_8 and $\text{Fe}_3(\text{CO})_{12}$. The bonding and structure of the norbornadiene fragment have been estimated by an X-ray structural study of this compound. All the results concerning the abovementioned reaction have been summarized.

Introduction

This paper concludes the series of articles concerning the structure and properties of the reaction products of norbornadiene with dodecacarbonyltriiron and sulfur. In our preliminary communication [1] the synthesis and structure of three isomeric complexes I–III of the composition $\text{Fe}_2(\text{CO})_6(\text{S}_2\text{C}_7\text{H}_8)$ were briefly reported. The synthesis of these isomers was discussed in detail [2], while the structures of I and III and of II were described in [3] and [4], respectively. IR, ^1H and ^{13}C NMR spectra of complexes I–III were considered in [2], while the R_f values and melting points were reported in [1,2]. The Mössbauer spectra of compounds I–III, along with data for other sulfur-containing iron-carbonyl complexes have been discussed in [5], and the results of thermal analysis and mass spectroscopy were discussed in [6]. The isolation and X-ray structural study of the fourth isomeric complex formed in the abovementioned reaction are the subject of the present paper.

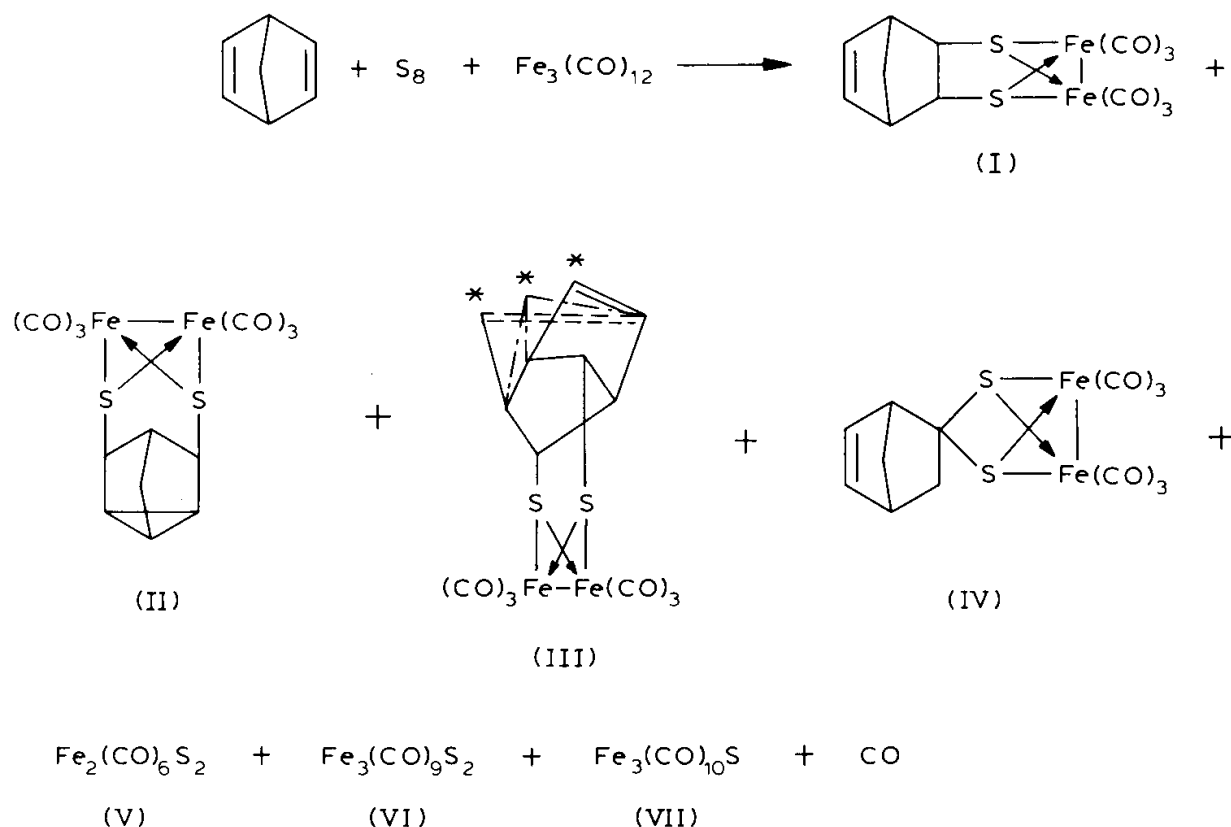
Results and discussion

The interaction of 1,3-cyclohexadiene and 1,5-cyclooctadiene with sulfur and $\text{Fe}_3(\text{CO})_{12}$ results in the implantation of sulfur atoms at one double bond with the formation of the corresponding dithiolatodiironhexacarbonyl complexes [2]. In the case of norbornadiene, together with the formation of the product of addition to one double bond (complex I), other products were also found: μ -(S,S' -tricyclo[2.2.1.0^{3,5}]hept-2,6-ylenedithiolato)hexacarbonyldiiron (II) and complex III, in which the C* atom occupies three positions with equal probability, corresponding