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CHARACTERIZATION OF A MINOR PRODUCT OF THE REACTION OF DIIRON NONACARBONYL WITH *cis*-BICYCLO[6.2.0]DECA-2,4,6-TRIENE: *trans*-DI-μ-BIS(2,3,4,5,6-*pentahapto*-TRICYCLO[6.2.0.$0^{2,6}$]DECA-2,4-DIEN-6-YL)DICARBONYLDIIRON(Fe–Fe)

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SUMMARY

The identity of a minor product obtained from the reaction of diiron nonacarbonyl with *cis*-bicyclo[6.2.0]deca-2,4,6-triene has been ascertained by X-ray crystallography. The product, with the formula $[(C_{10}H_{11})Fe(CO)_2]_2$, is a substituted $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2$ molecule in which the $h^5\text{-}C_5H_5$ groups are replaced by *pentahapto*-tricyclo[6.2.0.$0^{2,6}$]deca-2,4-dien-6-yl groups. The mechanism by which the $C_{10}H_{11}$ tricyclic system is formed from the initial bicyclo triolefin is obscure although $(C_{10}H_{11})FeH(CO)_2$ is a probable intermediate. The compound crystallizes in the monoclinic system, space group $P2_1/n$ with $a = 9.231(4)$, $b = 9.138(5)$, $c = 12.140(6)$Å, $\beta = 106.16(4)°$, and $Z = 2$. The intensities of 928 independent reflections ($2\theta_{max} = 45°$) with $I > 3\ \sigma(I)$, collected on a computer-controlled diffractometer with Mo-K_α radiation were used to solve and refine the structure to $R_1 = 0.051$ and $R_2 = 0.063$.

INTRODUCTION

It has been found that the reaction of *cis*-bicyclo[6.2.0]deca-2,4,6-triene, (I), with $Fe_2(CO)_9$ in anhydrous ether at *ca.* 25° for 90 h resulted in three metal carbonyl derivatives by column chromatography on alumina[1]. One of these products, (II), has been identified unambiguously[1,2] and fully characterized structurally[2]. When a solution of (II) in dry toluene is refluxed for about 24 h two products are obtained. The major product is (III), which has also been fully characterized[1,3]; the minor product forms the subject of this paper. The quantity of this red-black crystalline solid is so small[1] that it is difficult to characterize it beyond recordings its IR spectrum in the carbonyl stretching region. This contains two terminal bands and one bridging band[1].

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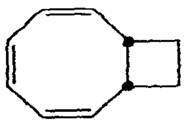
In this paper we report the complete identification and structural definition of this substance by X-ray crystallography, employing a sample consisting of one single crystal with an approximate mass of 30 micrograms.

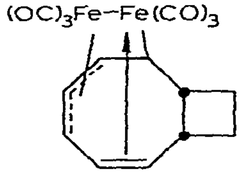
EXPERIMENTAL

Collection of X-ray data

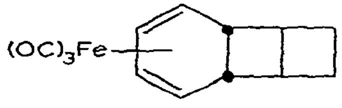
Red-black air-stable crystals of $[(C_{10}H_{11})Fe(CO)_2]_2$ were prepared as described previously[1] as an unidentified product from the thermolysis of $(C_{10}H_{12})Fe_2(CO)_6$. Of the twenty crystals from the initial preparation, one which measured 0.35 × 0.25 × 0.20 mm was selected for investigation. The crystal, mounted on a thin glass fiber, was examined using Mo-K_α radiation, on a Syntex $P\bar{1}$ computer-controlled 4-circle diffractometer equipped with a graphite-crystal, incident-beam monochromator. The operation of the diffractometer has been described previously[2]. Preliminary examination on the diffractometer showed the crystal to be monoclinic. Subsequent examination of collected data revealed systematic absences for $h0l$, $h+l=2n+1$ and $0k0$, $k=2n+1$. These absences fix the space group as $P2_1/n$, a non-standard setting of $P2_1/c$. Unit cell dimensions and an orientation matrix for data collection were determined at a temperature of 22° by least-squares refinement of the setting angles for fifteen carefully centered reflections. Unit cell dimensions and other crystal data are given in Table 1. The width at half-height for ω scans of several strong reflections was 0.25°.



