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**IRON CARBONYL COMPLEXES OF 2,3,5,6-TETRAKIS(METHYLENE)-7-OXABICYCLO[2.2.1]HEPTANE. CRYSTAL AND MOLECULAR STRUCTURE OF  $(C_{10}H_{10}O)Fe(CO)_3$  AND  $(C_9H_{10}CO)Fe_2(CO)_6$**

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### Summary

The reaction of 2,3,5,6-tetrakis(methylene)-7-oxabicyclo[2.2.1]heptane (I) with iron carbonyls in various solvents yields the  $(\eta^4-1,3\text{-diene})Fe(CO)_3$  isomers (II: *exo*; III: *endo*) and the bimetallic isomers bis[ $(\eta^4-1,3\text{-diene})Fe(CO)_3$ ] (IV: bis(*exo*); V: *endo,exo*). In weakly coordinating solvents, a parallel rearrangement of I occurs through C—O bond cleavage of the allylic ether by  $Fe_2(CO)_9$ , yielding an unsaturated ketone (VI) bonded to two  $Fe(CO)_3$  groups through a trimethylenemethane and a 1,3-diene system, respectively. The geometries of III and VI have been ascertained by X-ray crystal structure determinations.

### Introduction

Allylic C—O bonds can react with low valent metal carbonyls [1]. For instance, an elegant synthesis of unsaturated  $\delta$ -lactones has been developed by treatment of vinyl epoxides with  $Fe_2(CO)_9$  or  $Fe(CO)_5$  [2]. Deoxygenation of benzeneoxides [3] and benzooxanorbornadiene [4] has been observed by treating these compounds with iron carbonyls. These reactions probably involve the generation of allylic iron systems and may occur for instance by (a) initial com-

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plexation of the double bond by  $\text{Fe}(\text{CO})_4$  followed by cleavage of the C—O bond or (b) initial complexation of the oxygen function by the electrophilic  $\text{Fe}(\text{CO})_4$  and ring cleavage [5] (i.e. oxidative addition of  $\text{Fe}(\text{CO})_4$  into the allylic C—O bond [6]).

Recently, we reported that 5,6-bis(methylene)7-oxabicyclo[2.2.1]hept-2-ene (formally a bis(allyl)ether), when treated with iron carbonyls in excess, yielded a bis(iron) complex which eliminated the oxygen bridge upon heating to give the corresponding (*o*-quinodimethane) $\text{Fe}(\text{CO})_3$  complex in relatively good yield [7]. In the presence of iron carbonyls, the 2,3-bis(methylene)-7-oxabicyclo[2.2.1]heptane yielded only the expected *exo* and *endo* (1,3-diene) $\text{Fe}(\text{CO})_3$  complexes. The allylic C—O bond in these complexes as well as in the free ligand did not react [8]. In the 2,3,5,6-tetrakis(methylene)-7-oxabicyclo[2.2.1]heptane (I), the ether function is of the bis(allylic) type. It was hoped therefore that this oxygen bridge would prove more labile and more readily undergo oxidative additions with  $\text{Fe}(\text{CO})_4$  yielding rearranged and/or deoxygenated products.

We treated I with  $\text{Fe}_2(\text{CO})_9$  and  $\text{Fe}(\text{CO})_5$  under various conditions and found that, besides the formation of the expected (1,3-diene) $\text{Fe}(\text{CO})_3$  complexes, a parallel rearrangement of the tetraene I occurs which implies a C—O bond cleavage of the allylic ether.

### Reaction of I with Fe carbonyls

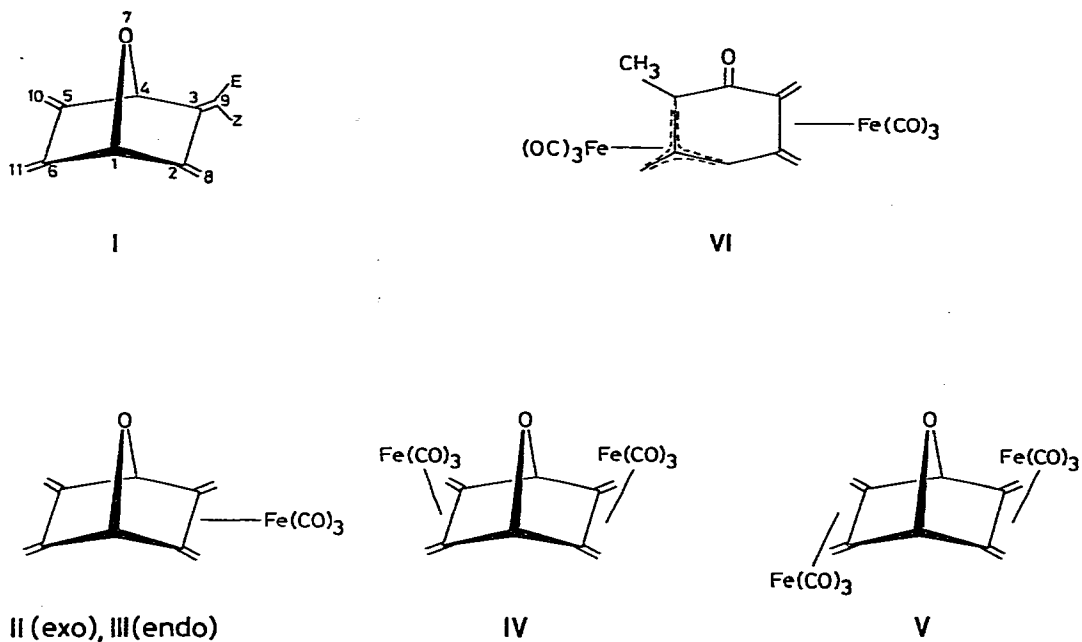
Iron carbonyls may form at least four complexes with 2,3,5,6-tetrakis(methylene)-7-oxabicyclo[2.2.1]heptane (I): the *exo*- and *endo*-*tetrahapto*-tricarbonyliron isomers (II and III) and the bis(*exo*)- and *endo,exo*-bis(*tetrahapto*-tricarbonyliron) isomers (IV and V). The molecular structure of III (*vide infra*) shows that the bis(*endo*)-bis(*tetrahapto*-tricarbonyliron) complex cannot be formed for steric reasons.

Reacting I with  $\text{Fe}_2(\text{CO})_9$  in *n*-hexane at room temperature gives II (33%), IV (9%), V (3%) and the rearranged product VI (1.5%) (Scheme 1) \*. The same reaction in benzene, *n*-hexane/THF or  $\text{CH}_3\text{CN}$  at higher temperature or irradiation of I with  $\text{Fe}(\text{CO})_5$  in *n*-pentane at  $-75^\circ\text{C}$  gave lower yields of the same complexes. The *endo* isomer III was obtained (7%) by reacting I with  $\text{Fe}_2(\text{CO})_9$  in methanol. Such a solvent effect on the *endo/exo* ratio of (1,3-diene) $\text{Fe}(\text{CO})_3$  isomers has been reported for the reaction of  $\text{Fe}_2(\text{CO})_9$  with bicyclo[4.2.1]nona-2,4,7-triene-9-one [9].

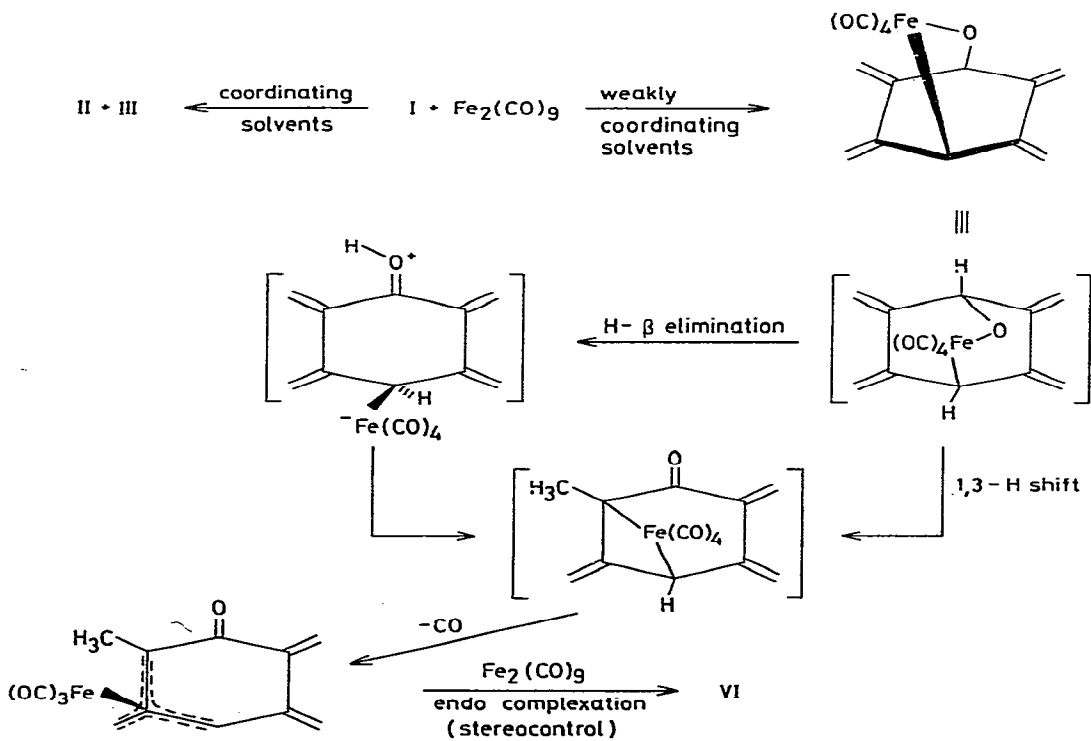
The rearranged product VI was obtained in very low yield and could have been formed by the reaction of  $\text{Fe}_2(\text{CO})_9$  with a precursor of ligand I present as an impurity, e.g. 2,3-bis(methylene)-5,6-bis(*exo*-chloromethyl)-7-oxabicyclo[2.2.1]heptane (VII). However, the direct reaction of VII with  $\text{Fe}_2(\text{CO})_9$  in *n*-hexane (or methanol) gave only the *exo* and *endo* isomers (VIII and IX) of the expected (*tetrahapto*-1,3-diene) $\text{Fe}(\text{CO})_3$  complex (see Experimental). The direct reaction of the monometallic complexes II and III with  $\text{Fe}_2(\text{CO})_9$  in *n*-hexane or ether/*n*-pentane yields stereospecifically the bimetallic isomers IV (40%) and V (45%), respectively. Likewise no evidence was found for the for-