to the positions of the C* atom in three different isomers (designated by the lines —, — — and - - - -). The isomers designated by the lines — and — — — are conformers of μ -(S,S' -bicyclo[2.2.1]hept-5-en-2,7-ylenedithiolato)hexacarbonyldiiron, while the isomer designated by the line - - - - corresponds to complex II. Reaction takes place without evolution of hydrogen sulfide.

An analogy of the reactions of norbornadiene and sulfur compounds is known. For instance, the addition of sulfur to one double bond in the course of the formation of complex I occurs in a similar way to the addition of di-, tri- and tetrasulfur compounds to the norbornadiene molecule [7–13].

In the case of complex II both double bonds of the norbornadiene molecule take part in the reaction, leading to the formation of two C–S and one C–C bond between them. The same behaviour of the norbornadiene double bonds has been structurally confirmed for one of its reaction products with 2,4-dinitrophenylsulfene chloride [14] and for one of the isomeric reaction products with *N,N*-dimethyl-4-nitrophenylsulfenamide [15].

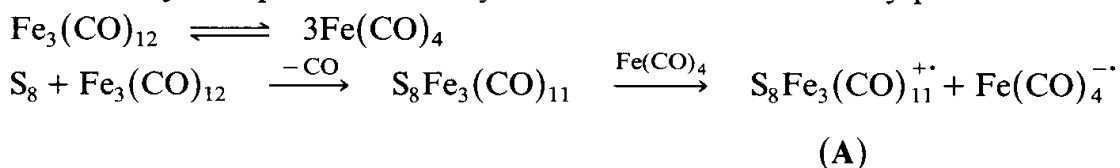
The formation of the product of Vagner–Meerwein rearrangement has been observed in the reaction of norbornene with 2,4-(NO₂)₂C₆H₃SCl in formic acid [16]



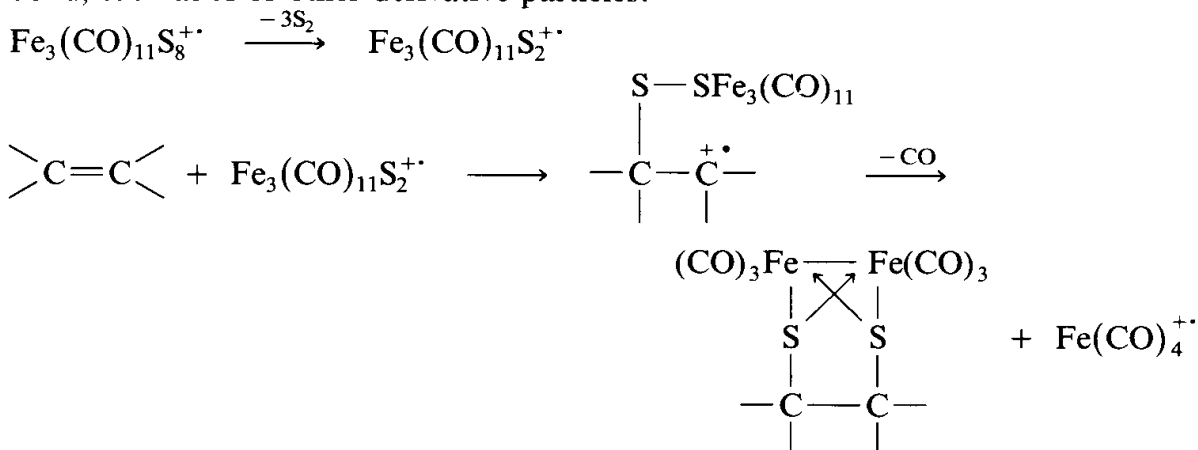
and in liquid SO_2 [17], and also in its reaction with the system phenylsulfene chloride/acetonitrile [18]. These reactions are likely to be similar to those resulting in the formation of conformers of complex III, designated by the lines — and — — —. In this case bonding of the sulfur atoms should have occurred with one of the carbon atoms of the former double bond of the norbornadiene molecule and the bridging carbon atom, with intramolecular migration of the hydrogen atom from the bridging carbon atom to the other carbon atom of the former norbornadiene double bond.

