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THE CRYSTAL AND MOLECULAR STRUCTURE OF μ-(1,2,6-η: 3-5-η-BICYCLO[6.10]NONA-1,3,5-TRIENE)HEXACARBONYLDIIRON (*Fe—Fe*), AND COMMENT ON ITS TEMPERATURE-DEPENDENT ^{1}H NMR SPECTRUM

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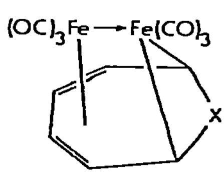
Summary

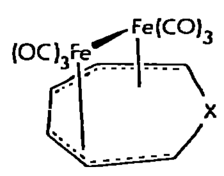
The crystal and molecular structure of $(C_9H_{10})Fe_2(CO)_6$ has been determined from a three-dimensional, X-ray crystal-structure analysis. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares. With all atoms located and refined the conventional R factor is 0.034, based on 2651 reflections measured with an automated General Electric XRD-6 diffractometer utilizing Mo-K_α radiation. Crystallographic data are: space group $P\bar{1}$ with a = 7.229(4), b = 14.699(4) and c = 7.696(2) Å, α = 87.53(2)°, β = 113.48(3)° and γ = 102.08(2)°, Z = 2 and ρ_{calcd} = 1.80 g/cm^3, ρ_{obsd} = 1.78 g/cm^3. Contrary to previous claims the structure of the molecule is of the asymmetric type already established for $(C_8H_{10})Fe_2(CO)_6$ and $(C_{10}H_{12})Fe_2(CO)_6$. The almost identical bond parameters amongst the three structures are noted. The lengthening of the Fe—C(carbonyl) *trans* to Fe—C σ bond is attributed to the *trans*-influence of the σ-carbon atom. The fluxional nature of the molecule is also demonstrated by extending the variable temperature ^{1}H NMR study down to —127°.

Introduction

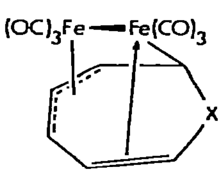
The structural features of several complexes containing an $Fe_2(CO)_6$ moiety bonded to a cyclic 1,3,5-triene have been previously established by single-crystal X-ray crystallography [1-3]. Although a priori one can consider three possible structures for these compounds, represented schematically by Ia, Ib and Ic, from the above studies the following consistent picture seems to be emerging. For complexes containing eight membered rings attached to the two iron atoms the skew structure Ic is found invariably [1, 3], and only in the case of (cycloheptatriene)hexacarbonyldiiron [2] is the symmetrical structure Ib observed. It is interesting to note that the possible structure Ia, albeit originally proposed [4] for this type of complexes, has yet to be observed.



(Ia)



(Ib)



(Ic)

A further interesting property of the complexes containing eight membered rings is their fluxional behaviour [3, 5]. At low temperatures the ^{1}H NMR spectrum can be explained in terms of the structure found in the solid state, whereas at room temperature rapid interconverion between the two enantiomers of Ic results in a time-averaged mirror plane for the molecule and concurrent simplification of the NMR spectrum.

It was therefore of some interest that ^{1}H [6] and ^{13}C [7] NMR results on (bicyclo[6.1.0]nonatriene)hexacarbonyldiiron were seemingly only consistent with a non-fluxional and symmetric structure in solution, i.e. with structures Ia and Ib. Since this would represent the first case where an eight membered ring would have changed its bonding pattern to an $Fe_2(CO)_6$ moiety a structure determination of the above complex was definitely in order. In view of the crystallographic results, which are reported here, the variable temperature ^{1}H NMR study of the complex was extended down to −127° and is also commented upon.

Experimental

Collection of X-ray data

The compound (bicyclo[6.1.0]nona-1,3,5-triene)hexacarbonyldiiron was prepared as described elsewhere [6]. Crystals suitable for X-ray study were obtained by slow crystallization from pentane under nitrogen. Preliminary examination of the compound using Weissenberg and precession techniques indicated only $\bar{1}$ symmetry. The crystal therefore belongs to the triclinic system with probable space group $P\bar{1}$. This choice is fully substantiated by the subsequent successful refinement of the data. For data collection a parallelipiped shaped crystal of dimensions 0.24 × 0.26 × 0.32 mm was chosen and mounted on a glass fiber; no evidence for crystal decomposition was found during the data collection process.