\* The optimisation of yields was not attempted.

SCHEME 1



SCHEME 2



mation of VI, nor for the epimerisation equilibrium  $IV \rightleftharpoons V$ , by heating each bimetallic isomer in refluxing toluene in the presence or absence of  $Fe_2(CO)_9$ , by irradiation in n-pentane in the presence or absence of  $Fe(CO)_5$ , or by adding dry HCl to a diethylether solution of IV or V. We conclude that VI is formed in n-hexane by a parallel and slower reaction in which  $Fe_2(CO)_9$  or  $Fe(CO)_4$  interacts directly with the oxygen bridge of ligand I or of a transient complex intermediate. We tentatively propose the mechanistic limits as shown in Scheme 2 for its formation..

The absence of VI when running the complexation reaction in methanol supports the hypothesis of an oxidative addition into the allylic C—O bond. This is made possible by coordination of the ether bridge (donor) and  $Fe(CO)_4$  (acceptor).

The crystal and molecular structures of III and VI have been determined to serve as a reference for the assignments of the spectroscopic data of all complexes and to ascertain the nature of the rearranged product VI.

#### Crystal structures of $(C_{10}H_{10}O)Fe(CO)_3$ (III) and $(C_9H_{10}CO)Fe_2(CO)_6$ (VI)

The X-ray diffractometer measurements were carried out with a Syntex P2<sub>1</sub> automatic four-circle diffractometer. The crystal data and methods used are summarised in Table 1.

*a) Complex III:* during the measurements the intensities of three check reflections fell to 70% of their starting value and the measured intensities were scaled accordingly. The crystal form was accurately measured as before [11] and used to correct the intensities for absorption. The computer programs used for the data reduction and structure analysis were taken from the "X-RAY 72" program system [12] and MULTAN [13]. Scattering factors for the neutral non-hydrogen atoms were taken from Cromer and Mann [14], and for hydrogen atoms from Stewart et al. [15]. Anomalous dispersion coefficients of Fe were taken from Cromer [16]. All the non-hydrogen atoms were obtained from a E map calculated with the phases generated by MULTAN after Patterson and Fourier methods had failed. This failure was due to the rather special position of the Fe atom (0, 3/4, 7/8). Hydrogen atom positions were obtained from a difference Fourier synthesis after refinement to  $R = 0.075$ . Final refinement to  $R = 0.032$  included isotropic extinction ( $Y_{\min} = 0.74$ ) and gave the positional and thermal parameters reported in Table 2\*. The perspective drawing was prepared by the program ORTEP [17]. Calculated bond lengths and angles are reported in Tables 3 and 4, respectively. The equations for several least-squares planes and some dihedral angles are presented in Table 5. A view of the molecular structure is given in Fig. 1, where the numbering scheme of the ligand is identical with that used for nomenclatural purposes.

*b) Complex VI:* the crystal was protected from the air by a sealed glass capillary. The computer programs used were the same as above and the structure was solved by Patterson and Fourier methods. All hydrogen atoms were found from a difference synthesis after preliminary refinement to  $R = 0.055$ . Final

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\* Lists of observed and calculated structure factors for both complexes are available from the authors on request.

TABLE 1  
SUMMARY OF CRYSTAL DATA, INTENSITY COLLECTION AND REFINEMENT

	III	VI
Formula	(C <sub>10</sub> H <sub>10</sub> O)Fe(CO) <sub>3</sub>	(C <sub>9</sub> H <sub>10</sub> CO)Fe <sub>2</sub> (CO) <sub>6</sub>
Molecular weight	286.08	425.95
Dimensions (mm)	0.15 × 0.23 × 0.26	0.07 × 0.30 × 0.42
Crystal class	Orthorhombic	Monoclinic
a (Å)	8.772(8)	13.734(2)
b (Å)	14.453(2)	7.304(1)
c (Å)	20.170(4)	17.353(2)
β (°)		106.08(1)
V (Å <sup>3</sup> )	2557	1672.6
Z	8	4
d <sub>calcd</sub> (g/cm <sup>3</sup> )	1.486	1.691
d <sub>obsd</sub> (g/cm <sup>3</sup> )	1.48(1)	1.69(1)
F <sub>000</sub>	1168	856
Space group	Pbca	P2 <sub>1</sub> /n
Systematic absences	hk0: h = 2n + 1 h0l: l = 2n + 1 0kl: k = 2n + 1	h0l: h + l = 2n + 1 0k0: k = 2n + 1
Radiation	Mo-K <sub>α</sub> , Nb filtered (λ 0.71069 Å)	same
μ (cm <sup>-1</sup> )	12.1	18.2
Scan method	2θ-θ	same
Background from	Scan profile interpretation [10]	same
(sin θ/λ) <sub>max</sub>	0.54	0.59
Data collected	+h, +k, +l	+h, +k, ±l
No. of unique reflections	1686	2495
No. of reflections <3σ	703	813
No. of observations/No. of variables	8.3	9.3
Structure solution	MULTAN and Fourier	Patterson and Fourier
Refinement method	Block diagonal least-squares	same
Function minimised	Σw( F <sub>o</sub>   -  F <sub>c</sub>  ) <sup>2</sup>	same
w	1/σ <sup>2</sup>	same
R	0.032	0.045
R <sub>w</sub>	0.027	0.049
Goodness of fit	1.80	3.89

refinement to  $R = 0.045$  gave the positional and thermal parameters listed in Table 6. Calculated bond lengths and angles are reported in Tables 7 and 8, respectively. The equations for several least-squares planes and some dihedral angles are presented in Table 9 and a view of the molecular structure is given in Fig. 2.

### Discussion

*a) Complex III:* the structure is composed of discrete monomeric (C<sub>10</sub>H<sub>10</sub>O)-Fe(CO)<sub>3</sub> molecules. All intermolecular contacts are equal to or greater than the sum of normal Van der Waals radii. There is essentially mirror symmetry for the whole molecule, with the mirror plane I (Table 5) passing through the Fe atom, O(7), one CO group and the midpoints of the bonds C(2)-C(3) and C(5)-C(6). The Fe(CO)<sub>3</sub> group is in the *endo* position with respect to the roof-shaped ligand. The arrangement of ligands about the iron atom is tetragonal pyramidal. Four coordination sites are occupied by 2 CO and the midpoints *m* and *m'* of the exocyclic C-C bonds of one *s-cis*-butadiene system, C(13)-