The new fourth product of the reaction of norbornadiene with sulfur and $\text{Fe}_3(\text{CO})_{12}$, complex IV, is formed as a result of gem-addition of the sulfur atoms to one of the carbon atoms at the double bond of norbornadiene together with intramolecular migration of the hydrogen atom to the neighbouring carbon atom of the former double bond. Formation of similar dithiodiironhexacarbonyls, containing a spirane carbon atom between the sulfur atoms, has been observed in reactions of thiobenzophenones [19] and nonaromatic thioketones [20] with $\text{Fe}_2(\text{CO})_9$. The character of bonding and the structure of the norbornadiene group in IV have been determined by X-ray structural analysis of this compound.

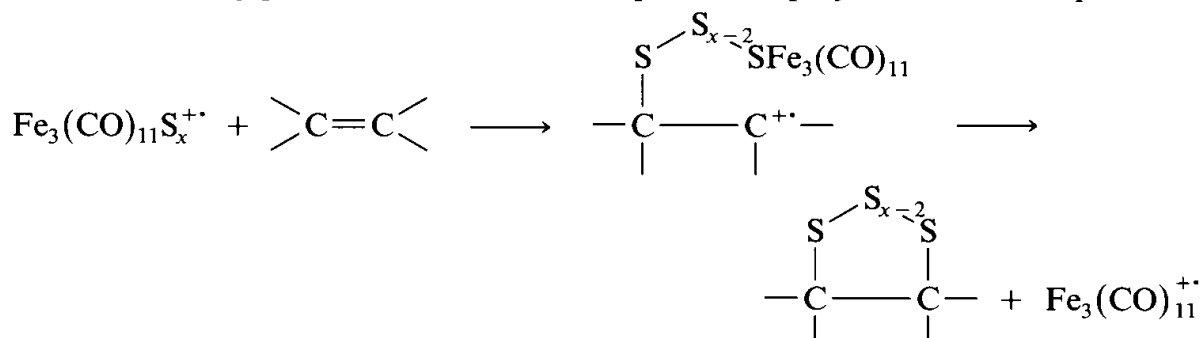
Taking into account that in the course of the interaction of iron carbonyls with Lewis bases, including sulfur, ironcarbonyl particles of radical character appear as a result of redox disproportionation [21], the following scheme of formation of ironcarbonyl complexes I–IV may be assumed as one of many possible:



The cation-radical A may then decay according to the β -rule, with the elimination of S_2 fragments, to the cation-radical $\text{Fe}_3(\text{CO})_{11}\text{S}_2^{+\cdot}$, which may then add to a double bond, such as A or other derivative particles:



The following path of formation of complexes via polysulfides is also possible:



