

## FLUXIONAL ORGANOMETALLIC MOLECULES

### XXXIV\*. THE STRUCTURE AND TEMPERATURE-DEPENDENT NMR SPECTRUM OF *cis*-(1,2,6-trihapto-; 3,4,5-trihapto-BICYCLO[6.2.0]DECA-1,3,5-TRIENE)HEXACARBONYLDIIRON(Fe-Fe)\*\*

F. A. COTTON and B. A. FRENZ

Department of Chemistry, Texas A&M University, College Station, Texas 77843 (U.S.A.)

G. DEGANELLO

Centro di Chimica e Tecnologia dei Composti Metallorganici degli Elementi di Transizione del C.N.R., Venice (Italy)

and A. SHAVER

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (U.S.A.)

(Received July 21st, 1972)

#### SUMMARY

The crystal structure and low temperature PMR spectra of the diironhexacarbonyl adduct of bicyclo[6.2.0]deca-1,3,5-triene have been determined. The entire body of data suggests that the ground state structure of the molecule is of the asymmetric *cis*-(1,2,6-trihapto-3,4,5-trihapto-cyclooctatriene)diironhexacarbonyl type previously found in (cyclooctatriene)diironhexacarbonyl and (cyclooctatetraene)diruthenium hexacarbonyl. Below  $-70^\circ$  the PMR spectrum broadens and the complex spectrum in the slow exchange limit ( $-130^\circ$ ) is consistent with such an instantaneous structure. Above  $-70^\circ$  the spectrum is indicative of a time-average plane of symmetry resulting from fluxionality of the molecule.

---

#### INTRODUCTION

Several molecules in which the  $\text{Fe}_2(\text{CO})_6$  moiety is bonded to a cyclic 1,3,5-triene have previously been studied by PMR spectroscopy<sup>1-5</sup> and X-ray crystallography<sup>6-8</sup>. Those to be discussed here are shown below as I-VI. The notation I(Fe) will be used to designate the compound of type I with  $\text{Fe}_2(\text{CO})_6$ , I(Ru) to designate the corresponding compound containing  $\text{Ru}_2(\text{CO})_6$ , etc. For each of the compounds there are three structures which might be considered as possible *a priori*. These are shown schematically as a, b and c. Compounds I(Ru) and II(Fe) have been studied crystallographically<sup>6,7</sup> and shown to have the c type structure. Studies of their PMR

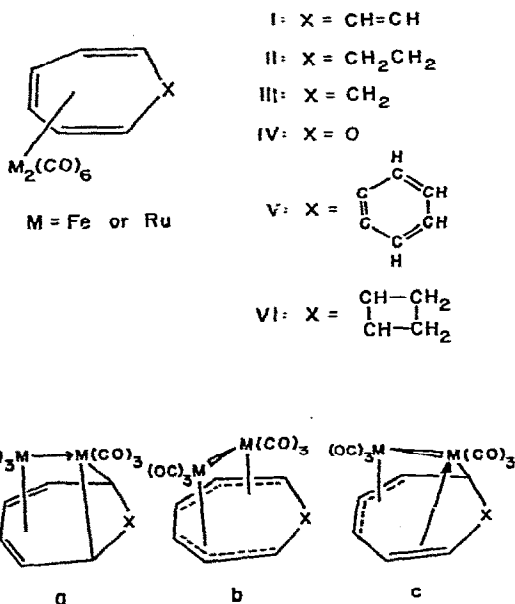
---

\* For Part XXXIII, see ref. 18.

\*\* Supported in part by The Robert A. Welch Foundation, which provided funds for the diffractometer, and by the National Science Foundation.

spectra from room temperature to temperatures in the range of  $-50$  to  $-100^\circ$  show that they are fluxional molecules. They have the structure **c** as their instantaneous structure, but at higher temperatures rapid oscillation between the two enantiomorphs creates a time-average plane of symmetry. For III(Fe) on the other hand, the crystal structure is of type **b**; the PMR spectrum is temperature-independent. No structure of type **a**, which was the first one proposed for molecules of this type, has yet been found. Compounds IV(Fe)<sup>9</sup> and V(Fe)<sup>10</sup> have apparent mirror symmetry in their room-temperature PMR spectra. For IV(Fe) this symmetry persists at  $-80^\circ$ , without line broadening, and the molecule may have a structure of type **b**. For V(Fe) there is no further information.

In this paper we are concerned with the structure and dynamics of VI(Fe). The preparation of this substance has previously been reported<sup>11</sup>. The PMR spectrum implies mirror symmetry down to a temperature of about  $-70^\circ$ . It was noted



that this might indicate that the molecule possesses a structure of type **b**, since the spectra of I(Ru) and II(Fe) showed the first evidences of collapse at temperatures of  $-7^\circ$  and  $-15^\circ$ , respectively.

In order to establish with certainty the structural and dynamical nature of VI(Fe) the crystal structure and additional low-temperature PMR measurements were undertaken. The results are reported here.