TABLE 2  
ATOMIC COORDINATES AND THERMAL PARAMETERS OF III

Atom	x	y	z	U <sub>11</sub> (or U)	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
C(1)	0.8657(5)	0.9277(3)	0.7877(2)	0.047(3)	0.053(3)	0.040(3)	0.003(2)	0.001(3)	0.015(3)
C(2)	0.8773(4)	0.8239(2)	0.7986(2)	0.037(3)	0.043(2)	0.038(2)	-0.001(2)	-0.003(2)	-0.003(2)
C(3)	0.7688(5)	0.8045(2)	0.8464(2)	0.036(3)	0.037(2)	0.048(2)	-0.005(2)	-0.009(2)	0.002(2)
C(4)	0.6955(5)	0.8988(3)	0.8619(2)	0.038(3)	0.057(3)	0.058(3)	0.000(2)	0.004(3)	0.008(2)
C(5)	0.8067(5)	0.9602(3)	0.8974(2)	0.046(3)	0.041(2)	0.049(3)	0.015(3)	0.001(2)	0.002(2)
C(6)	0.9236(5)	0.9799(3)	0.8473(2)	0.037(3)	0.033(2)	0.053(3)	0.007(2)	-0.001(2)	0.005(2)
C(8)	0.9665(5)	0.7529(4)	0.7730(2)	0.070(4)	0.056(3)	0.053(3)	-0.022(4)	0.012(3)	-0.003(3)
C(9)	0.7480(5)	0.7130(3)	0.8695(3)	0.046(3)	0.051(3)	0.059(3)	-0.009(2)	0.002(3)	-0.001(3)
C(10)	0.7926(6)	0.9937(4)	0.9581(3)	0.065(5)	0.057(3)	0.076(5)	0.000(4)	0.012(4)	0.004(3)
C(11)	1.0453(6)	1.0338(3)	0.8503(3)	0.062(4)	0.040(3)	0.072(4)	0.002(3)	0.003(3)	-0.003(3)
C(12)	1.0424(4)	0.6371(3)	0.8802(2)	0.037(2)	0.052(3)	0.093(3)	-0.001(2)	-0.001(3)	0.008(3)
C(13)	1.1562(5)	0.8130(3)	0.8754(3)	0.051(3)	0.041(3)	0.077(3)	-0.004(2)	-0.013(4)	0.006(3)
C(14)	0.9522(5)	0.7756(3)	0.9624(2)	0.056(3)	0.050(3)	0.066(3)	-0.010(3)	-0.009(3)	0.006(3)
Fe(1)	0.9785(5)	0.75312(4)	0.87712(3)	0.0369(3)	0.0372(3)	0.0541(3)	-0.0025(4)	-0.0027(4)	0.0025(4)
O(1)	1.0812(3)	0.5607(2)	0.8610(2)	0.064(2)	0.045(2)	0.173(3)	0.012(2)	-0.008(3)	0.000(3)
O(2)	1.2727(4)	0.8492(2)	0.8753(2)	0.052(2)	0.075(2)	0.132(3)	-0.022(2)	-0.019(3)	0.021(2)
O(3)	0.9345(4)	0.7872(2)	1.0183(2)	0.126(3)	0.103(3)	0.057(2)	-0.008(2)	-0.011(3)	0.003(2)
O(7)	0.7015(3)	0.9394(2)	0.7958(1)	0.041(2)	0.064(2)	0.060(2)	0.005(2)	-0.010(2)	0.014(2)
H(1)	0.896(3)	0.947(2)	0.746(1)	0.03(1)					
H(4)	0.602(4)	0.894(2)	0.878(2)	0.04(1)					
H(8E)	1.048(4)	0.771(2)	0.748(2)	0.04(1)					
H(8Z)	0.924(4)	0.691(2)	0.762(2)	0.06(1)					
H(9E)	0.692(4)	0.707(2)	0.907(2)	0.05(1)					
H(9Z)	0.746(4)	0.667(2)	0.840(2)	0.04(1)					
H(10E)	0.722(4)	0.974(2)	0.982(2)	0.03(1)					
H(10Z)	0.868(4)	1.036(2)	0.974(2)	0.05(1)					
H(11E)	1.104(4)	1.042(3)	0.813(2)	0.07(2)					
H(11Z)	1.068(5)	1.069(3)	0.887(2)	0.07(2)					

The e.s.d. of the last significant digit is given in parentheses. The temperature factor has the form  $e^{-T}$  where  $T = 2\pi^2 \sum h_i h_j U_{ij} a_i^* a_j^*$  for anisotropic atoms and  $T = 8\pi^2 U \sin^2 \theta / \lambda^2$  for isotropic atoms.

TABLE 3  
BOND LENGTHS (Å) IN III

Fe(1)—C(2)	2.083(4)	Fe(1)—C(12)	1.769(4)
Fe(1)—C(3)	2.079(4)	Fe(1)—C(13)	1.785(4)
Fe(1)—C(8)	2.103(4)	Fe(1)—C(14)	1.765(5)
Fe(1)—C(9)	2.107(5)	C(13)—O(2)	1.147(5)
C(12)—O(1)	1.156(5)	C(14)—O(3)	1.150(6)
C(1)—C(2)	1.519(5)	C(3)—C(4)	1.534(6)
C(1)—C(6)	1.508(6)	C(4)—C(5)	1.500(6)
C(1)—O(7)	1.459(5)	C(4)—O(7)	1.457(5)
C(2)—C(3)	1.382(5)	C(5)—C(6)	1.467(6)
C(2)—C(8)	1.389(6)	C(6)—C(11)	1.322(7)
C(3)—C(9)	1.421(6)	C(5)—C(10)	1.323(7)
C(1)—H(1)	0.93(3)	C(4)—H(4)	0.89(3)
C(8)—H(8E)	0.91(3)	C(10)—H(10E)	0.83(3)
C(8)—H(8Z)	0.99(3)	C(10)—H(10Z)	0.95(3)
C(9)—H(9E)	0.90(3)	C(11)—H(11E)	0.93(4)
C(9)—H(9Z)	0.90(3)	C(11)—H(11Z)	0.92(4)

The e.s.d. of the last significant digit is given in parentheses.

C(14)—m—m' defining the basal plane (Table 5). The apex-to-base and the basal angles are very similar to those found in several other (exocyclic 1,3-diene)Fe(CO)<sub>3</sub> structures [11]. The diene is perpendicular to the basal plane, the Fe atom lies 0.50(2) Å over it and the apical Fe—CO bond makes an angle of 8(1)° with the normal to the basal plane. The difference between the weighted average of Fe—C(8) and Fe—C(9) and the weighted average of Fe—C(2) and Fe—C(3) is 0.024(6) Å. The difference between C(2)—C(3) and the weighted aver-

(Continued on p. 258)

TABLE 4  
BOND ANGLES (°) IN III

C(2)—Fe(1)—C(3)	38.8(1)	C(12)—Fe(1)—C(13)	100.5(2)
C(2)—Fe(1)—C(8)	38.7(2)	C(12)—Fe(1)—C(14)	100.5(2)
C(3)—Fe(1)—C(9)	39.7(2)	C(13)—Fe(1)—C(14)	92.5(2)
Fe(1)—C(12)—O(1)	178.2(4)	Fe(1)—C(14)—O(3)	177.8(4)
Fe(1)—C(13)—O(2)	177.8(4)	C(1)—O(7)—C(4)	95.2(3)
C(2)—C(1)—C(6)	110.9(3)	C(3)—C(4)—C(5)	110.4(3)
C(2)—C(1)—O(7)	99.5(3)	C(3)—C(4)—O(7)	98.8(3)
C(6)—C(1)—O(7)	100.7(3)	C(5)—C(4)—O(7)	100.1(3)
C(1)—C(2)—C(3)	104.5(3)	C(2)—C(3)—C(4)	104.8(3)
C(1)—C(2)—C(8)	135.5(4)	C(4)—C(3)—C(9)	134.9(4)
C(3)—C(2)—C(8)	120.0(4)	C(2)—C(3)—C(9)	120.3(4)
C(4)—C(5)—C(6)	104.0(3)	C(1)—C(6)—C(5)	102.4(3)
C(4)—C(5)—C(10)	126.7(4)	C(1)—C(6)—C(11)	127.1(4)
C(6)—C(5)—C(10)	129.1(4)	C(5)—C(6)—C(11)	130.4(4)
H(1)—C(1)—C(2)	114(2)	H(4)—C(4)—C(3)	113(2)
H(1)—C(1)—C(6)	119(2)	H(4)—C(4)—C(5)	118(2)
H(1)—C(1)—O(7)	110(2)	H(4)—C(4)—O(7)	114(2)
H(8E)—C(8)—H(8Z)	115(3)	H(9E)—C(9)—H(9Z)	119(3)
H(8E)—C(8)—C(2)	116(2)	H(9E)—C(9)—C(3)	115(2)
H(8Z)—C(8)—C(2)	123(2)	H(9Z)—C(9)—C(3)	119(2)
H(10E)—C(10)—H(10Z)	123(2)	H(11E)—C(11)—H(11Z)	118(3)
H(10E)—C(10)—C(5)	118(2)	H(11E)—C(11)—C(6)	119(2)
H(10Z)—C(10)—C(5)	118(2)	H(11Z)—C(11)—C(6)	122(2)

the e.s.d. of the last significant digit is given in parentheses.