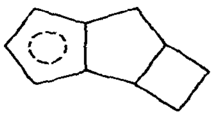
(I)



(II)



(III)



(IV)

Intensity data were collected with Mo-$K_{\alpha 1}$ radiation at 22° using the $\theta-2\theta$ scan technique and a variable scan rate of 2.0 to 24.0°/min depending on the intensity of the reflection. A symmetric scan range of $2\theta(\text{Mo-}K_{\alpha_1})-0.8°$ to $2\theta(\text{Mo-}K_{\alpha_2})+0.8°$ was used to measure 1518 reflections up to a maximum 2θ of 45.0°. Three standard reflections were measured after every 100 reflections to check on crystal and electronic stability. Only slight random variations were observed in these standards. Transmission factors varied from 0.63 to 0.73 in test calculations; an absorption correction was

TABLE 1

CRYSTAL DATA FOR $[(C_{10}H_{11})Fe(CO)_2]_2$

F.W. = 486.18	Monoclinic
a = 9.231(4) Å	Space group $P2_1/n$
b = 9.138(5) Å	$F(000) = 500$
c = 12.140(6) Å	Mo-K_α radiation
β = 106.16(4)°	$\mu = 15.43$ cm^{-1}
V = 983.6(8) Å^3	$Z = 2$
	$d_{\text{calcd.}} = 1.64$ g·cm^{-3}

not made. No extinction correction was deemed necessary. In the refinement of the structure, 928 reflections having $F_o^2 > 3\sigma \cdot (F_o^2)$ were used. The parameter p used in the calculation of standard deviations was set equal to 0.05 (ref. 2).

Solution and refinement of the structure[*]

A solution for one iron atom was determined using a three-dimensional Patterson function. Two cycles of least-squares refinement on this position gave the following agreement factors: $R_1 = (\Sigma| |F_o| - |F_c| |)/\Sigma|F_o| = 0.352$ and $R_2 = [\Sigma w \cdot (|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}} = 0.367$. The terms $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes and w is the weighting factor given as $4|F_o|^2/\sigma^2$ where σ is the e.s.d. of $|F_o|^2$. Based on this apparent solution, a difference Fourier synthesis revealed the position of two carbonyl groups and five carbon atoms of a ring system. After two additional least-squares cycles and a subsequent difference Fourier synthesis, all of the remaining non-hydrogen atoms were located. Two least-squares cycles on all non-hydrogen atoms, refining positional parameters, isotropic thermal parameters, and a scale factor reduced the discrepancy indexes to $R_1 = 0.080$ and $R_2 = 0.091$. All eleven hydrogen atoms were located on a difference Fourier synthesis based on the above refinement. The positional and anisotropic refinement of non-hydrogen atoms and positional refinement of hydrogen atoms including a scale factor (169 variables) converged to the final agreement factors of $R_1 = 0.051$ and $R_2 = 0.063$ with no parameter shift greater than 0.2 times its e.s.d. Hydrogen atoms were refined holding the temperature parameters constant at 4.0 Å^2.

The error in an observation of unit weight is 1.68. The final difference Fourier synthesis showed no residual electron density greater than 0.65 e·Å^{-3}, where the lowest hydrogen atom in a previous map appeared as 0.77 e·Å^{-3}. Atomic scattering factors were taken from the International Tables[4]. Anomalous dispersion effects

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[*] Computer programs used in data reduction and in the solution and refinement of the structure were as follows: DATARED by Frenz was used for data reduction. Absorption corrections were performed using the numerical subroutines of Coppen's DATAPP as included in AGNOST by Cahen. The Fourier program JIMDAP by Ibers is a version of Zalkin's FORDAP. NUCLS, a full-matrix least-squares program by Ibers and Doedens, closely resembles Busing and Levy's ORFLS program; the function minimized in the refinement is $\Sigma w \cdot (|F_o| - |F_c|)^2$. Atomic distances and angles were calculated using a local modification of Baur's SADIAN program. RSCAN by Doedens was used for an analysis of structure factors and ORTEP by Johnson was used for drawing illustrations on a Gerber plotter. The function and error program ORFFE by Busing, Martin, and Levy as modified by Brown, Johnson, and Thiessen was used. LIST by Snyder was used for listing the data.

were included in the calculated structure factors for iron using $\Delta f'$ and $\Delta f''$ values given by Cromer and Liberman[5]. No systematic trends were found in the data as a function of $\lambda^{-1} \cdot \sin\theta$, $|F_o|$, Miller indices, or reflection number.