## EXPERIMENTAL

*Collection of X-ray data.* Air-stable red-orange crystals of the compound were prepared as previously described<sup>11</sup> by reaction of *cis*-bicyclo[6.2.0]deca-2,4,6-triene and diiron nonacarbonyl.

Precession photographs revealed no symmetry elements; hence the crystals were assigned to the triclinic system and space group  $P\bar{1}$  was assumed.

A Syntex  $P\bar{1}$  computer-controlled 4-circle diffractometer equipped with a graphite-crystal, incident-beam monochromator was used to examine an irregularly shaped crystal of approximate dimensions  $0.21 \times 0.23 \times 0.14$  mm with faces 100,  $\bar{1}00$ ,  $0\bar{1}0$ ,  $011$ ,  $0\bar{1}\bar{1}$ ,  $01\bar{1}$ ,  $0\bar{1}1$ ,  $1\bar{1}\bar{1}$ ,  $1\bar{1}1$ ,  $1\bar{1}\bar{1}$ , and  $\bar{1}\bar{1}\bar{1}$ . The crystal was mounted in an arbitrary orientation along its long direction.

The diffractometer setting angles were positioned at  $2\theta = \omega = \chi = 0^\circ$  and a Polaroid film cassette was mounted in front of the counter at 9.8 cm from the crystal. The film was exposed to  $\text{Mo-K}_\alpha$  radiation for 15 min while the  $\phi$  axis was rotated through  $360^\circ$  at  $192^\circ/\text{min}$ . From this film, the X and Y coordinates of fourteen reflections were measured. These results were put into the computer, and, using the Syntex software package, the reflections were centered automatically.

From  $\omega$  scans of several strong reflections a width at half-height of  $0.18^\circ$  was measured. The setting angles for the reflections were used as input for the auto-indexing program. From the output a triclinic cell was selected and least-squares refinement of the 42 setting angles ( $\phi$  is held fixed) produced the orientation matrix to be used for data collection. The cell constants and calculated volume are:  $a = 8.442(1)$ ,  $b = 12.071(3)$ ,  $c = 8.410(3)$  Å,  $\alpha = 95.43(3)^\circ$ ,  $\beta = 102.10(2)^\circ$ ,  $\gamma = 105.96(1)^\circ$ ,  $V = 795.1(4)$  Å<sup>3</sup>. For  $Z = 2$  and mol.wt. 411.96 the calculated density is  $1.72 \text{ g}\cdot\text{cm}^{-3}$ .

Data were collected at  $24^\circ$  using  $\text{Mo-K}_\alpha$  radiation. The  $\theta$ - $2\theta$  scan technique with a variable scan rate from  $2.0$  to  $24.0^\circ/\text{min}$  with a symmetric scan range from  $2\theta(\text{Mo-K}_{\alpha_1}) - 0.8^\circ$  to  $2\theta(\text{Mo-K}_{\alpha_2}) + 0.8^\circ$  was used. The variable scan rate allows rapid data collection for intense reflections where a fast scan rate is used and assures good counting statistics for weak reflections where a slow scan rate is used. Stationary-crystal stationary-counter background counts were taken at each end of the  $2\theta$  scan range; the total background counting time is equal to the scan time. The Syntex data collection program corrects the scan count for background. For intense reflections where the counting rate floods the scintillation detector a coincidence correction is automatically applied to the data.

Data were collected in the range  $0^\circ < 2\theta (\text{Mo-K}_\alpha) \leq 45^\circ$ . The counter was placed 19 cm from the crystal with the counter aperture wide open at its 2 mm diameter. The takeoff angle was set at  $3^\circ$  and the width of the pulse height analyser was set to accept about 95% of the radiation when centered on the  $\text{Mo-K}_\alpha$  peak.

As a check on crystal and electronic stability, four representative reflections were measured periodically. A decrease in intensity ranging from 1.1 to 1.4% was observed for these standards; this decrease is not significant when compared to the standard deviations of the intensities based on counting statistics alone.

Data collection was terminated because of the comparatively few reflections beyond  $2\theta = 45^\circ$  which had significant intensities. A total of 2086 unique reflections were collected; of these 1576 had  $F_0^2 > 3\sigma(F_0^2)$ . Here  $\sigma(F_0^2)$  is the standard deviation for the observed intensity of a reflection and is calculated from

$$\sigma(F_0^2) = [S^2(C + R^2B) + (pF_0^2)^2]^{\frac{1}{2}}$$

where  $S$  is the scan rate,  $C$  is the total integrated peak count,  $R$  is the ratio of scan time to background counting time,  $B$  is the total background count, and the parameter  $p$

is set to 0.05. Lorentz and polarization corrections were applied\* to the data. The linear absorption coefficient of the substance for Mo- $K_{\alpha}$  radiation is  $19.0 \text{ cm}^{-1}$ . Preliminary calculations<sup>12</sup> showed transmission factors of  $76 \pm 4\%$ . An absorption correction was not applied. No effects owing to secondary extinction were observed in the data.