TABLE 5  
LEAST-SQUARES PLANES IN III

Plane	Atoms defining plane <sup>a</sup>	Equation of mean plane
I	O(7), Fe(1), C(12), O(1)	$-6.086X + 2.973Y + 13.919Z = 4.014$
II	H(1), C(1), O(7), C(4), H(4)	$1.289X + 13.077Y + 8.061Z = 19.578$
III	C(1), C(2), C(3), C(4)	$5.954X + 2.216Y + 14.485Z = 18.619$
IV	C(2), C(3), C(8), C(9)	$5.966X + 2.298Y + 14.434Z = 18.654$
V	C(13), C(14), m, m'	$-1.986X + 14.042Y + 1.381Z = 10.330$
VI	C(1), C(4), C(5), C(6)	$-4.519X + 11.648Y - 5.881Z = 2.258$
VII	C(5), C(6), C(10), C(11)	$-4.777X + 11.071Y - 7.054Z = 0.401$

Displacement of atoms from mean plane (Å)

Plane I	O(7) 0.000	Plane II	H(1) -0.031	Plane III	C(1) 0.001
	Fe(1) 0.001		C(1) 0.018		C(2) -0.002
	C(12) -0.001		O(7) 0.024		C(3) 0.002
	O(1) 0.001		C(4) 0.019		C(4) -0.001
			H(4) -0.031		
Plane IV	0.00 for the	Plane VI	C(1) 0.002	Plane VII	C(5) -0.006
Plane V	four atoms		C(4) -0.002		C(6) 0.006
			C(5) 0.002		C(10) 0.003
			C(6) -0.002		C(11) -0.003

Dihedral angle between planes (°)

I-II	89.3;	I-III	89.6;	I-IV	89.4;	I-V	89.7;	I-VI	89.5;	I-VII	88.8;
II-III	121.7;	II-VI	122.5;	III-IV	0.4;	III-VI	115.8;	IV-V	87.2;	VI-VII	4.5;

<sup>a</sup> m and m' are the midpoints of the C(2)-C(8) and C(3)-C(9) bonds, respectively.

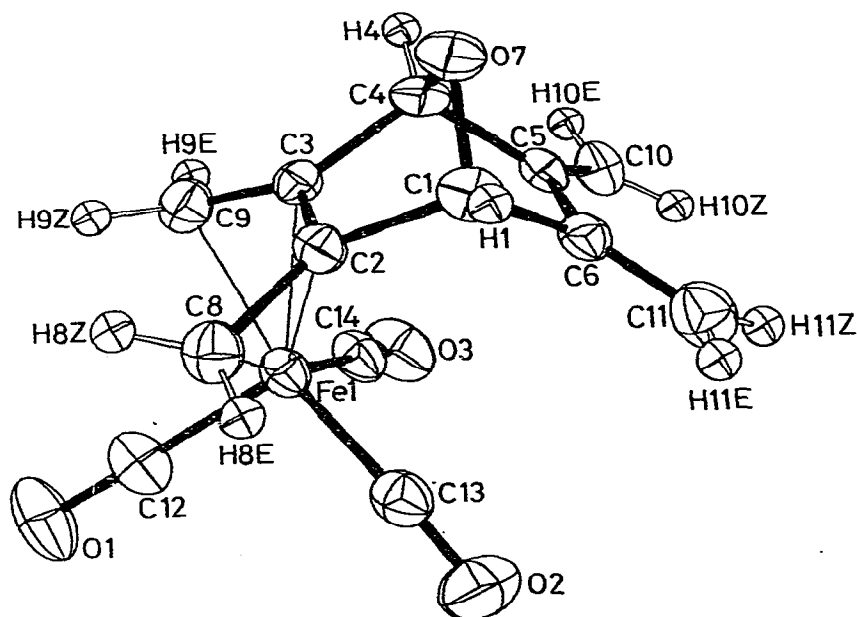


Fig. 1. Molecular structure of complex III.



TABLE 6  
ATOMIC COORDINATES AND THERMAL PARAMETERS OF VI

Atom	x	y	z	$U_{11}$ (or $U_1$ )	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Fe(1)	-0.02945(7)	0.0397(1)	0.28406(6)	0.0309(5)	0.0400(5)	0.0354(5)	-0.0028(4)	0.0051(4)	-0.0033(4)
C(11)	0.0118(6)	0.164(1)	0.2090(4)	0.047(4)	0.072(5)	0.036(4)	-0.013(4)	0.001(3)	0.001(4)
O(2)	0.0362(5)	0.239(1)	0.1609(4)	0.077(4)	0.121(6)	0.053(3)	-0.028(4)	0.016(3)	-0.027(4)
C(12)	-0.1816(6)	0.103(1)	0.2494(5)	0.049(5)	0.063(5)	0.052(4)	-0.003(4)	0.009(4)	-0.011(4)
O(3)	-0.2445(4)	0.148(1)	0.2288(4)	0.033(3)	0.138(7)	0.103(5)	0.019(4)	-0.006(3)	-0.026(5)
C(13)	-0.0396(6)	-0.183(1)	0.2364(4)	0.047(4)	0.056(5)	0.049(4)	-0.008(4)	0.005(3)	-0.011(4)
O(4)	-0.0428(5)	-0.3214(8)	0.2084(3)	0.096(5)	0.063(4)	0.069(3)	-0.005(3)	0.002(3)	-0.035(3)
Fe(2)	0.30694(6)	0.2335(1)	0.45040(6)	0.0243(4)	0.0406(5)	0.0351(5)	-0.0014(4)	0.0047(4)	-0.0024(4)
C(14)	0.2963(5)	0.066(1)	0.5233(5)	0.029(3)	0.050(4)	0.053(4)	0.002(3)	0.006(3)	0.002(4)
O(5)	0.2872(5)	-0.037(1)	0.5697(4)	0.064(4)	0.082(5)	0.084(4)	0.005(3)	0.021(3)	0.040(4)
C(15)	0.2923(5)	0.412(1)	0.5156(4)	0.037(4)	0.056(5)	0.046(4)	-0.001(3)	0.009(3)	-0.009(4)
O(6)	0.2843(5)	0.5268(9)	0.5583(4)	0.072(4)	0.077(4)	0.082(4)	-0.003(4)	0.025(3)	-0.035(4)
C(16)	0.4407(5)	0.248(1)	0.4653(4)	0.035(4)	0.068(5)	0.044(4)	-0.002(4)	0.010(3)	-0.006(4)
O(7)	0.5259(4)	0.259(1)	0.4740(4)	0.033(3)	0.125(6)	0.086(4)	-0.009(4)	0.015(3)	-0.018(4)
C(17)	0.0118(4)	0.2447(9)	0.3810(4)	0.030(3)	0.035(3)	0.033(3)	0.004(3)	0.003(3)	0.001(3)
C(2)	0.0380(5)	0.0570(9)	0.3981(4)	0.036(3)	0.036(4)	0.027(3)	-0.005(3)	0.002(3)	-0.004(3)
C(3)	0.1154(5)	-0.0118(9)	0.3673(4)	0.036(3)	0.028(3)	0.035(3)	0.002(3)	0.002(3)	0.002(3)
C(4)	0.1971(5)	0.1075(9)	0.3570(4)	0.031(3)	0.036(4)	0.031(3)	-0.004(3)	-0.002(3)	-0.003(3)
C(5)	0.1863(5)	0.299(1)	0.3567(4)	0.032(3)	0.046(4)	0.030(3)	-0.003(3)	0.002(3)	0.004(3)
C(6)	0.0911(5)	0.375(1)	0.3711(4)	0.044(4)	0.034(4)	0.038(4)	0.006(3)	-0.005(3)	0.001(3)
C(7)	-0.0744(7)	0.337(1)	0.4045(6)	0.048(5)	0.047(5)	0.051(5)	0.004(4)	0.015(4)	-0.016(5)
C(8)	-0.0420(6)	-0.068(1)	0.3945(4)	0.050(4)	0.038(4)	0.044(4)	-0.004(4)	0.014(3)	-0.005(3)
C(9)	0.2937(6)	0.041(1)	0.3561(5)	0.043(4)	0.054(5)	0.051(5)	-0.002(4)	0.013(4)	-0.011(4)
C(10)	0.2697(7)	0.409(1)	0.3529(5)	0.050(5)	0.042(5)	0.053(5)	-0.002(4)	0.010(4)	0.004(4)
O(1)	0.0800(4)	0.5396(7)	0.3748(4)	0.056(3)	0.025(3)	0.052(3)	0.000(2)	-0.001(3)	0.002(3)
H(3A)	0.121(4)	-0.112(9)	0.371(4)	0.05(2)	0.05(2)	0.05(2)			
H(71)	-0.085(6)	0.47(1)	0.369(5)	0.06(2)	0.06(2)	0.06(2)			
H(72)	-0.053(6)	0.40(1)	0.448(5)	0.07(3)	0.07(3)	0.07(3)			
H(73)	-0.125(7)	0.27(1)	0.405(5)	0.08(3)	0.08(3)	0.08(3)			
H(8A)	-0.026(5)	-0.20(1)	0.395(4)	0.05(2)	0.05(2)	0.05(2)			
H(8S)	-0.101(6)	0.00(1)	0.405(4)	0.06(2)	0.06(2)	0.06(2)			
H(9E)	0.309(5)	-0.07(1)	0.371(4)	0.03(2)	0.03(2)	0.03(2)			
H(9Z)	0.328(5)	0.10(1)	0.325(5)	0.06(2)	0.06(2)	0.06(2)			
H(10E)	0.256(4)	0.517(9)	0.357(4)	0.02(2)	0.02(2)	0.02(2)			
H(10Z)	0.305(5)	0.377(9)	0.324(4)	0.04(2)	0.04(2)	0.04(2)			

The e.s.d. of the last significant digit is given in parentheses. The temperature factor has the form  $e^{-T}$  where  $T = 2\pi^2 \sum_i h_i^2 U_{ii} + \sum_{i \neq j} h_i h_j U_{ij}$  for anisotropic atoms and  $T = 8\pi^2 U \sin^2 \theta / \lambda^2$  for isotropic atoms.