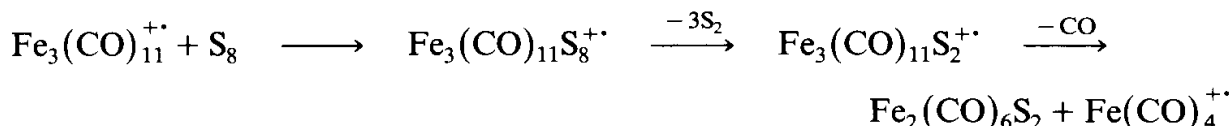
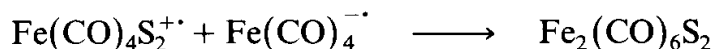
This plurality of directions of addition to norbornadiene may be due to delocalization of the positive charge in the norbornadiene fragment. The possibility of the delocalization of positive charge in the norbornadiene cation has been pointed out previously, for instance in [22–25]. Ironcarbonyl complexes of norbornadiene and other dienes cannot be formed in the presence of sulfur. This is obviously due to the fact that originally sulfur interacts with ironcarbonyl. The absence of norbornadiene polysulfides among the reaction products may be connected with the high reactivity of polysulfides towards $\text{Fe}_3(\text{CO})_{12}$. It has been experimentally proved [26,27] that polysulfides readily react with ironcarbonyls, forming dithiolatodiiironhexacarbonyl complexes. It is also noteworthy that, under the conditions carried out in the present work, norbornadiene does not react with $\text{Fe}_2(\text{CO})_6\text{S}_2$, $\text{Fe}_3(\text{CO})_9\text{S}_2$ or $\text{Fe}_3(\text{CO})_{10}\text{S}$.

The cation-radicals $\text{Fe}(\text{CO})_4^{+\cdot}$, $\text{Fe}_3(\text{CO})_{11}^{+\cdot}$, as well as the anion-radicals $\text{Fe}(\text{CO})_4^{-\cdot}$, may take part in interaction chains analogous to those described above, e.g.:



Along with the four complexes of the composition $\text{Fe}_2(\text{CO})_6(\text{S}_2\text{C}_7\text{H}_8)$, products of the interaction of sulfur with the $\text{Fe}_3(\text{CO})_{12}$ —compounds V and primarily VI were also formed. Complex VII was present in the reaction mixture only if the latter contained $\text{Fe}_3(\text{CO})_{12}$ [26], but since the reaction was carried out until the complete disappearance of $\text{Fe}_3(\text{CO})_{12}$ (TLC monitoring), compound VII could not be isolated from the reaction mixture.

One of the main initial reaction products, $\text{Fe}_2(\text{CO})_6\text{S}_2$, may be formed in different ways, e.g.:



As has been shown earlier by us [28], complex V is transformed under the action of ironcarbonyl into compound VI. On the basis of elemental analysis and IR and mass spectroscopy, complex IV was shown to contain a hydrocarbon fragment C_7H_8 bound to the $\text{Fe}_2(\text{CO})_6\text{S}_2$ group; thus it is an isomer of complexes I–III. However, for a long time single crystals suitable for an X-ray structural study could not be obtained.

The X-ray structural study confirms that complex IV is indeed the fourth isomeric product of the reaction of norbornadiene with sulfur and dodecacarbonyltriiron, in which the binuclear fragment $\text{Fe}_2(\text{CO})_6\text{S}_2$ is bound by its S-bridges to the bicyclo[2.2.1]hept-5-en-2,2-ylene fragment obtained from norbornadiene (Fig. 1). The normal Fe–Fe bond length in IV is 2.493(4) Å, which does not differ practically from 2.485 Å in $\text{Fe}_2(\text{CO})_6(\text{S}_2\text{CH}_2)$ [29] and 2.486 Å in $[\text{Fe}_2(\text{CO})_6\text{S}_2\text{C}]_2$ [30] and is close to the values of 2.469(3), 2.489(1) and 2.465(4) Å estimated in the isomeric complexes I–III [1,3,4]. The mean values for the Fe–S and C–S bond lengths, 2.256 and 1.825 Å, respectively, in compound IV are of the same order as in complexes with the analogous $\text{Fe}_2(\text{CO})_6\text{S}_2\text{C}$ base [29–32]. There is conformation that the non-planar Fe_2S_2 fragment in IV is of the butterfly type (the dihedral angle between the FeFeS planes is 91°).