The atomic coordinates, anisotropic thermal parameters and estimated standard deviations for non-hydrogen atoms are given in Table 2. The hydrogen atom coordinates and estimated standard deviations are given in Table 3. Root-

TABLE 2

POSITIONAL AND ANISOTROPIC THERMAL PARAMETERS AND THEIR STANDARD DEVIATIONS FOR NON-HYDROGEN ATOMS[a]

Atom	*x*	*y*	*z*	$\beta(1,1)$[b]	$\beta(2,2)$	$\beta(3,3)$	$\beta(1,2)$	$\beta(1,3)$	$\beta(2,3)$
Fe(1)	0.1305(1)	0.0583(1)	0.0338(1)	84(2)	92(2)	45(1)	−3(2)	26(1)	−1(1)
O(1)	0.0537(8)	0.2415(8)	0.2048(6)	179(12)	204(13)	92(6)	−10(11)	65(8)	−72(8)
O(2)	0.0818(7)	−0.1962(8)	0.1626(6)	131(11)	182(12)	93(6)	2(10)	18(7)	63(7)
C(1)	0.3808(12)	0.3265(12)	0.0335(9)	120(16)	152(16)	81(9)	−14(14)	28(10)	5(10)
C(2)	0.3375(9)	0.1700(10)	0.0366(8)	77(13)	105(13)	77(8)	−5(12)	28(8)	7(9)
C(3)	0.3629(10)	0.0504(12)	0.1160(8)	94(12)	151(15)	52(7)	13(14)	11(8)	1(12)
C(4)	0.3211(10)	−0.0749(12)	0.0516(8)	78(12)	123(15)	88(9)	9(14)	33(9)	5(11)
C(5)	0.2615(10)	−0.0387(11)	−0.0663(8)	82(13)	156(18)	74(9)	−14(13)	38(9)	−28(10)
C(6)	0.2757(10)	0.1138(11)	−0.0746(8)	97(15)	141(15)	62(8)	−18(12)	33(9)	−6(9)
C(7)	0.2578(13)	0.2278(13)	−0.1645(9)	139(17)	175(19)	76(9)	−24(15)	58(10)	25(11)
C(8)	0.3091(13)	0.3672(12)	−0.0946(9)	185(20)	142(17)	93(10)	−28(16)	44(12)	44(11)
C(9)	0.1914(16)	0.4605(14)	−0.0578(12)	196(21)	136(20)	143(14)	7(20)	19(15)	14(14)
C(10)	0.2825(14)	0.4457(14)	0.0643(10)	210(22)	145(16)	104(11)	−55(19)	53(12)	−25(13)
C(11)	0.0843(10)	0.1702(11)	0.1366(8)	118(15)	117(14)	65(8)	−26(13)	15(9)	−2(9)
C(12)	0.0420(10)	−0.1094(10)	0.0859(8)	90(13)	111(14)	68(8)	−10(11)	43(9)	−4(8)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits in this and all other Tables.

[b] The anisotropic temperature factor is in the form of $\exp\{-10^4[\beta(1,1)h^2+\beta(2,2)k^2+\beta(3,3)l^2+2\beta(1,2)hk+2\beta(1,3)hl+2\beta(2,3)kl]\}$.

TABLE 3

POSITIONAL PARAMETERS AND THEIR STANDARD DEVIATIONS FOR HYDROGEN ATOMS

Atom[a]	*x*	*y*	*z*
H(1)	0.503(10)	0.330(9)	0.070(7)
H(3)	0.384(10)	0.056(10)	0.189(7)
H(4)	0.304(10)	−0.170(10)	0.068(8)
H(5)	0.203(10)	−0.096(8)	−0.131(7)
H(7,1)	0.152(10)	0.249(9)	−0.219(7)
H(7,2)	0.317(10)	0.203(9)	−0.209(7)
H(8)	0.368(9)	0.432(9)	−0.127(7)
H(9,1)	0.167(10)	0.555(10)	−0.081(7)
H(9,2)	0.097(10)	0.414(10)	−0.073(7)
H(10,1)	0.340(9)	0.542(9)	0.091(7)
H(10,2)	0.237(9)	0.438(10)	0.120(7)

[a] The number of each hydrogen atom corresponds to the number of the carbon atom to which it is attached. The second numbers distinguish between the two hydrogen atoms attached to C(7), C(9), and C(10).