TABLE 7  
BOND LENGTHS (Å) IN VI

C(1)—C(2)	1.428(9)	C(3)—H(3)	0.74(6)
C(1)—C(6)	1.489(10)	C(7)—H(71)	1.11(9)
C(1)—C(7)	1.512(12)	C(7)—H(72)	0.88(8)
C(2)—C(3)	1.408(10)	C(7)—H(73)	0.84(9)
C(2)—C(8)	1.417(10)	C(8)—H(8A)	0.96(8)
C(3)—C(4)	1.467(10)	C(8)—H(8S)	1.00(8)
C(4)—C(5)	1.403(10)	C(9)—H(9E)	0.87(7)
C(4)—C(9)	1.417(11)	C(9)—H(9Z)	0.90(9)
C(5)—C(6)	1.504(10)	C(10)—H(10E)	0.82(7)
C(5)—C(10)	1.418(12)	C(10)—H(10Z)	0.81(8)
C(6)—O(1)	1.219(9)		
Fe(1)—C(1)	2.206(6)	Fe(2)—C(4)	2.096(6)
Fe(1)—C(2)	1.943(6)	Fe(2)—C(5)	2.031(6)
Fe(1)—C(3)	2.143(6)	Fe(2)—C(9)	2.125(9)
Fe(1)—C(8)	2.123(8)	Fe(2)—C(10)	2.071(9)
Fe(1)—C(11)	1.803(9)	Fe(2)—C(14)	1.794(8)
Fe(1)—C(12)	1.807(8)	Fe(2)—C(15)	1.775(8)
Fe(1)—C(13)	1.810(8)	Fe(2)—C(16)	1.787(7)
C(11)—O(2)	1.125(11)	C(14)—O(5)	1.135(11)
C(12)—O(3)	1.143(9)	C(15)—O(6)	1.144(11)
C(13)—O(4)	1.120(10)	C(16)—O(7)	1.141(9)

The e.s.d. of the last significant digit is given in parentheses.

TABLE 8  
BOND ANGLES (°) IN VI

C(2)—C(1)—C(6)	119.1(6)	C(1)—Fe(1)—C(2)	39.6(3)
C(2)—C(1)—C(7)	122.8(7)	C(1)—Fe(1)—C(3)	67.1(2)
C(6)—C(1)—C(7)	113.6(6)	C(1)—Fe(1)—C(8)	68.4(3)
C(1)—C(2)—C(3)	115.9(6)	C(2)—Fe(1)—C(3)	39.9(3)
C(1)—C(2)—C(8)	117.5(6)	C(2)—Fe(1)—C(8)	40.5(3)
C(3)—C(2)—C(8)	114.3(6)	C(3)—Fe(1)—C(8)	68.4(3)
C(2)—C(3)—C(4)	121.1(6)	C(1)—Fe(1)—C(11)	98.2(3)
C(3)—C(4)—C(5)	120.5(6)	C(1)—Fe(1)—C(12)	95.9(3)
C(3)—C(4)—C(9)	123.2(6)	C(3)—Fe(1)—C(11)	99.0(3)
C(5)—C(4)—C(9)	115.9(7)	C(3)—Fe(1)—C(13)	95.2(3)
C(4)—C(5)—C(6)	117.5(6)	C(8)—Fe(1)—C(12)	94.0(4)
C(4)—C(5)—C(10)	118.7(7)	C(8)—Fe(1)—C(13)	93.7(3)
C(6)—C(5)—C(10)	123.3(7)	C(11)—Fe(1)—C(12)	96.8(4)
C(1)—C(6)—C(5)	118.8(6)	C(11)—Fe(1)—C(13)	97.0(4)
C(1)—C(6)—O(1)	121.2(7)	C(12)—Fe(1)—C(13)	97.7(4)
C(5)—C(6)—O(1)	120.0(7)	Fe(1)—C(11)—O(2)	178.4(7)
		Fe(1)—C(12)—O(3)	177.7(8)
C(2)—C(3)—H(3)	114(5)	Fe(1)—C(13)—O(4)	177.8(7)
C(4)—C(3)—H(3)	122(5)	C(4)—Fe(2)—C(5)	39.7(3)
C(1)—C(7)—H(71)	103(5)	C(4)—Fe(2)—C(9)	39.2(3)
C(1)—C(7)—H(72)	112(6)	C(5)—Fe(2)—C(10)	40.4(3)
C(1)—C(7)—H(73)	117(7)	C(4)—Fe(2)—C(14)	93.7(3)
C(2)—C(8)—H(8A)	117(5)	C(5)—Fe(2)—C(15)	97.3(3)
C(2)—C(8)—H(8S)	110(5)	C(9)—Fe(2)—C(14)	94.9(4)
H(8A)—C(8)—H(8S)	121(7)	C(10)—Fe(2)—C(15)	91.1(4)
C(4)—C(9)—H(9E)	117(5)	C(14)—Fe(2)—C(16)	90.4(4)
C(4)—C(9)—H(9Z)	120(5)	C(14)—Fe(2)—C(16)	102.7(3)
H(9E)—C(9)—H(9Z)	118(7)	C(15)—Fe(2)—C(16)	99.0(3)
C(5)—C(10)—H(10E)	110(5)	Fe(2)—C(14)—O(5)	117.9(7)
C(5)—C(10)—H(10Z)	119(5)	Fe(2)—C(15)—O(6)	178.9(6)
H(10E)—C(10)—H(10Z)	121(7)	Fe(2)—C(16)—O(7)	179.2(7)

The e.s.d. of the last significant digit is given in parentheses.

TABLE 9

## LEAST-SQUARES PLANES IN VI

Plane	Atoms defining plane <sup>a</sup>	Equation of mean plane
I	C(1), C(3-10), O(1)	$0.154X + 0.006Y + 0.988Z = 6.023$
II	C(4), C(5), C(9), C(10)	$0.029X + 0.020Y + 0.999Z = 6.003$
III	C(14), C(15), m, m'	$0.999X + 0.049Y - 0.004Z = 1.594$
IV	C(1), C(3), C(12), C(13)	$-0.539X - 0.512Y + 0.669Z = 4.236$
V	C(1), C(8), C(11), C(13)	$0.906X - 0.257Y + 0.334Z = 0.117$
VI	C(3), C(8), C(11), C(12)	$-0.049X + 0.887Y + 0.459Z = 2.722$

## Displacement of atoms from mean plane (Å)

Plane I:	C(1)	-0.07	C(7)	0.13	Plane II:	C(4)	-0.01	
	C(3)	-0.07	C(8)	0.02		C(5)	0.01	
	C(4)	0.06	C(9)	0.13		C(9)	0.00	
	C(5)	-0.08	C(10)	0.04		C(10)	0.00	
	C(6)	-0.05	O(1)	-0.01	Plane IV:	0.00 for the four atoms		
Plane III:	C(14)	-0.05	Plane V:	C(1)	0.03	Plane VI:	C(3)	0.02
	C(15)	0.05		C(8)	-0.03		C(8)	-0.02
	m	0.06		C(11)	-0.03		C(11)	-0.02
	m'	-0.06		C(13)	0.03		C(12)	0.02

## Dihedral angle between planes (°)

II-III 89; IV-V 82; IV-VI 83; V-VI 83; VII-VIII <sup>b</sup> 5.

<sup>a</sup> m and m' are the midpoints of the C(4)-C(9) and C(5)-C(10) bonds, respectively. <sup>b</sup> Planes VII and VIII are defined by C(1), C(3), C(8) and C(11), C(12), C(13), respectively.