Least-squares refinement of 38 reflections with $2\theta > 30°$ gave the following cell dimensions and errors: a = 7.229(4), b = 14.699(4), c = 7.696(2) Å; α = 87.53(2)°, β = 113.48(3)° and γ = 102.08(2)°. With two molecules per unit cell the calculated and experimental densities are 1.80 and 1.78 g cm^{-3} respectively.

Intensity data were collected, on a General Electric quarter-circle automated XRD-6 diffractometer equipped with a Datex control unit, using Zr-filtered Mo-K_α radiation. The intensities were measured with a scintillation counter with the pulse height discriminator set to receive 95% of the Mo-K_α radiation with the window centered on the Mo-K_α peak. The data were collected using a coupled 2θ—ω scan technique with a scan rate of 2°/min and a range of $2\theta_{calcd}$ −0.67° to $2\theta_{calcd}$ +0.66°. Stationary background (B_1 and B_2) counts of 20 sec were taken at each of the limits of the scan. A total of 3364 independent reflections were measured with $2\theta < 55°$. A set of three standard reflections were monitored after every 75 relfections as a check on crystal and electronic stability. The standard deviations of these reflections, computed on the basis of the agreement among the 53 observations made for each standard, were less than the deviations based on counting statistics and a 1% machine error. No systematic trend in the variations could be detected.

The intensities (I = total count $(P)-B_1-B_2$, $\sigma(I) = [P + B_1 + B_2 + (pI)^2]^{1/2}$) were reduced to relative amplitudes, $|F_0|$ by application of Lorentz and polarization corrections. Of the 3364 unique reflections 2651 were accepted using the criterion $F_0^2 > 1.0\sigma(F_0^2)$ and used in the solution and refinement of the structure. A "p factor" [8] of 0.03 was used in the calculation of $\sigma(F_0^2)$. The maximum variation in intensity due to crystal absorption, as verified by a ϕ scan, was less than 3% and as a result no absorption corrections were applied to the data (μ = 20.6 cm^{-1} for Mo-K_α).

TABLE 1

FINAL ATOMIC POSITIONAL AND ISOTROPIC THERMAL PARAMETERS

Atom	x	y	z	B (Å^2) [a]
Fe(1)	0.40606(6)	0.30771(3)	0.72611(5)	2.73
Fe(2)	0.23370(6)	0.13090(3)	0.79822(5)	2.87
C(11)	0.5336(5)	0.4256(2)	0.7294(4)	3.53
C(12)	0.6211(5)	0.2818(2)	0.9205(4)	3.46
C(13)	0.4842(5)	0.2776(2)	0.5425(4)	3.70
C(21)	0.4357(5)	0.1166(2)	1.0202(4)	3.83
C(22)	0.3306(5)	0.0918(2)	0.6397(5)	4.14
C(23)	0.0920(5)	0.0176(2)	0.8080(4)	4.01
C(1)	0.2850(4)	0.3262(2)	0.9271(4)	2.71
C(2)	0.1382(5)	0.2921(2)	0.8616(4)	3.30
C(3)	0.0458(5)	0.4027(2)	0.6518(4)	3.63
C(4)	0.1265(4)	0.3533(2)	0.5414(4)	3.35
C(5)	0.0854(4)	0.2573(2)	0.5156(4)	3.19
C(6)	−0.0163(4)	0.1860(2)	0.6023(4)	3.27
C(7)	−0.0082(4)	0.1860(2)	0.7873(4)	3.16
C(8)	0.1645(4)	0.2337(2)	0.9410(4)	2.93
C(9)	0.1810(6)	0.4851(2)	0.7843(5)	4.11
O(11)	0.6316(4)	0.4972(2)	0.7275(3)	5.25
O(12)	0.7681(3)	0.2746(2)	1.0481(3)	5.05
O(13)	0.5351(4)	0.2638(2)	0.4251(3)	5.57
O(21)	0.5527(4)	0.1001(2)	1.1621(3)	5.97
O(22)	0.3907(5)	0.0642(2)	0.5414(4)	6.78
O(23)	0.0084(4)	−0.0563(2)	0.8161(4)	6.13
H(1)	0.397(4)	0.346(2)	1.046(4)	3.0(6)
H(2)	0.0511(4)	0.384(2)	0.927(4)	2.7(6)
H(3)	−0.099(5)	0.409(2)	0.596(4)	4.4(7)
H(4)	0.160(4)	0.389(2)	0.448(4)	3.6(7)
H(5)	0.103(4)	0.233(2)	0.409(4)	2.9(6)
H(6)	−0.120(5)	0.148(2)	0.522(4)	4.0(7)
H(7)	−0.096(4)	0.142(2)	0.818(4)	3.7(7)
H(8)	0.171(4)	0.217(2)	1.061(4)	2.9(6)
H(91)	0.318(5)	0.510(2)	0.781(4)	4.1(7)
H(92)	0.110(5)	0.530(2)	0.803(4)	4.6(7)

[a] For non-hydrogen atoms these are "equivalent" isotropic thermal parameters as calculated from the anisotropic thermal parameters by SFLS5.