*Measurements of proton magnetic resonance spectra.* The spectra were recorded at various temperatures in the range  $+26^{\circ}$  to  $-129^{\circ}$  using a Varian HA-100 spectrometer equipped with a variable temperature probe. Chemical shifts were measured against TMS as an internal reference. Temperatures were measured with a Digitec Digital Thermocouple Thermometer, C-C Type T. The solvent used was the ternary mixture of  $\text{CD}_2\text{Cl}_2/\text{CF}_2\text{Cl}_2/\text{TMS}$  in the volume ratio 5/1/0.75.

#### DETERMINATION AND REFINEMENT OF THE STRUCTURE

The positions of the two Fe atoms were readily located using a three-dimensional Patterson function\*. Fifteen additional atoms were found from a difference Fourier synthesis\*, which was calculated after one cycle of least-squares refinement of the Fe atoms. The remaining non-hydrogen atoms were located in a succeeding least-squares and difference Fourier procedure. Several cycles of least-squares refinement of a scale factor plus all 24 non-hydrogen atoms with isotropic temperature factors (97 variables) resulted in agreement factors  $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.074$  and  $R_2 = (\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2)^{1/2} = 0.082$ . One cycle of anisotropic refinement of the 24 atoms (217 variables) then reduced  $R_1$  and  $R_2$  to 0.041 and 0.042, respectively. A difference Fourier synthesis now revealed the positions of the twelve hydrogen atoms. Several least-squares cycles including positional and thermal parameters for the hydrogen atoms (265 variables) resulted in final  $R$  values of  $R_1 = 0.028$  and  $R_2 = 0.036$ , using the 1576 reflections significantly above background. In the final cycle no parameter shifted by more than half of its standard deviation. The error in an observation of unit weight was 1.10. A final difference Fourier synthesis revealed no residual electron density above  $0.24 \text{ e } \text{\AA}^{-3}$ , where the peak height was  $0.50 \text{ e } \text{\AA}^{-3}$  for H atoms in a previous map. A list of structure amplitudes is available on request from F.A.C.

Atomic scattering factors for Fe, O, and C were those of Ibers<sup>12</sup>, while values for H were taken from Stewart, Davidson and Simpson<sup>13</sup>. Anomalous dispersion effects for iron were included in  $F_c$ <sup>14</sup>; the values of  $\Delta f'$  and  $\Delta f''$  were those of Cromer and Liberman<sup>15</sup>. The function minimized in the least-squares procedure was  $\Sigma w (|F_o| - |F_c|)^2$ , where  $w$  is  $4F_o^2/\sigma^2(F_o^2)$ . A check on agreement factors as a function of  $\lambda^{-1} \sin \theta$ ,  $F_o$ , and various classes of Miller indices revealed no unaccountable trends, thus suggesting that the weighting scheme is a reasonable one.

The final atomic parameters are given in Table 1 for the non-hydrogen atoms, and in Table 2 for the hydrogen atoms. Root-mean-square amplitudes of vibration are given in Table 3. The direction and shapes of the thermal ellipsoids are all reasonable.

\* The following computer programs written for the IBM 360 were used: DATARED, a data reduction program by Frenz; AGNOST, an absorption correction program by Cahen based on Coppens' DATAP and Tompa analytical subroutines of Cullen's program; JIMDAP, a version of Zalkin's FORDAP Fourier program modified by Ibers; NUCLS, a least-squares program by Ibers and Doedens which closely resembles Busing and Levy's ORFLS program; SADIAN, a program for calculating atomic distances and angles by Baur; RSCAN, a structure factor analysis program by Doedens; ORTEP, a plotting program by Johnson; ORFFE, a function and error program by Busing, Martin, and Levy and modified by Brown, Johnson, and Thiessen; and LIST, a data listing program by Snyder.