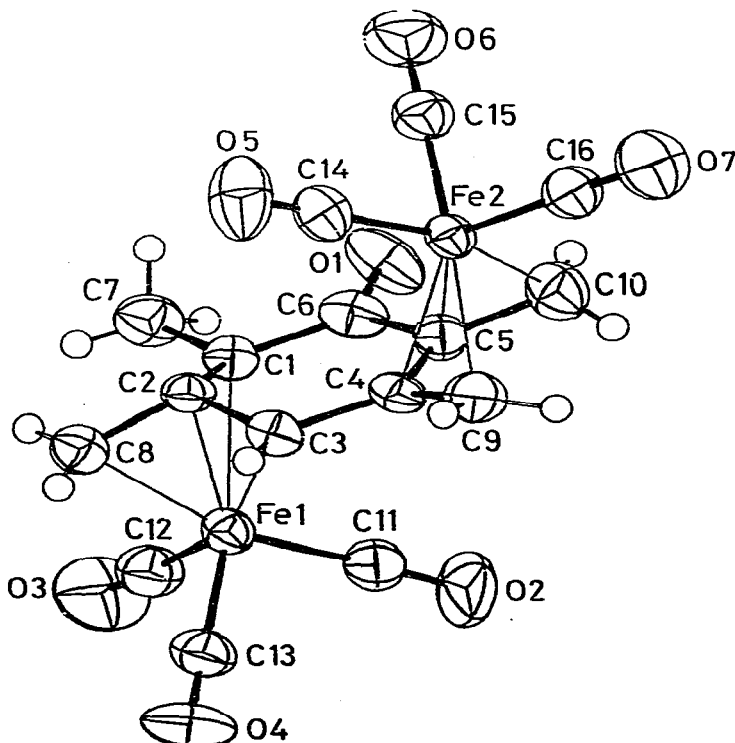


Fig. 2. Molecular structure of complex VI.

age of C(2)—C(8) and C(3)—C(9) is 0.023(7) Å. This difference was found to be 0.013(16) Å from a statistical comparison of 41 structures of the type (1,3-diene)Fe(CO)<sub>3</sub> [11]; the three C—C distances are thus not statistically different. The "terminal" C—C averaged distances are 1.405(4) and 1.323(5) Å for the bonded and the free diene group respectively. The corresponding "inner" C—C distances are 1.382(5) and 1.467(6) Å. Complexation causes thus the terminal C—C bonds to become longer by 0.063(7) Å, whereas the inner C—C bond becomes shorter by 0.046(9) Å. Complexation does not modify the averaged sum of angles at an "inner" C atom (360.0(6) for the bonded and 359.9(6)° for the free diene), which thus maintain its planarity. However, the *s-cis*-butadiene "bite" narrows since the angle C(3)—C(2)—C(8) is significantly smaller than C(6)—C(5)—C(10), while C(1)—C(2)—C(3) and C(4)—C(5)—C(6) are equal (Table 4). The reliability of hydrogen atom positions may be judged by considering pairs of H atoms related by plane I (Table 5), a plane of symmetry which is not required crystallographically. The averaged differences in related bond angles is 2.8°. H(Z) atoms deviate from the bonded diene plane away from the metal by 43° and H(E) atoms deviate towards the metal by 16°. These deviations are quite similar to those found in other (*exocyclic* 1,3-diene)-Fe(CO)<sub>3</sub> structures [11] and the resulting non-planarity at the "terminal" C atoms has been attributed to an electronic factor [18]. However, these deviations may as well be explained by a steric factor. The averaged Fe...H(Z) distance of 2.53(5) Å is indeed greater than the sum of the Fe covalent radius (1.17 Å [19,20]) and the Van der Waals radius of hydrogen (1.20 Å [20]), but would reduce to 2.05(4) Å if the calculation is made with H(Z) atoms lying in the diene plane.

*b) Complex VI:* the structure is composed of discrete monomeric (C<sub>9</sub>H<sub>10</sub>CO)Fe<sub>2</sub>(CO)<sub>6</sub> molecules. The ligand is a ketone derived from ligand I by oxygen bridge cleavage and a proton 1,3-shift (Fig. 2). The ketone is planar, except for C(2), with one *s-cis*-butadiene bonded to a Fe(CO)<sub>3</sub> group. The coordination polyhedron at Fe(2) is quite similar to that found in complex III. The second Fe(CO)<sub>3</sub> group (Fe(1)) is in a *trans* position with respect to Fe(2) and is bonded to the four carbon atoms of a substituted trimethylenemethane fragment. Fe(1) is located directly beneath the central carbon atom C(2) which deviates by 0.30 Å from plane I (Table 9) away from Fe(1). The six atoms C(1), C(3), C(8), C(11), C(12), C(13) describe a distorted octahedron as indicated by the dihedral angles between plane IV—VI (Table 9). Carbon—carbon distances (average 1.41 Å) and interatomic angles (average 115.9°) within the trimethylenemethane system are in good agreement with those reported for (phenyltrimethylenemethane)Fe(CO)<sub>3</sub> (1.416 Å and 115.2° respectively) [21]. The trigonal-pyramidal trimethylenemethane fragment and the Fe(CO)<sub>3</sub> moiety adopt a mutually staggered conformation, as observed for all (trimethylenemethane)Fe(CO)<sub>3</sub> complexes so far [21,22].

### Spectroscopic properties

The <sup>1</sup>H and <sup>13</sup>C NMR data of ligand I and its Fe complexes are reported in Table 10 and their IR and mass spectral data in the experimental part. The assignments of the NMR spectra were deduced from the multiplicity of the signals

TABLE 10

<sup>1</sup>H NMR AND <sup>13</sup>C NMR SPECTRAL DATA FOR IRON CARBOXYLS OF I<sup>a</sup>

	I	II	III	IV	V
H(1), H(4)	5.15s	5.07s(0.08) <sup>b</sup>	5.16s(-0.01)	5.15bs(0)	5.48s(-0.33)
H(8E), H(9E)	4.85s	2.23dd(2.62) <sup>e</sup>	2.06d(2.79)	2.33dd(2.52) <sup>e</sup>	2.34d(2.51)
H(8Z), H(9Z)	4.95s	0.59d(4.36)	0.54d(4.41)	0.76d(4.19)	0.78d(4.17)
H(10E), H(11E)	4.85	5.42(-0.57)	5.38s(-0.53)	2.33dd	2.34d
H(10Z), H(11Z)	4.95	5.60s(-0.65)	5.38s(-0.43)	0.76d	0.29d(4.03)
2J(H(8E)-H(8Z)) <sup>c</sup>	<0.6	3.2 ± 0.3	3.4 ± 0.3	2.6 ± 0.3	3.2 ± 0.3
2J(H(10E)-H(10Z))		<0.6	<0.6	2.6 ± 0.3	3.0 ± 0.3
C(1), C(4)	85.6d	81.5d(4.1) <sup>b</sup>	83.6d	80.4d(5.2)	81.2d(4.4)
C(2), C(3)		107.1s(38.6)	118.5s		111.4s(34.3)
C(5), C(6)	145.7bs	143.4(2.3)	145.3s	111.6s(24.1)	116.6s(29.1)
C(8), C(9)		32.6t(70.1)	30.2t		33.4t(69.3)
C(10), C(11)	102.7t	104.1t(-1.4)	101.7t	33.9t(68.8)	33.9t(68.8)
CO		210.1s <sup>d</sup>	209.6s	210.0s	209.9s
1J(C(1)-H(1))	163 ± 2	160 ± 2	163 ± 2	160 ± 2	164 ± 2
1J(C(8)-H(8))	160 ± 1	160 ± 1	161 ± 1	162 ± 1	163 ± 1
1J(C(10)-H(10))		160 ± 1	160 ± 1	162 ± 1	163 ± 1

<sup>a</sup> In CDCl<sub>3</sub> at room temperature; <sup>13</sup>C NMR spectrum width 3750 Hz, 4096 points. <sup>b</sup> From left to right:  $\delta$  (in ppm relative to TMS), multiplicity (s: singlet; bs: broad singlet; d: doublet; t: triplet) and, in parentheses,  $\Delta\delta = \delta(\text{ligand}) - \delta(\text{complex})$ . <sup>c</sup> Coupling constant in Hz. <sup>d</sup> CO exchange blocked at -50°C;  $\delta(\text{CO})$  208.4(2C) and 214.0 ppm (1C); coalescence occurs at -33°C. <sup>e</sup>  $J(\text{H}(8\text{E})-\text{H}(1)) \approx 0.4$  Hz.

and by comparison of  $\Delta\delta = \delta(\text{ligand I}) - \delta(\text{complex})$  with the corresponding values for the diene 2,3-bis(methylene)bicyclo[2.2.2]octane [23], the tetraene 2,3,5,6-tetrakis(methylene)bicyclo[2.2.2]octane [11] and their tricarbonyl-iron complexes.

The NMR spectra of II and III show resonances attributable to two uncoordinated C—C double bonds. The different positions of the iron atoms do not affect chemical shifts significantly enough to decide which isomer is the *exo* one in solution. However, a long range coupling between H(1) and H(8Z) is observed in II but not in III. Since the molecular structure of III and a model of II show that the dihedral angle between the planes defined by H(1)—C(1)—C(8) and by H(8E)—C(8)—C(1) are close to zero and  $90^\circ$  in III and II respectively, and since II and III do not epimerise in solution, we can attribute with certainty the *exo* configuration in solution to the isomer II.