TABLE 2

ANISOTROPIC THERMAL PARAMETERS (Å^2)[a]

Atom	10^3U_{11}	10^3U_{22}	10^3U_{33}	10^3U_{12}	10^3U_{13}	10^3U_{23}
Fe(1)	33.3(2)	37.8(2)	29.6(2)	7.3(2)	9.9(2)	2.8(2)
Fe(2)	40.9(3)	30.8(2)	34.6(2)	10.9(2)	10.8(2)	1.5(2)
C(11)	47(2)	49(2)	36(2)	6(1)	17(1)	3(1)
C(12)	41(2)	49(2)	42(2)	11(1)	17(1)	5(1)
C(13)	44(2)	53(2)	41(2)	9(1)	15(1)	1(1)
C(21)	56(2)	37(2)	47(2)	19(1)	12(2)	2(1)
C(22)	64(2)	45(2)	55(2)	21(2)	26(2)	4(2)
C(23)	66(2)	36(2)	48(2)	11(2)	21(2)	3(1)
C(1)	38(1)	34(1)	29(1)	9(1)	10(1)	1(1)
C(2)	44(2)	38(2)	47(2)	12(1)	20(1)	2(1)
C(3)	38(2)	42(2)	52(2)	15(1)	9(1)	8(1)
C(4)	42(2)	45(2)	34(2)	12(1)	8(1)	13(1)
C(5)	38(2)	45(2)	29(1)	11(1)	3(1)	0(1)
C(6)	31(2)	37(2)	42(2)	4(1)	1(1)	−3(1)
C(7)	35(2)	35(2)	52(2)	7(1)	19(1)	5(1)
C(8)	44(2)	37(2)	35(1)	15(1)	18(1)	5(1)
C(9)	57(2)	34(2)	65(2)	17(1)	21(1)	5(1)
O(11)	75(2)	51(2)	63(2)	−14(1)	31(1)	2(2)
O(12)	40(1)	84(2)	56(1)	19(1)	5(1)	14(1)
O(13)	72(2)	97(2)	53(1)	19(1)	35(1)	−5(1)
O(21)	85(2)	70(2)	52(1)	36(1)	−2(1)	11(1)
O(22)	125(3)	77(2)	92(2)	47(2)	9(2)	4(2)
O(23)	105(2)	39(1)	88(2)	−3(1)	46(2)	4(1)

[a] The U's are the mean square amplitudes of vibrations in Å^2 from the general temperature factor expression: $\exp[-2\pi(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$

Solution and refinement of the structure

The positions of the two iron atoms were located from a three-dimensional Patterson map*. Two cycles of least-squares refinement of the scale factor and the positional and thermal parameters for the two iron atoms were followed by a difference-Fourier synthesis which revealed the positions of all the remaining non-hydrogen atoms. Three cycles of least-squares refinement of the scale factor plus all 23 non-hydrogen atoms with isotropic temperature factors gave agreement factors $R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0| = 0.083$ and $R_2 = \{\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2\}^{1/2} = 0.088$. A difference-Fourier map at this point revealed the locations of all 10 hydrogen atoms. Four cycles of least-squares where the 23 atoms were refined anisotropically and the 10 hydrogen atoms isotropically gave the final values of $R_1 = 0.034$ and $R_2 = 0.033$. The final cycle of refinement

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* The following crystallographic programs were used in this structural analysis: C.T.P. Prewitt's SFLS5, structure factor calculation and least squares refinement of parameters, modified by B.M. Foxman and M.J. Bennett, for rigid body routine and by W.L. Hutcheon and M.J. Bennett for hindered rotor; A. Zalkin's FORDAP, Fourier summation for Patterson or Fourier maps; M.E. Pippy and F.R. Ahmed's NRC-22, calculates least-squares planes; W. Busing and H.A. Levy's ORFFE, calculates bond lengths, angles, and associated standard deviations, modified by B. Penfold for IBM 360; M. Cowie's PUBE, sorts data according to any desired sequence of h, k or l; R.C. Elder's PUBTAB, prints structure factor amplitude tables, modified by M. Cowie to work in conjunction with PUBE; C. Johnson's ORTEP, Fortran thermal ellipsoid plot program for crystallographic illustrations.

showed no parameter shift greater than one-fifth of one esd. The error in an observation of unit weight was 0.66, an indication of slight overestimation of $\sigma(F_0)$. A difference-Fourier map computed at this point did not have any feature greater than 0.35 eÅ^{-3}. Comparatively, in a previous map, the hydrogen atoms were located at 0.66 eÅ^{-3}.