TABLE 4

ROOT-MEAN-SQUARE AMPLITUDES OF THERMAL VIBRATION (Å)

Atom	*Min*	*Intermed*	*Max*
Fe(1)	0.159(2)	0.188(2)	0.199(2)
O(1)	0.157(13)	0.265(9)	0.341(9)
O(2)	0.190(11)	0.230(9)	0.330(9)
C(1)	0.212(15)	0.235(14)	0.261(14)
C(2)	0.168(15)	0.208(14)	0.233(13)
C(3)	0.182(14)	0.205(14)	0.255(13)
C(4)	0.167(14)	0.227(14)	0.248(13)
C(5)	0.161(15)	0.206(14)	0.276(14)
C(6)	0.178(15)	0.208(13)	0.250(13)
C(7)	0.156(17)	0.257(14)	0.286(15)
C(8)	0.174(17)	0.272(14)	0.303(15)
C(9)	0.235(17)	0.274(15)	0.335(16)
C(10)	0.214(16)	0.258(14)	0.317(16)
C(11)	0.190(15)	0.217(13)	0.248(15)
C(12)	0.156(15)	0.212(13)	0.232(13)

mean-square amplitudes of thermal vibration are given in Table 4. A listing of structure factors is available on request*.

RESULTS

A perspective view of the structure and the atomic numbering scheme is shown in Fig. 1. Tables 5 and 6 list the bond lengths and bond angles, respectively, with their estimated standard deviations. Table 7 gives selected weighted least-squares planes, dihedral angles, and the deviations of individual atoms from least-squares planes.

The structure consists of individual molecules with no intermolecular contacts differing significantly from the sum of the Van der Waals' radii. The molecule has a crystallographic center of symmetry and, therefore, only half of the dimeric molecule constitutes the asymmetric unit. Each iron atom has one terminal carbonyl group and shares two bridging carbonyl groups with the symmetry-related iron atom. The $C_{10}H_{11}$ fused-ring system consists of a cyclopentadienyl ring fused in a nearly planar fashion to a second five-membered saturated ring. The saturated five-membered ring is in turn fused to a non-planar four-membered ring. The center of symmetry lies between the iron atoms, and thus a *trans* relationship between the pair of $C_{10}H_{11}$ moieties is rigorously imposed.

The infrared spectrum in the carbonyl stretching region, measured on a solution in carbon disulfide, is shown in Fig. 2.

DISCUSSION

It is clear from the crystal structure that the title compound is a homolog of

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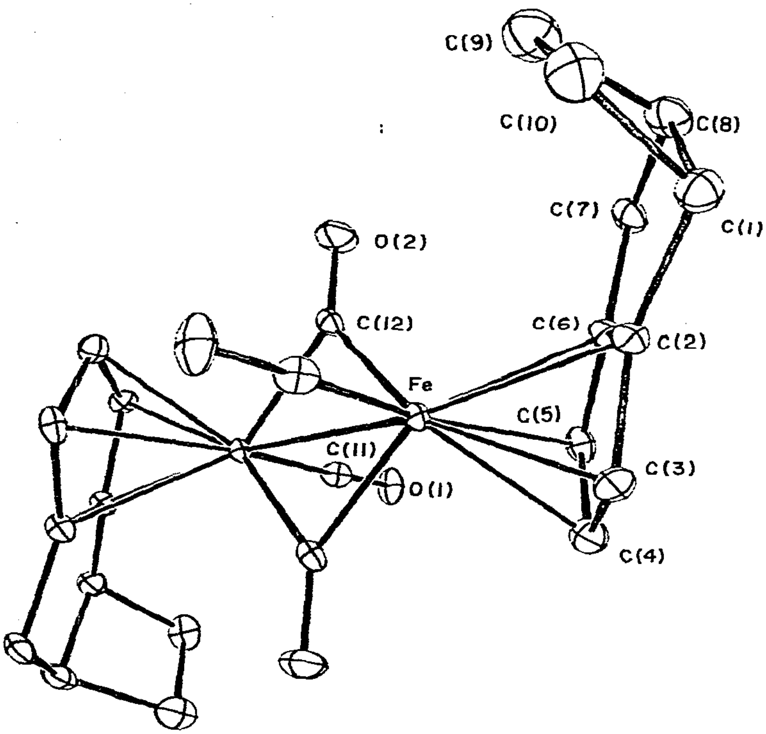
* The Table of structure factors has been deposited as NAPS Document No. 02153. Order from ASIS/NAPS c/o Microfiche Publications, 305 E, 46th St., New York, N.Y. 10017. Remit in advance for each NAPS accession number $1.50 for microfiche or $5.00 for photocopies up to 30 pages, 15¢ for each additional page. Make checks payable to Microfiche Publications.