Complex IV, which is the main product of the reaction of II and  $\text{Fe}_2(\text{CO})_9$ , must be the bis(*exo*) isomer as the magnetic equivalence of C(1,4) and that of C(2,3,5,6) require  $C_{2v}$  symmetry. Complex V must then be the *endo*, *exo*-diiron isomer as the non-equivalence of C(2,3) and C(5,6) implies the loss of a mirror plane defined by C(1), O(7) and C(4).

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data of VI are reported in Table 11. The numbering scheme is indicated in Fig. 2 (H(8A) is the proton in the *anti* position with respect to the methyl group). The  $^1\text{H}$  resonances appear as two singlets, four doublets and two doublets of doublets, and their assignment is based on selective irradiations. The two pairs of signals having a coupling constant of 2.6 Hz are clearly due to the methylene protons of the *s-cis*-butadiene system, since the  $^2J(\text{E}-\text{Z})$  characteristic for (*exocyclic* 1,3-diene) $\text{Fe}(\text{CO})_3$  complexes falls in the range 2.6–3.4 Hz [11,23]. H(9E) and H(10E) are distinguished by their signal multiplicity since only the former can couple with H(3). The same argument was used to distinguish between H(8A) and H(8S), since only H(8A) can experience a M coupling with H(3). The  $^{13}\text{C}$  resonances of VI appear as eight singlets, one doublet, two triplets, one triplet of doublets and one quartet. Their assignment remains tentative, even though several arguments are

TABLE 11  
 $^1\text{H}$  AND  $^{13}\text{C}$  NMR DATA OF COMPLEX VI<sup>a</sup>

H(3)	3.59bs (1) <sup>b</sup>	C(1,2)	86.0s, 84.3s
H(7)	1.77s (3)	C(3)	65.3bd ( $160 \pm 2$ ) <sup>g</sup>
H(8S)	3.22d (1; 1.3) <sup>c</sup>	C(4,5)	115.5s, 109.1bs <sup>j</sup>
H(8A)	2.59dd (1; $\sim 0.3$ ) <sup>d</sup>	C(6)	194.0s
H(9E)	2.45dd (1; 0.6) <sup>e</sup>	C(7)	13.4q ( $130 \pm 1$ )
H(9Z)	0.21d (1; 2.6) <sup>f</sup>	C(8)	41.6bt ( $160 \pm 1$ ) <sup>i</sup>
H(10E)	2.26d (1; 2.6) <sup>f</sup>	C(9)	48.6td ( $162 \pm 1$ ) <sup>h</sup>
H(10Z)	0.75d (1)	C(10)	34.1t ( $162 \pm 1$ )
		CO	208.8s (3C), 208.1s (2C), 206.3s (1C)

<sup>a</sup> In  $\text{CDCl}_3$  at room temperature. <sup>b</sup> From left to right:  $\delta$  (in ppm relative to TMS), multiplicity, relative intensity, coupling constant in Hz. <sup>c</sup>  $^2J(\text{8A}-\text{8S})$ . <sup>d</sup>  $^4J(\text{8A}-\text{3})$ . <sup>e</sup>  $^4J(\text{9E}-\text{3})$ . <sup>f</sup>  $^2J(\text{E}-\text{Z})$ . <sup>g</sup>  $^1J(\text{C}-\text{H})$ . <sup>h</sup>  $^3J(\text{C}(9)-\text{H}(3)) \sim 4$  Hz. <sup>i</sup>  $^3J(\text{C}(8)-\text{H}(3)) < 2$  Hz; dihedral angle between C(8)—C(2) and C(3)—H(3)  $\sim 40^\circ$ . <sup>j</sup>  $^3J(\text{C}(5)-\text{H}(3)) \sim 3$  Hz; long range  $^3J(\text{C}-\text{H})$  coupling constants are assumed to be nil for dihedral angle approaching  $90^\circ$  and are reported to be maximum when the dihedral angle is  $0$  or  $180^\circ$  [30].

based on the molecular structure. The atoms C(1), C(3 to 10), H(8A, 8S) and H(3) are coplanar within experimental error (plane I, Table 9), whereas C(2) and H(9E, 10E) deviate from the plane towards Fe(2), and H(9Z, 10Z) away from Fe(2). A non zero  $^3J(\text{C-H})$  is thus expected between C(1) and H(8A, S), C(5) and H(9E), and C(9) and H(3). Of the two singlets appearing in the usual region for "inner" carbon atoms of a *s-cis*-butadiene system (100–120 ppm), the one with the larger width was thus assigned to C(5). C(1) and C(2) are undistinguishable by their line width (induced shifts were not observed by adding  $\text{Yb}(\text{dpm})_3$  or other  $\beta$ -diketonato complexes of Yb, Eu or Pr). The triplet of doublets, the broad triplet and the narrow one were assigned to C(9), C(8) and C(10) respectively, since the dihedral angle between C(8)–C(2) and C(3)–H(3) is greater than that between C(9)–C(4) and C(3)–H(3), and C(10) does not experience any  $^3J$  coupling. The broad doublet is clearly related to C(3), as confirmed by single frequency proton decoupling. The relative intensities of the singlets appearing in the C(bonded carbonyl) region show that the intramolecular CO exchange of the (trimethylenemethane) $\text{Fe}(\text{CO})_3$  moiety is blocked at room temperature.

## Experimental

All reactions were carried out in an atmosphere of argon and the solvents were purified, dried and degassed by standard methods [24]. Mass spectra at 70 eV were measured with a Hewlett-Packard GC-MS 5980; IR spectra in n-hexane and in KBr pellets with a Perkin-Elmer 577 spectrophotometer; UV spectra in isooctane with a Beckman Acta V spectrophotometer;  $^1\text{H}$  NMR spectra with a Bruker WP-80 and a Bruker WP-60 spectrometer in the CW and the FT modes, respectively;  $^{13}\text{C}$  NMR spectra with a Bruker WP-60 instrument (15.08 MHz) in the FT mode and using a deuterium lock. The melting points (uncorrected) were measured with a Tottoli apparatus. E. Manzer (Mikrolabor, ETH, Zürich) carried out the microanalyses.

The 2,3,5,6-tetrakis(methylene)-7-oxabicyclo[2.2.1]heptane(I) was prepared according to ref. 25 and to a somewhat modified procedure that will be described elsewhere [26] \*.

### Preparation of complexes

a)  $\text{Fe}_2(\text{CO})_9$  (13.5 g; 37 mmol) and I (2.3 g; 15.7 mmol) were stirred at room temperature in n-hexane (320 ml) for 100 h. After filtration and removal of solvent, the residue was taken up in n-hexane and chromatographed on a 150 × 2 cm column packed with silica gel (acid alumina, activity grade I should not be used as it decomposes complex VI). First n-hexane was used as eluent to separate the  $\text{Fe}(\text{CO})_5$  and  $\text{Fe}_3(\text{CO})_{12}$  formed, then a mixture n-hexane/(1 to 50 v%) dichloromethane. After recrystallisation from n-pentane/diethylether at  $-25^\circ\text{C}$ , the successive fractions of eluate yielded the complexes II (30%), VI (1.5%), V (3%) and IV (9%). Overall yield 43.5%.

II: yellow crystals, m.p.  $91-94^\circ\text{C}$ . Analysis. Found: C, 54.63; H, 3.42.  $\text{C}_{13}\text{H}_{10}\text{FeO}_4$  calcd.: C, 54.58; H, 3.52%. Mass spectrum,  $m/e$ : 286 ( $M^+$ ; 14), 258

\* We wish to thank Miss B. Staempfli for her technical assistance.

( $M^+ - \text{CO}$ ; 66), 230 ( $M^+ - 2 \text{ CO}$ ; 86), 202 ( $M^+ - 3 \text{ CO}$ ; 100), 187 (5), 172 (34), 158 (6), 146 ( $I^+$ ; 29), 134 (5), 118 (9). IR (n-hexane):  $\nu(\text{CO})$  2063 ( $A'(1)$ ), 1988 ( $A'(2)$ ) and  $1981 \text{ cm}^{-1}$  ( $A''$ ; assigned according to Adams [27]). UV spectrum,  $\lambda_{\text{max}}$  in nm ( $\epsilon$  in  $\text{M}^{-1} \text{ cm}^{-1}$ ): 298 (4000), 220 (22000).

IV: yellow crystals, m.p. 172–174°C (dec.). Analysis. Found: C, 45.78; H, 2.54.  $\text{C}_{16}\text{H}_{10}\text{Fe}_2\text{O}_7$  calcd.: C, 45.12; H, 2.37%. Mass spectrum: 426 ( $M^+$ ; 3), 398 (9), 370 (30), 342 (1), 314 (6), 286 (11), 258 (100) (successive losses of 6 CO), 230 (6), 202 (4), 184 (3), 146 ( $I^+$ ; 2), 128 (9), 112 (5). IR spectrum:  $\nu(\text{CO})$  2060, 1990 and  $1982 \text{ cm}^{-1}$ . UV spectrum: 302 (5530), 223 (32900) nm.