E I

## POSITIONAL AND ANISOTROPIC THERMAL PARAMETERS AND THEIR STANDARD DEVIATIONS FOR NON-HYDROGEN ATOMS\*

x	y	z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
-0.18794(7)	0.22296(5)	0.13330(6)	159.3(12)	68.6(6)	120.4(10)	44.5(6)	30.7(8)	19.0(6)
0.16127(7)	0.32241(9)	0.25994(6)	163.7(12)	49.1(5)	118.7(10)	18.7(6)	53.9(8)	11.8(5)
-0.2031(6)	0.3674(4)	0.1296(6)	255(11)	87(5)	181(9)	72(6)	70(8)	40(5)
-0.1750(6)	0.1855(4)	-0.0732(6)	218(10)	94(4)	146(9)	77(5)	24(7)	23(5)
-0.4126(6)	0.1590(4)	0.0770(5)	178(11)	102(4)	137(7)	61(5)	24(7)	15(4)
0.1716(6)	0.3011(3)	0.0521(5)	235(10)	64(4)	157(9)	30(5)	72(7)	20(4)
0.1677(6)	0.4731(4)	0.2616(5)	216(10)	65(4)	177(8)	19(5)	89(7)	17(4)
0.3858(6)	0.3624(3)	0.3316(5)	185(10)	63(4)	173(8)	12(5)	80(7)	12(4)
-0.2165(5)	0.4584(3)	0.1277(5)	434(11)	98(4)	337(9)	133(5)	131(8)	67(5)
-0.1787(5)	0.1563(3)	-0.2074(4)	392(10)	159(4)	136(6)	110(5)	61(6)	5(4)
-0.5566(5)	0.1206(3)	0.0395(5)	157(7)	174(5)	247(7)	58(4)	9(6)	11(4)
0.1951(5)	0.2879(3)	-0.0768(4)	404(10)	128(4)	161(6)	61(5)	147(7)	28(4)
0.1782(5)	0.5696(3)	0.2634(5)	370(9)	61(3)	320(9)	55(4)	142(7)	40(4)
0.5316(4)	0.3971(3)	0.3704(5)	160(7)	108(3)	302(8)	-1(4)	76(6)	13(4)
0.2035(5)	0.1950(4)	0.5585(5)	148(8)	78(4)	111(7)	14(4)	28(6)	21(4)
0.1727(6)	0.3073(4)	0.5203(5)	160(8)	59(4)	113(6)	-1(5)	48(6)	0(4)
0.0155(6)	0.3191(4)	0.4506(5)	200(10)	61(4)	117(7)	37(5)	75(7)	10(4)
-0.1455(5)	0.2300(4)	0.3921(5)	143(8)	91(4)	124(7)	46(5)	58(6)	29(4)
-0.1761(5)	0.1171(4)	0.3082(5)	134(8)	69(4)	136(7)	23(5)	24(6)	26(4)
-0.0756(5)	0.0912(3)	0.2060(5)	156(8)	46(3)	110(6)	20(4)	3(6)	8(4)
0.1105(5)	0.1409(3)	0.2442(5)	137(8)	48(3)	109(6)	26(4)	40(5)	8(3)
0.1890(5)	0.1089(4)	0.4064(5)	139(7)	57(3)	140(7)	18(4)	18(6)	26(4)
0.3812(6)	0.1285(5)	0.4591(6)	149(9)	109(5)	213(9)	61(6)	43(8)	53(6)
0.3908(6)	0.2003(5)	0.6219(6)	175(10)	94(5)	175(9)	18(5)	-17(7)	34(5)

norm of the thermal ellipsoid is  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ . Parameters x, y, and z are in fractional coordinates. Numbers in parentheses in this and other tables are the estimated standard deviations in the last significant digits.

TABLE 2

## POSITIONAL AND ISOTROPIC THERMAL PARAMETERS AND THEIR STANDARD DEVIATIONS FOR HYDROGEN ATOMS

Atom <sup>a</sup>	x	y	z	B
H(1)	0.139(5)	0.171(3)	0.623(5)	3.5(9)
H(2)	0.257(4)	0.371(3)	0.586(4)	2.6(7)
H(3)	0.011(4)	0.388(3)	0.473(4)	3.2(8)
H(4)	-0.227(5)	0.239(3)	0.437(5)	4.0(9)
H(5)	-0.278(5)	0.065(3)	0.302(5)	4.1(10)
H(6)	-0.123(5)	0.018(3)	0.137(5)	3.1(8)
H(7)	0.153(4)	0.114(3)	0.156(4)	2.3(7)
H(8)	0.125(4)	0.028(3)	0.409(4)	2.7(7)
H(9,1)	0.438(5)	0.166(3)	0.395(5)	3.2(9)
H(9,2)	0.412(5)	0.067(4)	0.458(5)	4.5(10)
H(10,1)	0.468(5)	0.276(4)	0.651(5)	4.3(9)
H(10,2)	0.414(6)	0.157(4)	0.718(6)	6.1(11)

<sup>a</sup> Hydrogens are numbered according to the carbon atoms to which they are attached.

TABLE 3

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

Atom	Min	Intermed	Max
Fe(1)	0.1930(9)	0.2048(9)	0.2304(9)
Fe(2)	0.1795(9)	0.1876(9)	0.2364(9)
C(1,1)	0.211(7)	0.242(6)	0.288(7)
C(1,2)	0.200(6)	0.229(6)	0.284(6)
C(1,3)	0.209(6)	0.224(6)	0.270(6)
C(2,1)	0.204(6)	0.219(6)	0.278(6)
C(2,2)	0.200(6)	0.221(6)	0.284(6)
C(2,3)	0.194(6)	0.216(6)	0.273(6)
O(1,1)	0.199(5)	0.322(5)	0.378(5)
O(1,2)	0.206(5)	0.303(4)	0.364(5)
O(1,3)	0.213(5)	0.298(4)	0.348(5)
O(2,1)	0.193(5)	0.292(4)	0.366(5)
O(2,2)	0.194(5)	0.295(4)	0.358(4)
O(2,3)	0.203(5)	0.291(4)	0.328(4)
C(1)	0.190(6)	0.205(6)	0.250(6)
C(2)	0.180(6)	0.186(6)	0.259(6)
C(3)	0.169(6)	0.205(6)	0.257(6)
C(4)	0.180(6)	0.212(6)	0.248(6)
C(5)	0.185(6)	0.203(6)	0.243(6)
C(6)	0.173(6)	0.186(6)	0.241(6)
C(7)	0.173(6)	0.189(6)	0.211(6)
C(8)	0.184(6)	0.202(6)	0.239(5)
C(9)	0.196(7)	0.245(7)	0.289(6)
C(10)	0.200(7)	0.238(7)	0.304(6)