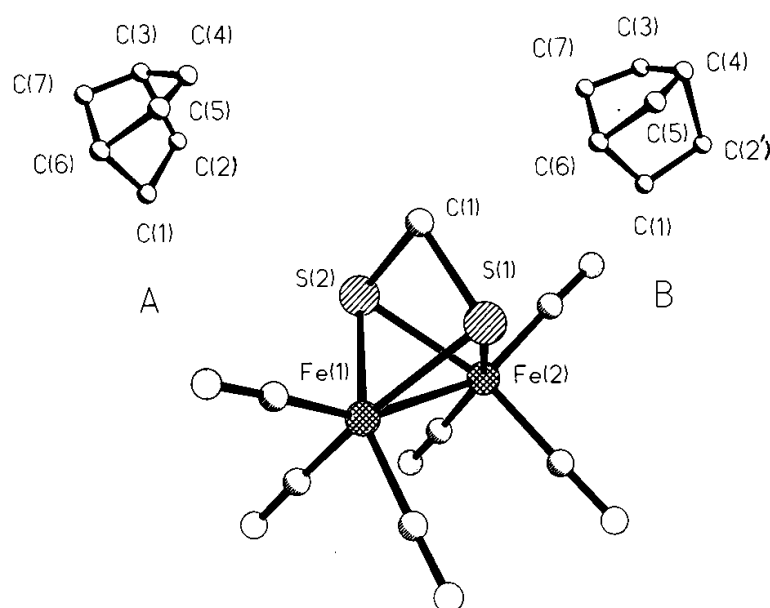


Fig. 1. The structure of compound IV.

The carbon atoms of the C_7H_8 fragment are distorted, i.e. a molecule of IV consists of the two conformers statistically substituting each other (with a 50% population). The six-membered ring in conformer A consists of atoms C(1)–C(6),

Table 1

Atomic coordinates ($\times 10^3$; for Fe and S $\times 10^{-4}$) and their equivalent temperature factors ($\times 10^2$) ($U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$) for compound IV

Atom	x	y	z	U_{eq}
Fe(1)	7771(3)	998(3)	4351(3)	6.1
Fe(2)	8251(3)	2692(3)	2378(3)	6.6
S(1)	6372(6)	650(6)	2362(6)	8.6
S(2)	8948(6)	613(5)	2307(6)	7.9
O(11)	697(2)	–187(2)	558(2)	13
O(21)	617(2)	251(2)	629(2)	13
O(31)	1021(2)	241(2)	621(2)	13
O(12)	1093(2)	466(2)	350(2)	10
O(22)	676(2)	478(2)	350(2)	12
O(32)	850(2)	338(2)	–66(2)	13
C(1)	731(3)	–48(2)	132(2)	10
C(2)	785(4)	–49(4)	–44(4)	6
C(2')	694(4)	–40(5)	–37(4)	6
C(3)	744(3)	–257(4)	–80(3)	14
C(4)	610(3)	–252(4)	–87(3)	13
C(5)	548(3)	–278(2)	49(3)	13
C(6)	685(4)	–221(2)	154(2)	13
C(7)	783(3)	–287(2)	50(4)	13
C(11)	725(2)	–75(2)	506(2)	7
C(21)	678(2)	190(2)	555(2)	9
C(31)	920(2)	181(2)	544(2)	9
C(12)	983(2)	387(2)	306(2)	8
C(22)	735(2)	393(2)	307(2)	9
C(32)	839(3)	307(2)	51(2)	10

Table 2

Bond lengths (Å) in the $\text{Fe}_2\text{S}_2(\text{CO})_6$ fragment for compound IV

Fe(1)–Fe(2)	2.493(4)	Fe(1)–S(1)	2.244(6)
Fe(1)–S(2)	2.254(6)	Fe(1)–C(11)	1.77(2)
Fe(1)–C(21)	1.78(2)	Fe(1)–C(31)	1.69(2)
Fe(2)–S(1)	2.269(6)	Fe(2)–S(2)	2.257(6)
Fe(2)–C(12)	1.72(2)	Fe(2)–C(22)	1.74(2)
Fe(2)–C(32)	1.77(2)	S(1)–C(1)	1.80(2)
S(2)–C(1)	1.85(2)	O(11)–C(11)	1.16(3)
O(21)–C(21)	1.13(3)	O(31)–C(31)	1.19(3)
O(12)–C(12)	1.19(3)	O(22)–C(22)	1.16(3)
O(32)–C(32)	1.14(3)		

while in conformer **B** this ring is formed of atoms C(1)–C(2′)–C(4)–C(3)–C(7)–C(6). In conformer **A** the C(7) is bridging in the C(1)–C(6) six-membered ring, whereas in the six-membered ring C(1)–C(2′)–C(4)–C(3)–C(7)–C(6) of conformer **B** the C(5)