V: yellow crystals, m.p. 171–173°C (dec.). Analysis. Found: C, 45.78; H, 2.46.  $\text{C}_{16}\text{H}_{10}\text{Fe}_2\text{O}_7$  calcd.: C, 45.12; H, 2.37%. Mass spectrum: 426 ( $M^+$ ; 1), 398 (19), 370 (42), 342 (20), 314 (23), 286 (74), 258 (100) (successive losses of 6 CO), 243 (7), 230 (19), 202 (60), 177 (21), 149 (95), 128 (29), 112 (38). IR spectrum:  $\nu(\text{CO})$  2060, 1987 and  $1979 \text{ cm}^{-1}$ . UV spectrum: 284 (6470), 219 (38500) nm.

VI: orange crystals, m.p. 170–172°C (dec.). Analysis. Found: C, 45.10; H, 2.48.  $\text{C}_{16}\text{H}_{10}\text{Fe}_2\text{O}_7$  calcd.: C, 45.12; H, 2.37%. Mass spectrum: 426 ( $M^+$ ; 8), 398 (8), 370 (68), 342 (26), 314 (63), 286 (100), 258 (95) (successive losses of 6 CO), 243 (10), 230 (10), 228 (10), 202 (31), 184 (10), 146 (16), 128 (18), 112 (50). IR spectrum:  $\nu(\text{CO})$  2080, 2063, 2018, 2014, 1995 and  $1983 \text{ cm}^{-1}$ ;  $\nu(\text{C}=\text{O})$   $1633^{-1}$ . UV spectrum: 307sh (6320), 244sh(12460), 233 (13400) nm.

b) Complex III was obtained by stirring  $\text{Fe}_2(\text{CO})_9$  (40 mmol) and I (16.4 mmol) in dry methanol (500 ml) at room temperature for 69 h. The same workup as in method (a) yielded, after recrystallisation, the complexes II (8%), III (7%), V (9%) and IV (8%). Overall yield 32%.

III: yellow crystals, m.p. 92–94°C. Analysis. Found: C, 54.60; H, 3.46.  $\text{C}_{13}\text{H}_{10}\text{FeO}_4$  calcd.: C, 54.58; H, 3.52%. Mass spectrum: 286 ( $M^+$ ; 1), 258 ( $M^+ - \text{CO}$ ; 9), 230 ( $M^+ - 2 \text{ CO}$ ; 38), 202 ( $M^+ - 3 \text{ CO}$ ; 40), 177 (26), 172 (18), 149 (100). IR spectrum:  $\nu(\text{CO})$  2060, 1984 and  $1978 \text{ cm}^{-1}$ . UV spectrum: 282 (3090), 253sh (6970), 219 (19700) nm.

The same reaction in benzene or in n-hexane/THF (1/1) at 60°C, or in  $\text{CH}_3\text{CN}$  at room temperature gave lower yields of the same complexes. Irradiation of I (high pressure Hg lamp HPK 125; pyrex vessel) and  $\text{Fe}(\text{CO})_5$  in n-pentane at  $-75^\circ\text{C}$  resulted in the polymerisation of the ligand.

c) II was found to be the only complex formed in the reaction of  $\text{Fe}_2(\text{CO})_9$  (27 mmol) with I (20 mmol) in diethylether (500 ml) for 8 days at room temperature. Yield, 25% after chromatography (method a) and recrystallisation from n-pentane at  $-25^\circ\text{C}$ . The *exo* isomer II (0.18 mmol) is converted into the *diexo* complex IV by treatment with  $\text{Fe}_2(\text{CO})_9$  (0.35 mmol) in ether/pentane (30 ml;  $30^\circ\text{C}$ ; 48 h). Yield, 40% after chromatography and recrystallisation. Likewise, the *endo* isomer III (0.1 mmol) is converted into the *endo-exo* complex V by treatment with  $\text{Fe}_2(\text{CO})_9$  (0.15 mmol) in n-hexane (30 ml;  $25^\circ\text{C}$ ; 46 h; yield 45%) or with (benzalacetone) $\text{Fe}(\text{CO})_3$  [28] (0.1 mmol) in benzene (30 ml;  $70^\circ\text{C}$ ; 40 h).

#### Epimerisation attempts

No evidence was found for the epimerisation equilibrium  $\text{IV} \rightleftharpoons \text{V}$  under the

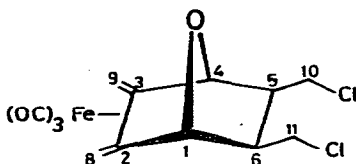


following conditions: by heating each isomer in refluxing toluene for 10 h in the presence or absence of  $\text{Fe}_2(\text{CO})_9$ , by irradiation of each isomer (high pressure Hg lamp HPK 125; pyrex vessel) in *n*-pentane for 10 h at  $-10^\circ\text{C}$  in the presence or absence of  $\text{Fe}(\text{CO})_5$ . Each isomer was also recovered unchanged from a solution in diethylether containing excess dry HCl (molar ratio complex/acid = 1/20) after 20 days.

#### Other reactions

As complex VI was only obtained in low yield (method a), it could have been formed by the reaction of  $\text{Fe}_2(\text{CO})_9$  with a precursor of ligand I present as an impurity, e.g. 2,3-bis(methylene)-5,6-bis(*exo*-chloromethyl)-7-oxabicyclo-[2.2.1]heptane (VII) [29]. Thus, the direct reaction of VII and  $\text{Fe}_2(\text{CO})_9$  was examined under the same conditions as in method (a):  $\text{Fe}_2(\text{CO})_9$  (1.4 mmol) and VII (200 mg; 0.9 mmol) were stirred in *n*-hexane (100 ml) at room temperature for 93 h. After removal of solvent, the residue was taken up in *n*-hexane and chromatographed on a  $40 \times 1$  cm column packed with silica gel. Elution with *n*-hexane brought down a single yellow band which yielded complex VIII after recrystallisation from *n*-pentane at  $-25^\circ\text{C}$ . Yield 21%. No evidence was found for the formation of VI under these or more drastic conditions.

#### SCHEME 3



#### VIII(*exo*), IX(*endo*)

VIII: yellow crystals, m.p.  $115-117^\circ\text{C}$ . Analysis. Found: C, 43.64; H, 3.40.  $\text{C}_{13}\text{Cl}_2\text{H}_{12}\text{FeO}_4$  calcd.: C, 43.50; H, 3.37%. Mass spectrum (peaks corresponding to  $^{35}\text{Cl}$ ): 358 ( $M^+$ ; 7), 330 ( $M^+ - \text{CO}$ ); 13), 302 ( $M^+ - 2 \text{CO}$ ; 100), 274 ( $M^+ - 3 \text{CO}$ ; 42), 238 (17), 202 (50). IR spectrum:  $\nu(\text{CO})$  2074, 1992 and  $1984 \text{ cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ ; TMS): H(1, 4) 4.81 (s; 2H), H(5, 6) 2.72 (m; 2H), H(8E, 9E) 2.14 (dd; 2H;  $^2J(\text{E}-\text{Z})$  2.6 Hz;  $^4J(\text{H}(8\text{E})-\text{H}(1))$  0.5 Hz), H(8Z, 9Z) 0.46 (d; 2H), H(10, 11) 3.76 ppm (m; 4H).

The same reaction in methanol (100 ml) at room temperature (1.8 mmol VII; 1.8 mmol  $\text{Fe}_2(\text{CO})_9$ ; 92 h) yielded after chromatography and recrystallisation the two isomers VIII (25%) and IX (6%).

IX: yellow crystals, m.p.  $162-165^\circ\text{C}$ . Analysis. Found: C, 43.33; H, 3.37.  $\text{C}_{13}\text{Cl}_2\text{H}_{12}\text{FeO}_4$  calc.: C, 43.50; H, 3.37%. Mass spectrum: 358 ( $M^+$ ; 12), 330 ( $M^+ - \text{CO}$ ; 100), 302 ( $M^+ - 2 \text{CO}$ ; 83), 274 ( $M^+ - 3 \text{CO}$ ; 53), 238 (17), 202 (50). IR spectrum:  $\nu(\text{CO})$  2062, 1989 and  $1973 \text{ cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ ; TMS): H(1, 4) 5.15 (s; 2H), H(5, 6) 2.80 (m; 2H), H(8E, 9E) 2.08 (d; 2H;  $^2J(\text{E}-\text{Z})$  3.3 Hz), H(8Z, 9Z) 0.54 (d; 2H), H(10, 11) 3.64 ppm (m; 4H). The long range coupling between H(8E) and H(1) is only observed in one isomer (VIII). Since this coupling was also observed in II (but not in III) and in the

*exo* isomer of the analogous ( $\eta^4$ -2,3-bis(methylene)-7-oxabicyclo[2.2.1]heptane)Fe(CO)<sub>3</sub> complex [8], we attribute the *exo* configuration to the isomer VIII.

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