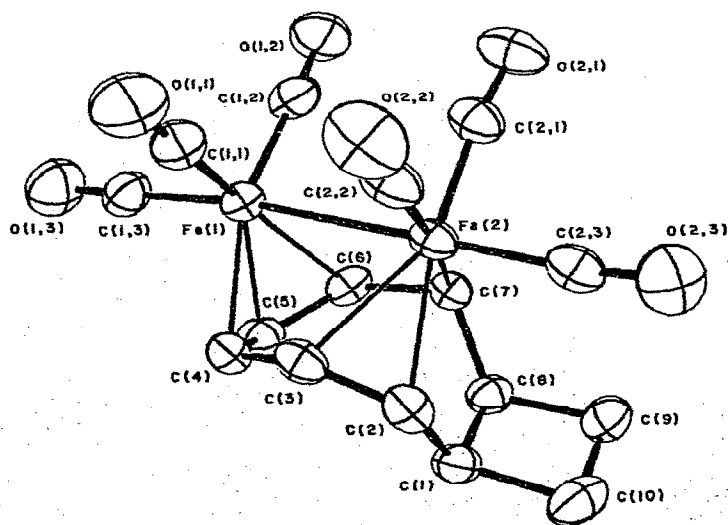


Fig. 1. The molecular structure of  $(C_{10}H_{12})Fe_2(CO)_6$  as found in the crystal. The 40% probability ellipsoids are shown.

## RESULTS

The molecular structure is represented in Fig. 1, which also shows the atom numbering scheme. The bond lengths and bond angles are recorded in Tables 4 and 5. The structure is further characterized by the planes and dihedral angles recorded in Table 6. A schematic drawing of the several planes defined by the non-carbonyl carbon atoms is presented as Fig. 2.

The way in which the proton magnetic resonance spectrum varies with temperature is shown in Fig. 3.

TABLE 4

## SELECTED BOND DISTANCES (Å)

<i>Fe-Fe distance</i>	2.786(2)		
<i>Fe-carbonyl distances</i>			
Fe(1)-C(1,1)	1.786(5)	Fe(2)-C(2,1)	1.769(4)
Fe(1)-C(1,2)	1.786(5)	Fe(2)-C(2,2)	1.803(4)
Fe(1)-C(1,3)	1.779(6)	Fe(2)-C(2,3)	1.775(6)
		av Fe-C	1.783(12)
<i>Carbonyl C-O distances</i>			
C(1,1)-O(1,1)	1.136(5)	C(2,1)-O(2,1)	1.146(5)
C(1,2)-O(1,2)	1.141(5)	C(2,2)-O(2,2)	1.146(5)
C(1,3)-O(1,3)	1.138(5)	C(2,3)-O(2,3)	1.148(5)
		av C-O	1.143(5)
<i>Fe-ring distances (bonding)</i>			
Fe(1)-C(4)	2.120(4)	Fe(2)-C(2)	2.199(4)
Fe(1)-C(5)	2.042(4)	Fe(2)-C(3)	2.214(4)
Fe(1)-C(6)	2.140(4)	Fe(2)-C(7)	2.099(4)
<i>Fe-ring distances (non-bonding)</i>			
Fe(1)-C(1)	4.440(5)	Fe(2)-C(1)	3.075(4)
Fe(1)-C(2)	3.797(5)	Fe(2)-C(4)	3.007(4)
Fe(1)-C(3)	2.795(4)	Fe(2)-C(5)	3.348(5)
Fe(1)-C(7)	2.960(4)	Fe(2)-C(6)	2.883(4)
Fe(1)-C(8)	4.153(4)	Fe(2)-C(8)	3.005(4)
Fe(1)-C(9)	5.476(5)	Fe(2)-C(9)	3.683(5)
Fe(1)-C(10)	5.776(5)	Fe(2)-C(10)	3.892(5)
<i>C-C ring distances</i>			
C(1)-C(2)	1.501(6)	C(5)-C(6)	1.399(6)
C(1)-C(8)	1.531(6)	C(6)-C(7)	1.472(6)
C(1)-C(10)	1.541(6)	C(7)-C(8)	1.521(5)
C(2)-C(3)	1.385(6)	C(8)-C(9)	1.534(6)
C(3)-C(4)	1.436(6)	C(9)-C(10)	1.425(7)
C(4)-C(5)	1.403(6)		
<i>C-H distances</i>			
C(1)-H(1)	0.86(4)	C(7)-H(7)	0.95(3)
C(2)-H(2)	0.97(3)	C(8)-H(9)	0.98(3)
C(3)-H(3)	0.88(4)	C(9)-H(9,1)	0.88(4)
C(4)-H(4)	0.89(4)	C(9)-H(9,2)	0.89(4)
C(5)-H(5)	0.91(4)	C(10)-H(10,1)	1.00(4)
C(6)-H(6)	0.93(4)	C(10)-H(10,2)	0.98(5)
		av C-H	0.93(5)