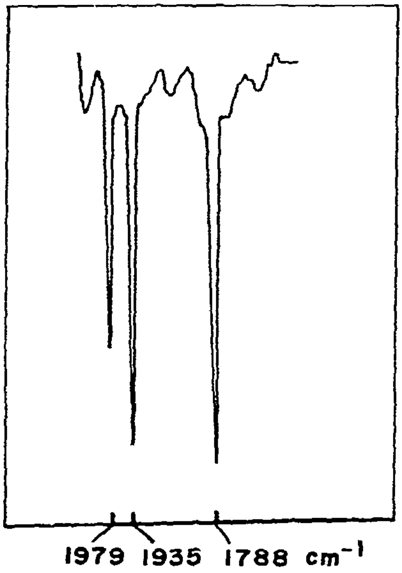


Fig. 1. An ORTEP rendering of the structure, showing the atom numbering scheme. The carbon atoms of the tricyclic ligand are numbered in accord with the scheme used in the chemical nomenclature. The atoms are represented by thermal ellipsoids enclosing 50% of the electron density.

Fig. 2. The carbonyl stretching region of the infrared spectrum, recorded on a solution in CS_2.

TABLE 5. BOND LENGTHS (Å)

Fe–Fe	2.553(2)	Fe–C(11)	1.755(10)
Fe–C(2)	2.159(8)	Fe–C(12)	1.925(9)
Fe–C(3)	2.100(9)	Fe[a]–C(12)	1.892(9)
Fe–C(4)	2.101(10)	C(11)–O(1)	1.149(10)
Fe–C(5)	2.133(9)	C(12)–O(2)	1.200(10)
Fe–C(6)	2.184(9)		
C(1)–C(2)	1.49(1)	C(1)–H(1)	1.09(8)
C(1)–C(8)	1.56(1)	C(3)–H(3)	0.85(8)
C(1)–C(10)	1.53(2)	C(4)–H(4)	0.92(9)
C(2)–C(3)	1.43(1)	C(5)–H(5)	0.98(8)
C(2)–C(6)	1.41(1)	C(7)–H(7,1)	1.03(9)
C(3)–C(4)	1.38(1)	C(7)–H(7, 2)	0.91(8)
C(4)–C(5)	1.42(1)	C(8)–H(8)	0.97(9)
C(5)–C(6)	1.41(1)	C(9)–H(9,1)	0.92(8)
C(6)–C(7)	1.49(1)	C(9)–H(9,2)	0.94(8)
C(7)–C(8)	1.53(2)	C(10)–H(10,1)	1.04(8)
C(8)–C(9)	1.54(2)	C(10)–H(10,2)	0.89(8)
C(9)–C(10)	1.49(2)		

[a] Symmetry equivalent iron atom ($\bar{x},\bar{y},\bar{z}$).

TABLE 6

BOND ANGLES (DEG.)