Atomic scattering factors for neutral Fe, O and C were those of Cromer and Mann [9], while for H the tabulation of Stewart, Davidson and Simpson [10] was used. The atomic scattering factors for iron were corrected for the real ($\Delta f' = 0.35$ e) and imaginary ($\Delta f'' = 0.845$ e) part of the anomalous dispersion [11]. The function minimized in the least-squares refinement was $\Sigma w(|F_0| - |F_c|)^2$, where $w = 1/\sigma^2\ (F_0)$.

The final positional and thermal parameters with their associated standard deviations, estimated from the inverse matrix, are given in Tables 1 and 2. A listing of the observed and calculated structure factors is available*.

Results

Figures 1 and 2 show two stereoscopic views of the molecule containing the numbering scheme used in the present study. Intramolecular distances and bond angles are collected in Tables 3 and 4, with their estimated standard deviations. Table 5 gives the equations of the planes which define the organic ligand, the deviations of individual atoms from these planes and the dihedral angles between pairs of planes. Figure 3 summarizes the corresponding bond distances in the three similar $Fe_2(CO)_6$ containing molecules: $(C_8H_{10})Fe_2(CO)_6$, $(C_{10}H_{12})Fe_2(CO)_6$ and $(C_9H_{10})Fe_2(CO)_6$. Finally Fig. 4 shows the variable temperature ^{1}H NMR of $(C_9H_{10})Fe_2(CO)_6$ extended to −127°.

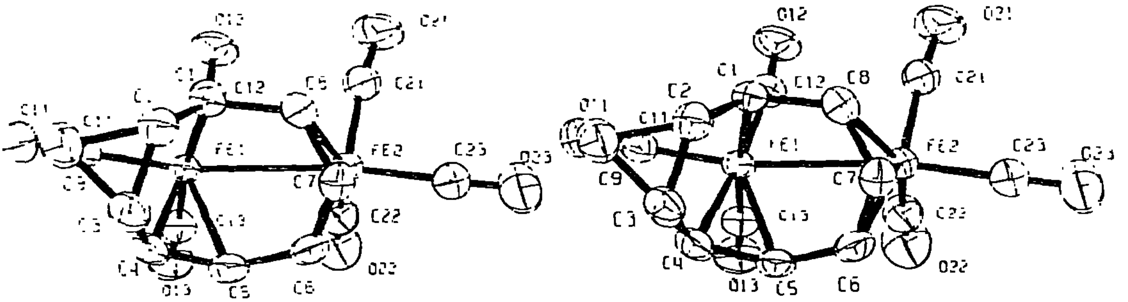

Fig. 1. Stereoview of the $(C_9H_{10})Fe_2(CO)_6$ molecule, emphasizing the asymmetric arrangement of the $Fe_2(CO)_6$ unit with respect to the organic ligand.

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* See NAPS document No. 02510 for 13 pages of supplementary material. Order from ASIS/NAPS c/o Microfiche Publications, 440 Park Avenue South, New York, N.Y. 10016. Remit in advance for each NAPS accession number. Make checks payable to Microfiche Publications. Photocopies are $ 5.00. Microfiches are $ 1.50. Outside of the United States and Canada, postage is $ 2.00 for a photocopy or $0.50 for a fiche.