TABLE 5: SELECTED BOND ANGLES (Deg.)

<i>Ring atoms</i>			
C(2)-C(1)-C(8)	114.2(3)	C(5)-C(6)-C(7)	124.9(4)
C(2)-C(1)-C(10)	115.9(4)	C(6)-C(7)-C(8)	109.4(3)
C(8)-C(1)-C(10)	89.8(3)	C(1)-C(8)-C(7)	114.1(3)
C(1)-C(2)-C(3)	124.9(4)	C(1)-C(8)-C(9)	89.5(3)
C(2)-C(3)-C(4)	128.7(4)	C(7)-C(8)-C(9)	120.3(4)
C(3)-C(4)-C(5)	127.0(4)	C(8)-C(9)-C(10)	90.2(3)
C(4)-C(5)-C(6)	122.6(4)	C(1)-C(10)-C(9)	89.5(3)
<i>Ring atoms and H atoms</i>			
H(1)-C(1)-C(2)	104(2)	H(7)-C(7)-C(8)	112(2)
H(1)-C(1)-C(8)	117(2)	H(8)-C(8)-C(1)	114(2)
H(1)-C(1)-C(10)	115(3)	H(8)-C(8)-C(7)	107(2)
H(2)-C(2)-C(1)	115(2)	H(8)-C(8)-C(9)	111(2)
H(2)-C(2)-C(3)	116(2)	H(9,1)-C(9)-C(8)	114(3)
H(3)-C(3)-C(2)	113(2)	H(9,1)-C(9)-C(10)	115(2)
H(3)-C(3)-C(4)	116(2)	H(9,1)-C(9)-H(9,2)	103(4)
H(4)-C(4)-C(3)	113(2)	H(9,2)-C(9)-C(8)	115(3)
H(4)-C(4)-C(5)	116(2)	H(9,2)-C(9)-C(10)	120(3)
H(5)-C(5)-C(4)	116(2)	H(10,1)-C(10)-C(1)	112(2)
H(5)-C(5)-C(6)	120(2)	H(10,1)-C(10)-C(9)	118(2)
H(6)-C(6)-C(5)	114(2)	H(10,1)-C(10)-H(10,2)	107(3)
H(6)-C(6)-C(7)	117(2)	H(10,2)-C(10)-C(1)	115(3)
H(7)-C(7)-C(6)	110(2)	H(10,2)-C(10)-C(9)	115(3)
<i>Ring atoms and Fe atoms</i>			
Fe(1)-C(4)-C(3)	101.9(3)	Fe(2)-C(2)-C(1)	111.1(3)
Fe(1)-C(4)-C(5)	67.3(2)	Fe(2)-C(2)-C(3)	72.3(2)
Fe(1)-C(5)-C(4)	73.2(2)	Fe(2)-C(3)-C(2)	71.1(2)
Fe(1)-C(5)-C(6)	74.3(2)	Fe(2)-C(3)-C(4)	109.1(3)
Fe(1)-C(6)-C(5)	66.7(2)	Fe(2)-C(7)-C(6)	106.3(2)
Fe(1)-C(6)-C(7)	108.7(2)	Fe(2)-C(7)-C(8)	111.2(3)
<i>Fe coordination sphere</i>			
C(1,1)-Fe(1)-C(1,2)	100.4(2)	C(2,1)-Fe(2)-C(2,2)	93.7(2)
C(1,1)-Fe(1)-C(1,3)	92.8(2)	C(2,1)-Fe(2)-C(2,3)	92.0(2)
C(1,1)-Fe(1)-C(4)	96.6(2)	C(2,1)-Fe(2)-C(2)	164.5(2)
C(1,1)-Fe(1)-C(5)	135.2(2)	C(2,1)-Fe(2)-C(3)	151.4(2)
C(1,1)-Fe(1)-C(6)	156.7(2)	C(2,1)-Fe(2)-C(7)	86.0(2)
C(1,1)-Fe(1)-Fe(2)	87.8(2)	C(2,1)-Fe(2)-Fe(1)	84.8(2)
C(1,2)-Fe(1)-C(1,3)	91.4(2)	C(2,2)-Fe(2)-C(2,3)	91.5(2)
C(1,2)-Fe(1)-C(4)	159.6(2)	C(2,2)-Fe(2)-C(2)	100.8(2)
C(1,2)-Fe(1)-C(5)	124.4(2)	C(2,2)-Fe(2)-C(3)	87.0(2)
C(1,2)-Fe(1)-C(6)	89.7(2)	C(2,2)-Fe(2)-C(7)	170.6(2)
C(1,2)-Fe(1)-Fe(2)	95.2(2)	C(2,2)-Fe(2)-Fe(1)	97.5(1)
C(1,3)-Fe(1)-C(4)	99.0(2)	C(2,3)-Fe(2)-C(2)	82.3(2)
C(1,3)-Fe(1)-C(5)	88.4(2)	C(2,3)-Fe(2)-C(3)	116.5(2)
C(1,3)-Fe(1)-C(6)	108.0(2)	C(2,3)-Fe(2)-C(7)	97.9(2)
C(1,3)-Fe(1)-Fe(2)	173.2(1)	C(2,3)-Fe(2)-Fe(1)	170.6(1)
C(4)-Fe(1)-C(5)	39.4(2)	C(2)-Fe(2)-C(3)	36.6(1)
C(4)-Fe(1)-C(6)	70.5(2)	C(2)-Fe(2)-C(7)	80.6(2)
C(4)-Fe(1)-Fe(2)	74.2(1)	C(2)-Fe(2)-Fe(1)	98.5(1)
C(5)-Fe(1)-C(6)	39.0(2)	C(3)-Fe(2)-C(7)	88.8(2)
C(5)-Fe(1)-Fe(2)	86.4(1)	C(3)-Fe(2)-Fe(1)	66.9(1)
C(6)-Fe(1)-Fe(2)	70.2(1)	C(7)-Fe(2)-Fe(1)	73.1(1)
<i>Fe atoms and carbonyl atoms</i>			
Fe(1)-C(1,1)-O(1,1)	178.4(5)	Fe(2)-C(2,1)-O(2,1)	173.1(4)
Fe(1)-C(1,2)-O(1,2)	174.9(5)	Fe(2)-C(2,2)-O(2,2)	177.4(4)
Fe(1)-C(1,3)-O(1,3)	178.2(4)	Fe(2)-C(2,3)-O(2,3)	173.6(4)