C(2)–Fe–C(3)	39.3(4)	Fe–Fe–C(11)	94.4(3)
C(2)–Fe–C(6)	37.9(3)	Fe–C(11)–O(1)	178.9(9)
C(3)–Fe–C(4)	38.4(4)	Fe–C(12)–Fe^a	83.9(4)
C(4)–Fe–C(5)	39.3(4)	Fe–C(12)–O(2)	135.6(7)
C(5)–Fe–C(6)	38.0(4)	Fe^a–C(12)–O(2)	140.4(7)
Angles within cyclopentadienyl ring at atom specified			
C(2)	108.3(8)	C(5)	106.5(9)
C(3)	106.5(8)	C(6)	108.3(9)
C(4)	110.2(9)		
Angles within central five-membered ring at atom specified			
C(1)	102.3(8)	C(7)	102.8(8)
C(2)	111.4(8)	C(8)	109.6(9)
C(6)	112.5(9)		
Angles within four-membered ring at atom specified			
C(1)	87.6(8)	C(9)	89.5(10)
C(8)	88.9(9)	C(10)	91.7(9)
C(1)–C(2)–C(3)	139.1(9)	C(5)–C(6)–C(7)	138.9(9)
C(2)–C(1)–C(10)	119.8(9)	C(7)–C(8)–C(9)	119.1(10)

^{a} Symmetry equivalent iron atom ($\bar{x},\bar{y},\bar{z}$).

trans-[(h^5-C_5H_5)Fe(CO)$_2$]$_2$, in which the simple (h^5-C_5H_5) groups are replaced by the polycyclic cyclopentadienyl derivative. The infrared spectrum in CS_2 solution is very similar to the spectra of [(h^5-C_5H_5)Fe(CO)$_2$]$_2$ and [(h^5-indenyl)Fe(CO)$_2$]$_2$ in non-polar solvents as reported by Manning[7,8]. The appearance of two bands of similar intensities in the terminal region indicates that both *cis* and *trans* isomers are present in comparable quantities presumably rapidly interconverting as has been shown to be the case for [(h^5-C_5H_5)Fe(CO)$_2$]$_2$[9]. The infrared frequencies mentioned earlier[1] for this compound were in error (particularly for the bridging CO band) because of a misreading of the spectrum trace.

The dimensions of this structure are nearly identical to those with which comparisons can be made in the prototypal molecule, *trans*-[(h^5-C_5H_5)Fe(CO)$_2$]$_2$[6]. The Fe–Fe distance here, 2.553(2) Å, is slightly longer than that [2.534(2) Å] in the prototypal molecule by an amount which may be real, but scarcely seems chemically significant. The Fe–C(bridging) distances of 1.910(5) and 1.918(5) Å in the prototype differ insignificantly. In the present compound, there appears to be a greater difference, 0.033 (13) Å, but still, it is less than three times the standard deviation for the difference. In any event, it is so small in comparison with the expected mean amplitude of thermal vibrations that it seems unlikely to be important. A comparison of the mean Fe–C-(cyclopentadienyl) distances in the two compounds, 2.11 and 2.14Å, is not meaningful. The greater average value in the present case can be traced clearly to the fact that the bridgehead carbon atoms, C(2) and C(6), are further from the iron atom than are the other three atoms by an average of 0.06 Å. This is due to a tilting rather than a bending of the cyclopentadienyl ring, which is essentially planar (see plane I, Table 7).

TABLE 7

WEIGHTED LEAST-SQUARES PLANES AND DIHEDRAL ANGLES

Plane	*Atoms defining plane*	*Equation of mean plane*[a]
I	C(2), C(3), C(4), C(5), C(6)	$9.126x-0.954y-4.611z=2.745$
II	C(1), C(2), C(6), C(7), C(8)	$8.982x-1.911y-4.425z=2.578$
III	C(1), C(8), C(9), C(10)	$6.117x+6.844y-2.234z=4.553$
IV	C(1), C(8), C(10)	$6.835x+6.121y-1.881z=4.538$
V	C(8), C(9), C(10)	$-5.100x-7.571y+2.888z=-4.630$

Displacement (Å) of atoms from mean plane

Plane I	*Plane II*	*Plane III*	*Plane IV*	*Plane V*
C(2) 0.005(8)	C(1) 0.070(11)	C(1) −0.064(11)	C(9) −0.302	C(1) 0.313
C(3) −0.016(9)	C(2) −0.033(8)	C(8) 0.062(11)		
C(4) 0.019(9)	C(6) 0.011(9)	C(9) −0.101(14)		
C(5) −0.014(9)	C(7) 0.031(11)	C(10) 0.082(13)		
C(6) 0.007(9)	C(8) −0.085(12)			
C(1) −0.888	C(9) −1.482			
C(7) 0.264	C(10) −1.177			
C(8) 0.162				

Dihedral angles between planes (deg.)