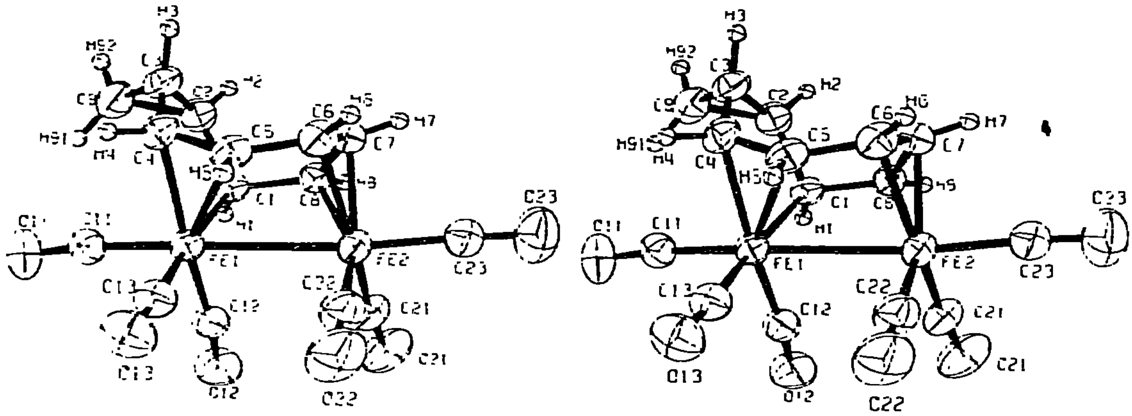

Fig. 2. Stereoview of $(C_9H_{10})Fe_2(CO)_6$ molecule, showing the locations of the hydrogen atoms and the geometry of the organic ligand.

Discussion

It is clear from Figs. 1 and 2 that, at least in the solid state, the structure found for this complex is not the symmetrical type, Ia or Ib as previously postulated, but is analogous to the structures of $(C_8H_{10})Fe_2(CO)_6$ and $(C_{10}H_{12})Fe(CO)_6$, depicted schematically by Ic. Each, well separated, monomeric

(continued on p. 219)

TABLE 3

INTRAMOLECULAR DISTANCES (Å) IN $(C_9H_{10})Fe_2(CO)_6$

Fe(1)—Fe(2)	2.773(1)		
Fe(1)—C(11)	1.780(3)	Fe(2)—C(21)	1.780(3)
Fe(1)—C(12)	1.773(3)	Fe(2)—C(22)	1.794(3)
Fe(1)—C(13)	1.819(3)	Fe(2)—C(23)	1.779(3)
C(11)—O(11)	1.143(3)	C(21)—O(21)	1.137(3)
C(12)—O(12)	1.145(3)	C(22)—O(22)	1.135(4)
C(13)—O(13)	1.142(3)	C(23)—O(23)	1.140(4)
Fe(1)—C(1)	2.108(3)	Fe(2)—C(7)	2.047(3)
Fe(1)—C(4)	2.179(3)	Fe(2)—C(6)	2.129(3)
Fe(1)—C(5)	2.223(3)	Fe(2)—C(8)	2.154(3)
C(1)—C(2)	1.511(4)	C(6)—C(7)	1.402(4)
C(2)—C(3)	1.497(4)	C(7)—C(8)	1.407(4)
C(3)—C(4)	1.488(4)	C(8)—C(1)	1.478(4)
C(4)—C(5)	1.387(4)	C(9)—C(2)	1.490(4)
C(5)—C(6)	1.446(4)	C(9)—C(3)	1.509(4)
C(1)—H(1)	0.96(3)	C(6)—H(6)	0.86(3)
C(2)—H(2)	0.94(3)	C(7)—H(7)	0.90(3)
C(3)—H(3)	0.98(3)	C(8)—H(8)	0.93(3)
C(4)—H(4)	0.95(3)	C(9)—H(91)	0.99(3)
C(5)—H(5)	0.96(3)	C(9)—H(92)	0.97(3)