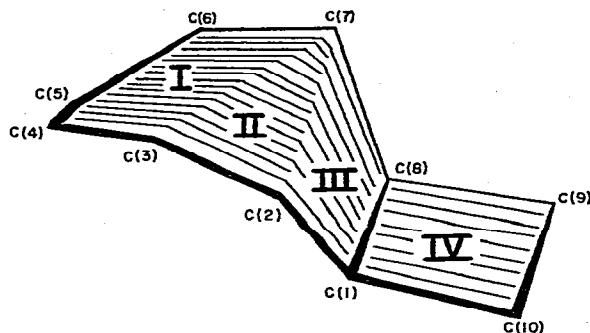


Fig. 2. A perspective view of the four planes defined by the atoms of the  $(C_{10}H_{12})$  fused ring system in  $(C_{10}H_{12})Fe_2(CO)_6$ .

## DISCUSSION

It is immediately evident from Fig. 1 that the molecular structure found in the crystal is qualitatively analogous to the structures of  $(C_8H_8)Ru_2(CO)_6$ <sup>6</sup> and  $(C_8H_{10})Fe_2(CO)_6$ <sup>7</sup>.

A comparison of bond distances and bond angles with the corresponding dimensions for the  $(C_8H_8)Ru_2(CO)_6$  and  $(C_8H_{10})Fe_2(CO)_6$  structures is given in Fig. 4. The similarity of the structures is seen to be semiquantitative. In each structure one metal atom is symmetrically bonded to the ring carbon atoms (C(2), C(3)) comprising the formal double bond; metal carbon distances of ca. 2.2 Å for Fe and 2.3 Å for Ru are found. This same metal atom is also bonded at ca. 2.1 Å to a single carbon atom (C(7)) across the ring from the formal double bond. A second metal atom is bonded to the allyl portion (C(4), C(5), C(6)) of the eight-membered ring. In each structure the distance from the central allyl carbon atom to the metal atom is shorter than from the two outer allyl carbon atoms to the metal atom. Also the allyl-metal bonding is not precisely symmetrical, the C(6)-metal bonds being consistently longer (0.02 to 0.07 Å) than C(4)-metal bonds.

The C-C bond distances in the eight-membered ring show a satisfactory relationship with the expected bond orders. The shortest bond (1.30 Å) is found for the double bond in the  $C_8H_8$  ring of the Ru structure. Next, the formal double bond attached to one metal atom has a C-C distance of  $1.39 \pm 0.01$  Å in each structure. The two C-C distances in the allyl portion of each molecule are in the range 1.39 to 1.42 Å, with a mean of 1.405 Å. The remaining C-C single bonds have distance ranging from 1.44 to 1.55 Å with an average length of 1.50 Å. The C-C bond that is mutually shared by the four- and eight-membered rings in the present work has a length of 1.531(6) Å; this is not significantly different from the 1.52(2) Å bond found in  $(C_8H_{10})Fe_2(CO)_6$  where the four-membered ring is replaced by two hydrogen atoms.