Planes	*Planes*
I–II 6.1	II–III 60.8
I–III 54.8	IV–V 16.3

[a] Equations have the form $Ax+By+Cz=D$, where x, y and z are fractional monoclinic coordinates.

The mean C–C distance in the cyclopentadienyl rings in the present case is 1.41(2) Å, in good accord with the values found in a host of other h^5-C_5H_5 rings (1.39–1.42 Å).

Ring conformations

The unique component of this structure is the tricyclo ligand. The cyclopentadienyl ring is fused to the cyclopentane ring so that the best least-squares planes through these rings are roughly coplanar. As indicated in Table 7, the dihedral angle between the least-squares planes for the five-membered rings is only 6.1°. A similar conformation was found for the fused cyclopentadienyl and cyclopentane rings in $(C_8H_9)Re(CO)_3$[10].

The four-membered ring is fused to the cyclopentane ring in *cis*-fashion with respect to the iron carbonyl moiety; the dihedral angle between the four- and five-membered rings is 60.8°. The C–C distances in the four-membered ring range from 1.49(2) to 1.56(1) Å with an average value of 1.53(3) Å; this is comparable to that (1.548±.003 Å) found in the electron diffraction study of cyclobutane in the gas phase[11]. The four-membered ring is non-planar in both structures. In the present work the dihedral angle is 16.4°, whereas a larger value of 27° was obtained from a best fit of experimental and computed proton NMR spectra of cyclobutane in a nematic solvent[12]. The original electron diffraction study[13] gave a dihedral angle of 20° (+10°, −20°). Substituted cyclobutane structures have dihedral angles varying from 0° to 33°, while organometallic compounds with cycloalkanes fused to cyclobutane have dihedral angles ranging from 1° to 16°. The conformation of four-membered rings will be discussed *in extenso* in a subsequent paper[3].

The central five-membered ring presents some features of special interest. In the previous example of a complex containing a five-membered ring fused to a *pentahapto*-cyclopentadienyl ring, *viz.*, trimethylene-1,2-cyclopentadienylrhenium tricarbonyl[10], the cyclopentane ring has an envelope configuration with four atoms coplanar within 0.04 Å and the fifth atom lying 0.35 Å from this plane. The central five-membered ring in $[(C_{10}H_{11})Fe(CO)_2]_2$ can also be described as envelope-shaped. As presented in Table 8, atoms C(1), C(2), C(6), and C(7) lie within 0.024 Å of their least-squares plane, while C(8) lies 0.18 Å from this plane. Thus the distortion in the cyclopentane ring is approximately half of that found in the rhenium complex. Another approximate envelope configuration can be described by using atoms C(2), C(6), C(7), and C(8) to define the "planar" part (maximum deviation, 0.020 Å) with C(1) lying 0.17 Å from this plane (Table 8).

TABLE 8

WEIGHTED LEAST-SQUARES PLANES AND RELATED DATA FOR THE CENTRAL FIVE-MEMBERED RING IN $[(C_{10}H_{11})Fe(CO)_2]_2$

Plane	*Atoms defining plane*	*Equation of mean plane*
VI	C(1), C(2), C(6), C(7)	$8.905x-2.301y-4.166z=2.481$
VII	C(2), C(6), C(7), C(8)	$9.081x-1.523y-4.101z=2.650$
VIII	C(2), C(6), C(7)	$9.023x-1.817y-4.095z=2.587$

Distances (Å) of atoms from planes

Plane	*C(1)*	*C(2)*	*C(6)*	*C(7)*	*C(8)*	*Description*
VI	0.020(11)	−0.018(8)	0.024(9)	−0.023(12)	−0.178	Envelope[a]
VII	0.173	0.006(8)	−0.014(9)	0.020(11)	0.014(12)	Envelope[b]
VIII	0.119	0.0	0.0	0.0	−0.077	Half-chair

[a] Dihedral angle is 11.5°. [b] Dihedral angle is 10.7°.