TABLE 4. INTRAMOLECULAR BOND ANGLES (°) IN $(C_9H_{10})Fe_2(CO)_6$

Fe(1)—C(11)—O(11)	172.2(2)	Fe(2)—C(21)—O(21)	173.8(3)
Fe(1)—C(12)—O(12)	173.0(3)	Fe(2)—C(22)—O(22)	177.8(3)
Fe(1)—C(13)—O(13)	176.2(3)	Fe(2)—C(23)—O(23)	177.2(3)
C(11)—Fe(1)—C(12)	92.4(1)	C(21)—Fe(2)—C(22)	99.6(1)
C(11)—Fe(1)—C(13)	89.9(1)	C(21)—Fe(2)—C(23)	90.4(1)
C(11)—Fe(1)—C(1)	97.3(1)	C(21)—Fe(2)—C(6)	157.9(1)
C(11)—Fe(1)—C(4)	85.5(1)	C(21)—Fe(2)—C(7)	121.1(1)
C(11)—Fe(1)—C(5)	120.1(1)	C(21)—Fe(2)—C(8)	87.8(1)
C(11)—Fe(1)—Fe(2)	168.5(1)	C(21)—Fe(2)—Fe(1)	98.6(1)
C(12)—Fe(1)—C(13)	96.1(1)	C(22)—Fe(2)—C(23)	92.2(1)
C(12)—Fe(1)—C(1)	86.2(1)	C(22)—Fe(2)—C(6)	100.4(1)
C(12)—Fe(1)—C(4)	166.0(1)	C(22)—Fe(2)—C(7)	139.3(1)
C(12)—Fe(1)—C(5)	147.1(1)	C(22)—Fe(2)—C(8)	154.8(1)
C(12)—Fe(1)—Fe(2)	80.0(1)	C(22)—Fe(2)—Fe(1)	84.7(1)
C(13)—Fe(1)—C(1)	172.4(1)	C(23)—Fe(2)—C(6)	97.9(1)
C(13)—Fe(1)—C(4)	97.7(1)	C(23)—Fe(2)—C(7)	89.6(1)
C(13)—Fe(1)—C(5)	85.5(1)	C(23)—Fe(2)—C(8)	111.2(1)
C(13)—Fe(1)—Fe(2)	99.4(1)	C(23)—Fe(2)—Fe(1)	170.9(1)
C(1)—Fe(1)—C(4)	80.4(1)	C(6)—Fe(2)—C(7)	39.2(1)
C(1)—Fe(1)—C(5)	88.6(1)	C(6)—Fe(2)—C(8)	70.1(1)
C(1)—Fe(1)—Fe(2)	73.8(1)	C(6)—Fe(2)—Fe(1)	74.0(1)
C(4)—Fe(1)—C(5)	36.1(7)	C(7)—Fe(2)—C(8)	39.0(1)
C(4)—Fe(1)—Fe(2)	99.7(1)	C(7)—Fe(2)—Fe(1)	86.6(1)
C(5)—Fe(1)—Fe(2)	67.7(1)	C(8)—Fe(2)—Fe(1)	70.4(1)
Fe(1)—C(1)—C(2)	111.9(2)	Fe(2)—C(6)—C(5)	102.5(2)
Fe(1)—C(1)—C(8)	105.7(2)	Fe(2)—C(6)—C(7)	67.3(2)
Fe(1)—C(4)—C(3)	111.4(2)	Fe(2)—C(7)—C(6)	73.6(2)
Fe(1)—C(4)—C(5)	73.3(2)	Fe(2)—C(7)—C(8)	74.6(2)
Fe(1)—C(5)—C(4)	69.9(2)	Fe(2)—C(8)—C(1)	108.7(2)
Fe(1)—C(5)—C(6)	107.6(2)	Fe(2)—C(8)—C(7)	66.4(2)
C(8)—C(1)—C(2)	107.4(2)	C(7)—C(8)—C(1)	123.3(3)
C(1)—C(2)—C(3)	115.0(3)	C(3)—C(2)—C(9)	60.7(2)
C(2)—C(3)—C(4)	115.0(2)	C(2)—C(3)—C(9)	59.4(2)
C(3)—C(4)—C(5)	123.9(3)	C(2)—C(9)—C(3)	59.9(2)
C(4)—C(5)—C(6)	129.3(3)	C(1)—C(2)—C(9)	125.1(3)
C(5)—C(6)—C(7)	128.4(3)	C(4)—C(3)—C(9)	121.0(3)
C(6)—C(7)—C(8)	122.3(3)		
H(1)—C(1)—C(2)	113(2)	H(6)—C(6)—C(5)	114(2)
H(1)—C(1)—C(8)	111(2)	H(6)—C(6)—C(7)	115(2)
H(2)—C(2)—C(1)	111(2)	H(7)—C(7)—C(6)	120(2)
H(2)—C(2)—C(3)	118(2)		
H(2)—C(2)—C(9)	118(2)	H(7)—C(7)—C(8)	116(2)
H(3)—C(3)—C(4)	120(2)	H(8)—C(8)—C(7)	116(2)
H(3)—C(3)—C(2)	116(2)		
H(3)—C(3)—C(9)	111(2)	H(8)—C(8)—C(1)	117(2)
H(4)—C(4)—C(3)	115(2)	H(91)—C(9)—C(2)	120(2)
H(4)—C(4)—C(5)	117(2)	H(91)—C(9)—C(3)	117(2)
H(5)—C(5)—C(4)	117(2)	H(91)—C(9)—H(92)	117(2)
H(5)—C(5)—C(6)	113(2)	H(92)—C(5)—C(2)	116(2)
		H(92)—C(5)—C(3)	116(2)