Table 3

Bond lengths (Å) in the C_7H_8 groups (**A** and **B**) for compound IV

C(1)–C(2)	1.69(4)	C(3)–C(4)	1.38(5)
C(1)–C(2′)	1.60(4)	C(3)–C(7)	1.34(4)
C(1)–C(6)	1.59(2)	C(4)–C(5)	1.40(4)
C(2)–C(3)	1.85(5)	C(5)–C(6)	1.61(4)
C(2′)–C(4)	1.92(5)	C(6)–C(7)	1.57(4)

Table 4

Bond angles (degrees) in the $\text{Fe}_2\text{S}_2(\text{CO})_6$ fragment for compound IV

Fe(2)–Fe(1)–S(1)	57.0(2)	Fe(2)–Fe(1)–S(2)	56.5(2)
Fe(2)–Fe(1)–C(11)	155.6(7)	Fe(2)–Fe(1)–C(21)	99.8(7)
Fe(2)–Fe(1)–C(31)	99.5(8)	S(1)–Fe(1)–S(2)	71.4(2)
S(1)–Fe(1)–C(11)	103.9(7)	S(1)–Fe(1)–C(21)	94.7(7)
S(1)–Fe(1)–C(31)	156.4(8)	S(2)–Fe(1)–C(11)	105.4(7)
S(2)–Fe(1)–C(21)	156.3(7)	S(2)–Fe(1)–C(31)	94.5(8)
C(11)–Fe(1)–C(21)	97(1)	C(11)–Fe(1)–C(31)	98(1)
C(21)–Fe(1)–C(31)	91(1)	Fe(1)–Fe(2)–S(1)	56.0(2)
Fe(1)–Fe(2)–S(2)	56.4(2)	Fe(1)–Fe(2)–C(12)	98.2(7)
Fe(1)–Fe(2)–C(22)	99.1(7)	Fe(1)–Fe(2)–C(32)	153.8(8)
S(1)–Fe(2)–S(2)	70.9(2)	S(1)–Fe(2)–C(12)	154.0(7)
S(1)–Fe(2)–C(22)	93.1(7)	S(1)–Fe(2)–C(32)	104.6(8)
S(2)–Fe(2)–C(12)	93.0(7)	S(2)–Fe(2)–C(22)	155.2(8)
S(2)–Fe(2)–C(32)	102.8(8)	C(12)–Fe(2)–C(22)	94(1)
C(12)–Fe(2)–C(32)	99(1)	C(22)–Fe(2)–C(32)	99(1)
Fe(1)–S(1)–Fe(2)	67.1(2)	Fe(1)–S(1)–C(1)	91.3(7)
Fe(2)–S(1)–C(1)	89.5(7)	Fe(1)–S(2)–Fe(2)	67.1(2)
Fe(1)–S(2)–C(1)	89.7(7)	Fe(2)–S(2)–C(1)	88.6(7)
Fe(1)–C(21)–O(21)	178(2)	Fe(1)–C(11)–O(11)	176(2)
Fe(2)–C(12)–O(12)	179(2)	Fe(1)–C(31)–O(31)	179(2)
Fe(2)–C(32)–O(32)	177(2)	Fe(2)–C(22)–O(22)	178(2)

Table 5

Bond angles (degrees) in the $S_2C_7H_8$ groups (**A** and **B**) for compound IV

S(1)–C(1)–C(2)	131(2)	S(1)–C(1)–C(2')	104(2)
S(2)–C(1)–C(2)	99(2)	S(2)–C(1)–C(2')	125(2)
S(1)–C(1)–S(2)	92(1)	S(1)–C(1)–C(6)	116(2)
C(2)–C(1)–C(6)	103(2)	C(2')–C(1)–C(6)	106(2)
S(2)–C(1)–C(6)	113(2)	C(1)–C(2')–C(4)	96(2)
C(1)–C(2)–C(3)	95(2)	C(2')–C(4)–C(3)	83(2)
C(2)–C(3)–C(4)	83(2)	C(2')–C(4)–C(5)	96(2)
C(2)–C(3)–C(7)	100(2)	C(4)–C(3)–C(7)	114(3)
C(3)–C(4)–C(5)	110(3)	C(4)–C(5)–C(6)	99(2)
C(1)–C(6)–C(5)	99(2)	C(1)–C(6)–C(7)	103(2)
C(5)–C(6)–C(7)	98(2)	C(3)–C(7)–C(6)	99(2)

atom acts as a bridge. Conformers **A** and **B** contain C(4)–C(5) (1.40(4) Å) and C(3)–C(7) (1.34(4) Å) double bonds, respectively. The atomic coordinates and their anisotropic temperature factors, bond lengths and bond angles for compound IV are listed in Tables 1–5.