An alternative description is obtained by examining the deviations of C(1) and C(8) from the plane defined by C(2), C(6), and C(7); these deviations are +0.12 and −0.08 Å. Thus the central five-membered ring has a conformation similar to the well-known "half-chair" low-energy conformation of C_5H_{10} itself in which there is a two-fold axis of symmetry.

The conformational ambiguity of the central five-membered ring in $[(C_{10}H_{11})Fe(CO)_2]_2$ contrasts with the relatively simple description of the terminal five-membered ring in $(C_{11}H_{14})Fe(CO)_3$[14]. Here four carbon atoms are definitely planar [maximum deviation, 0.004(6) Å] with the fifth carbon atom positioned 0.58 Å from the plane, thus uniquely defining an envelope conformation. For the present structure, in the absence of the outer four-membered ring, it would seem reasonable that the cyclopentadienyl ring would enforce coplanarity of C(1), C(2), C(6) and C(7) and thus cause an envelope configuration in which C(8) would be the out-of-plane atom. Evidently, however, this would introduce an excessive amount of strain into the fused four-membered ring. Thus, the distorted half-chair conformation is adopted, even at the expense of bending the two bonds to the cyclopentadienyl ring out of coplanarity with that ring and thus weakening the Fe–C bonding. Once again, in this molecule, as in others, we see a complex interplay of forces leading to mutual conformational interactions between fused rings.

Mechanism of formation

Now that the identity and structure of the substance are known, there remains the interesting question of how it is formed*. Of particular concern is the origin of the ligand (IV). It will be clear that under the circumstances, no definitive answer can be given. However, the following sequence of steps appears to us to be plausible.

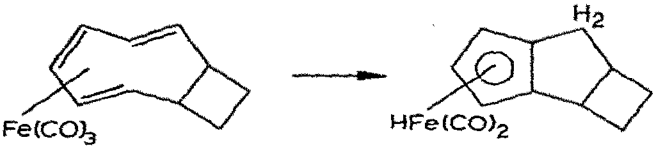
The first stage may involve breaking of the C_1–C_8 bond in (II) accompanied, or closely followed, by loss of $Fe(CO)_3$, eqn. (1). Rupture of a metal–metal bond assisted by the aromatic solvent has been invoked previously in a related system[15].

$$(\mathrm{II}) \xrightarrow[\mathrm{ArH}]{\mathrm{Heat}} \underset{(\mathrm{V})}{(C_{10}H_{12})Fe(CO)_3} \; [+\mathrm{ArH}\cdot Fe(CO)_3] \qquad (1)$$

Neither of the two products of this first step should be stable, particularly under the reaction conditions. The arene · $Fe(CO)_3$ species presumably decomposes promptly to unidentified products.

The species (V) rearranges mainly to (III), which is the major reaction product. However, at the high temperature of the thermolysis reaction a second, minor, rearrangement pathway, leading to the title compound, also occurs.

We believe that the next steps may involve loss of CO and transfer of a ring hydrogen atom to iron, followed by cyclization to give the substituted cyclopentadienyl ring. Whether closure of the C_4 ring precedes, accompanies, or follows these steps is uncertain. The combined effects of closing the cyclopentadienyl ring, and hydrogen transfer, eqn. (2),could generate (VI). Whatever the details of its formation,



(VI)

(2)

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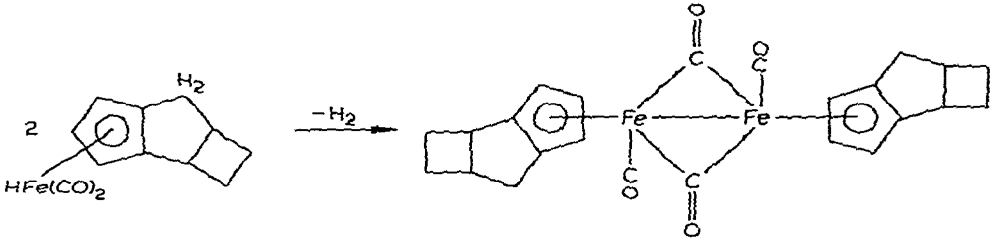
* Although only a minute quantity is obtained in each run, its formation has since been found to be consistently reproducible.

(VI) seems a very probable intermediate, which would then rapidly undergo reaction (3) to generate the final product.



(3)

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