TABLE 5

LEAST-SQUARES PLANES IN (BICYCLO[6.1.0]NONATRIEN)HEXACARBONYLDIIRON[a]

	Equations of planes			
	L	*M*	*N*	*D*
Plane I ($C_6C_7C_8$)	−0.5381	0.8251	−0.1722	2.6819
Plane II ($C_1C_8C_6C_5$)	−0.8721	0.4745	−0.1196	2.8199
Plane III ($C_1C_4C_5$)	0.9983	0.0574	−0.0063	−1.5727
Plane IV ($C_1C_2C_3C_4$)	−0.6167	−0.7762	−0.1270	−3.1480
Plane V ($C_2C_3C_9$)	0.9743	−0.2142	−0.0692	−4.3460

DISTANCES AND DEVIATIONS FROM LEAST-SQUARES PLANES (Å)

	Plane II		Plane IV	
Plane I—Fe(2) 1.683	C_1	0.041	C_1	0.011
	C_8	−0.055	C_2	−0.025
	C_6	0.063	C_3	0.027
	C_5	−0.047	C_4	−0.013

ANGLES BETWEEN LEAST-SQUARES PLANES (°)

Plane I—Plane II	151.8	Plane II—Plane V	160.9
Plane II—Plane III	146.4	Plane III—Plane IV	130.3
Plane II—Plane IV	100.7	Plane IV—Plane V	65.7

[a] The equations of the planes are $Lx + My + Nz = D$, where *L*, *M* and *N* are direction cosines referred to the orthogonal coordinate system where $x = a$, y is in the *ab* plane and z is c^*.

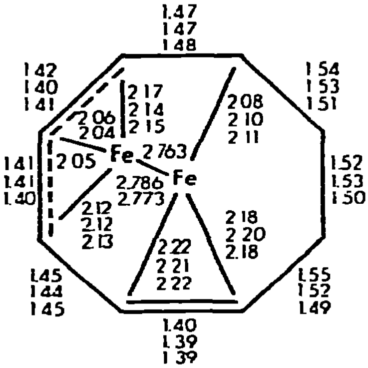

Fig. 5. Schematic drawing of the C_8 ring bonded to an Fe—Fe moiety for $(C_8H_{10})Fe_2(CO)_6$, $(C_{10}H_{12})Fe_2(CO)_6$ and $(C_9H_{10})Fe_2(CO)_6$. Bond distances for the compounds are listed in the above order from top to bottom. The standard deviations on the bond lengths are ca 0.02 Å for the first and ca. 0.005 Å for the last two compounds.