The distortion of the C_7H_8 fragment in IV, caused by the presence of two conformers, apparently leads to considerable errors in the determination of the geometrical parameters in this fragment and to certain differences in the values of bond lengths and bond angles (Tables 2–5) from the anticipated standard values [33].

Experimental

The IR spectra were recorded in KBr pellets with a UR-20 spectrophotometer. The mass-spectra were measured with a Varian MAT-311A instrument having a direct inlet into the ion source at 80 °C and an ionization energy of 70 eV. In order to control the presence of H_2S in the gaseous reaction products a flask containing a saturated aqueous solution of $CdCl_2$ was installed at the outlet. The yield of IV was determined relative to iron used for the reaction, and the R_f value was defined for n-heptane on Silufol plates (Kavalier, Czechoslovakia) with a fixed silica gel layer. The X-ray measurements were performed with a Syntex-P1 diffractometer ($\lambda(Mo-K_\alpha)$, graphite monochromator, $\theta/2\theta$ scan, $3 \leq 2\theta \leq 51^\circ$). Crystals of IV are triclinic, a 10.152 (6), b 9.385(6), c 9.110(6) Å, α 96.95(4), β 89.51(4), γ 107.15(4)°, V 823(1) Å³, $Z = 2$, space group $P\bar{1}$. The structure was solved by the heavy-atom method and refined by the least-squares technique in an anisotropic full-matrix approximation to $R = 0.0778$ ($R_w = 0.0810$) for 1124 independent reflections with $F^2 \geq 2\sigma$. Crystals of IV were obtained from heptane at $-18^\circ C$.

Synthesis of IV

The mixture of norbornadiene (40 ml, 393.5 mmol), sulfur (7.70 g, 0.24 g-at) and $Fe_3(CO)_{12}$ (32.0 g, 63.5 mmol) in 400 ml of benzene was stirred for 14 h at 80 °C under an Ar flow. Norbornadiene and benzene were removed under reduced pressure. The residue was extracted by hexane in a Soxhlet apparatus until the solvent became colourless. The hexane solution was evaporated to minimal volume and chromatography was carried out on a silica gel column with hexane as eluent.

The reagents and reaction products were eluted in the following order: S₈, IV, V, VI, I, III, II. TLC monitoring in the course of the reaction showed that Fe₃(CO)₁₂ was eluted after III, and *R_f* for the complexes VII and II, which were the last to be eluted, coincided. Complexes V and VI were obtained with yields of 2 and 16%, respectively.

Compound IV is red-orange, with m.p. 100–103° C, yield 2%, *R_f* = 0.40. The IR spectrum gives (ν , cm⁻¹): 2080, 2038, 2015, 2004, 1966 (C≡O). The mass spectrum is as follows (*m/z*, the relative intensities are given in parentheses) 436(52) Fe₂(CO)₆S₂C₇H₈⁺, 408(6) Fe₂(CO)₅S₂C₇H₈⁺, 380(57) Fe₂(CO)₄S₂C₇H₈⁺, 352(73) Fe₂(CO)₃S₂C₇H₈⁺, 324(81) Fe₂(CO)₂S₂C₇H₈⁺, 296(91) Fe₂(CO)S₂C₇H₈⁺, 268(94) Fe₂S₂C₇H₈⁺, 242(94) Fe₂S₂C₅H₆⁺, 190(13) Fe₂S₂CH₂⁺, 176(98) Fe₂S₂⁺, 144(100) Fe₂S⁺, 112(25) Fe₂⁺. Fragmentation of IV under electron impact is analogous to that of I–III [6]. Found: C, 35.68; H, 1.80; Fe, 25.47; S, 14.83. C₁₃H₈Fe₂O₆S₂ calcd.: C, 35.81; H, 1.85; Fe, 25.61; S, 14.71%.

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