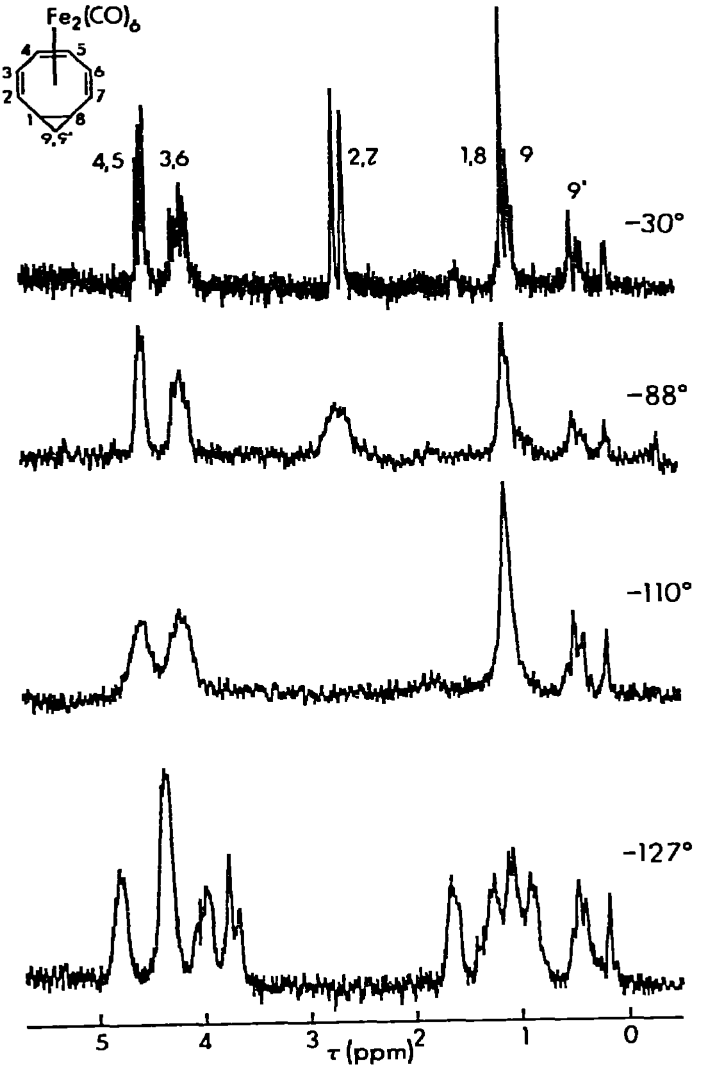

Fig. 4. ^1H NMR spectra (100 MHz) of $(C_9H_{10})Fe_2(CO)_6$ at various temperatures in CD_2Cl_2/CHF_2Cl (20/80 vol./vol.). Note the different assignments of the protons 2, 7 and 1, 8 from that previously suggested.

unit consists of two $Fe(CO)_3$ groups lying on the same side of the organic ligand and joined together by an Fe—Fe bond. The bonding is completed by a η^3-allyl linkage, $C_6C_7C_8$, to Fe_2 and by a combination of η^2-olefin, C_4C_5, and C_1-to-metal single bonds to Fe_1. Thus each iron atom achieves the favoured 18 electron configuration.

The similarities in the three structures can be even more appreciated when the corresponding bond lengths are compared. Not unexpectedly, the average Fe—C(carbonyl) and C—O distances are similar, 1.789(8) and 1.140(5) as compared to 1.78(2) and 1.13(2)Å in $(C_8H_{10})Fe_2(CO)_6$ [1] and 1.783(12) and 1.143(5)Å in $(C_{10}H_{12})Fe_2(CO)_6$ [3]. More significant is the amazing similarity of the remaining Fe—Fe, Fe—C and C—C bond lengths. Indeed inspection of Fig. 3, which summarizes these distances in the above three compounds, clearly demonstrates the quantitative similarity in the structures. Since, as has been discussed previously [3], the observed bond lengths and angles are entirely consistent with the observed structure, discussion of the distances and bonding in the molecule is deemed redundant and unnecessary. It is nevertheless interesting to note that the length of the Fe—C(carbonyl) bond *trans* to the metal—carbon σ bond is significantly longer than the other Fe—C(carbonyl) bond distances ($Fe_1—C_{13}$) = 1.819(3) vs. 1.783(4) Å (the average distance for the others). Similar behaviour of these distances can also be seen in $(C_{10}H_{12})Fe_2(CO)_6$ [1.803(4) and 1.779(4) Å] the other accurately determined structure for these complexes of this type. The significance of the observations lies in the fact that the lengthening is in the direction expected from the known greater structural *trans*-influence of a σ-carbon atom [12] as compared to the other bonding units in the above two molecules.

The geometry of the C_9H_{10} group can be seen in Figs. 1 and 2. Not unexpectedly, upon coordination to the metal, the ligand adopts a highly distorted geometry. Table 5 lists the five individual planes that can be identified within the organic group together with the dihedral angles made by these planes. The geometry and the joining of the cyclopropane ring to the eight membered ring in an *exo* fashion parallels in the structure of $(C_{10}H_{12})Fe_2(CO)_6$. The distances and angles within the cyclopropane ring are as expected [13].

In view of the almost identical structure found in the solid state between this complex and others [1, 3] which are known to be fluxional [3, 5], the solution behaviour reported for the present compound was rather puzzling. To see whether the existing discrepancies between solid state and solution behaviours were only artifacts of the limited variable temperature ^1H NMR investigation it was decided to extend such a study down to the lowest accessible temperature. Figure 4 clearly shows that the molecule $(C_9H_{10})Fe_2(CO)_6$ is fluxional and therefore it is, in all respects, similar to the previouslt reported $(C_8H_{10})Fe_2(CO)_6$ and $(C_{10}H_{12})Fe_2(CO)_6$ complexes.

No more will be said about the variable temperature behaviour of the complex since further NMR studies, both ^1H and ^{13}C, are in progress in order to elucidate the rearrangement processes involved and to evaluate the associated rate parameters. These results will form the body of a future publication [14].

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