The geometry of the  $C_{10}H_{12}$  group in the present structure is depicted schematically in Fig. 2. Table 6 gives equations for planes I, II, III, and IV, as labeled in the figure. Plane I includes the allyl carbon atoms; the formal double bond is included in plane II. Planes I and II meet at an angle of  $41^\circ$ ; the angle between planes I and III is  $84^\circ$ , while the angle between II and III is  $45^\circ$ . The  $C_8$  ring geometry parallels that

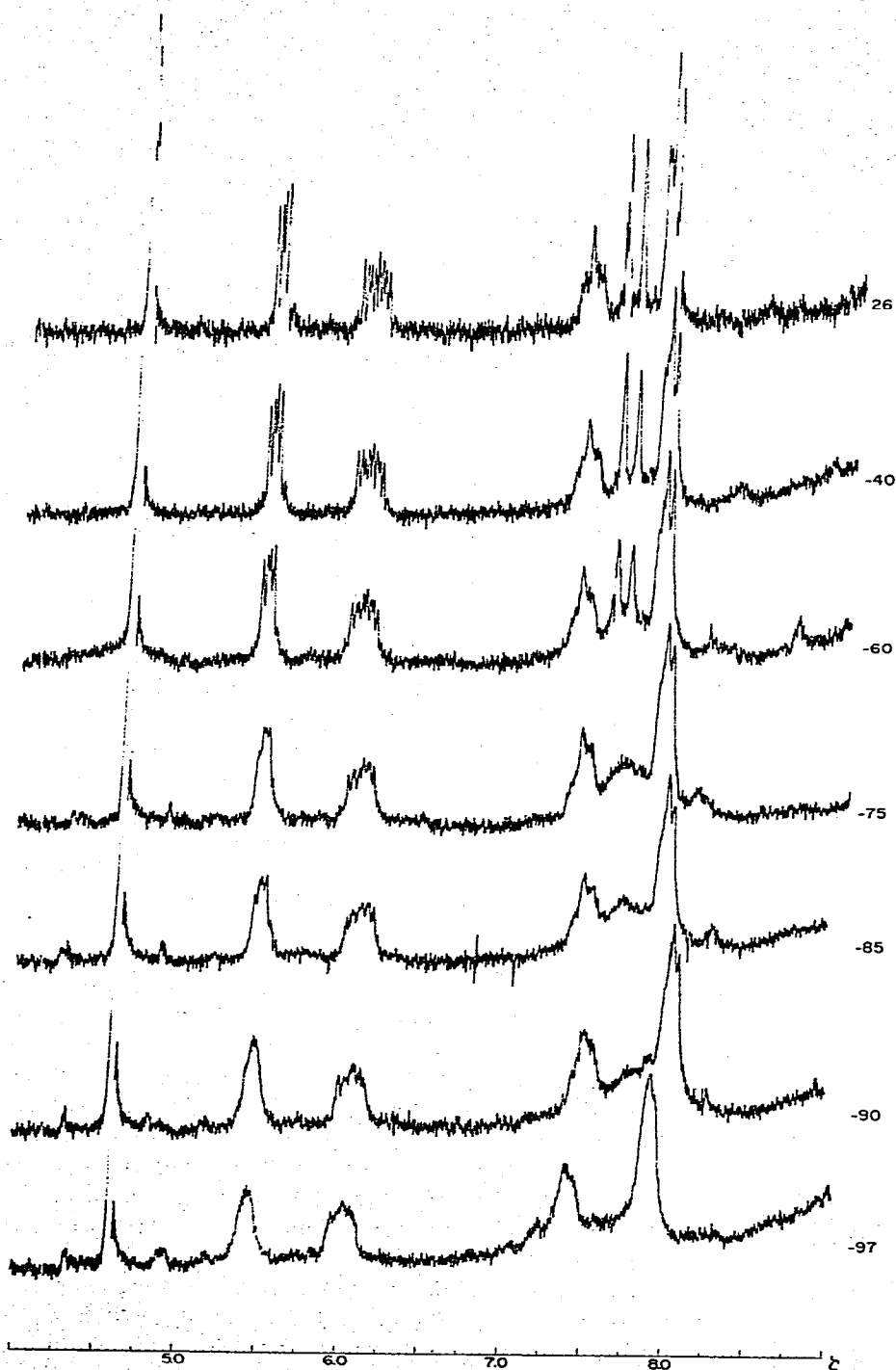


Fig. 3. The PMR spectra (100 MHz) of  $(C_{10}H_{12})Fe_2(CO)_6$  at various temperatures (from  $+26^\circ$  to  $-129^\circ$ ) in  $CD_2Cl_2/CF_2Cl_2/TMS$ .

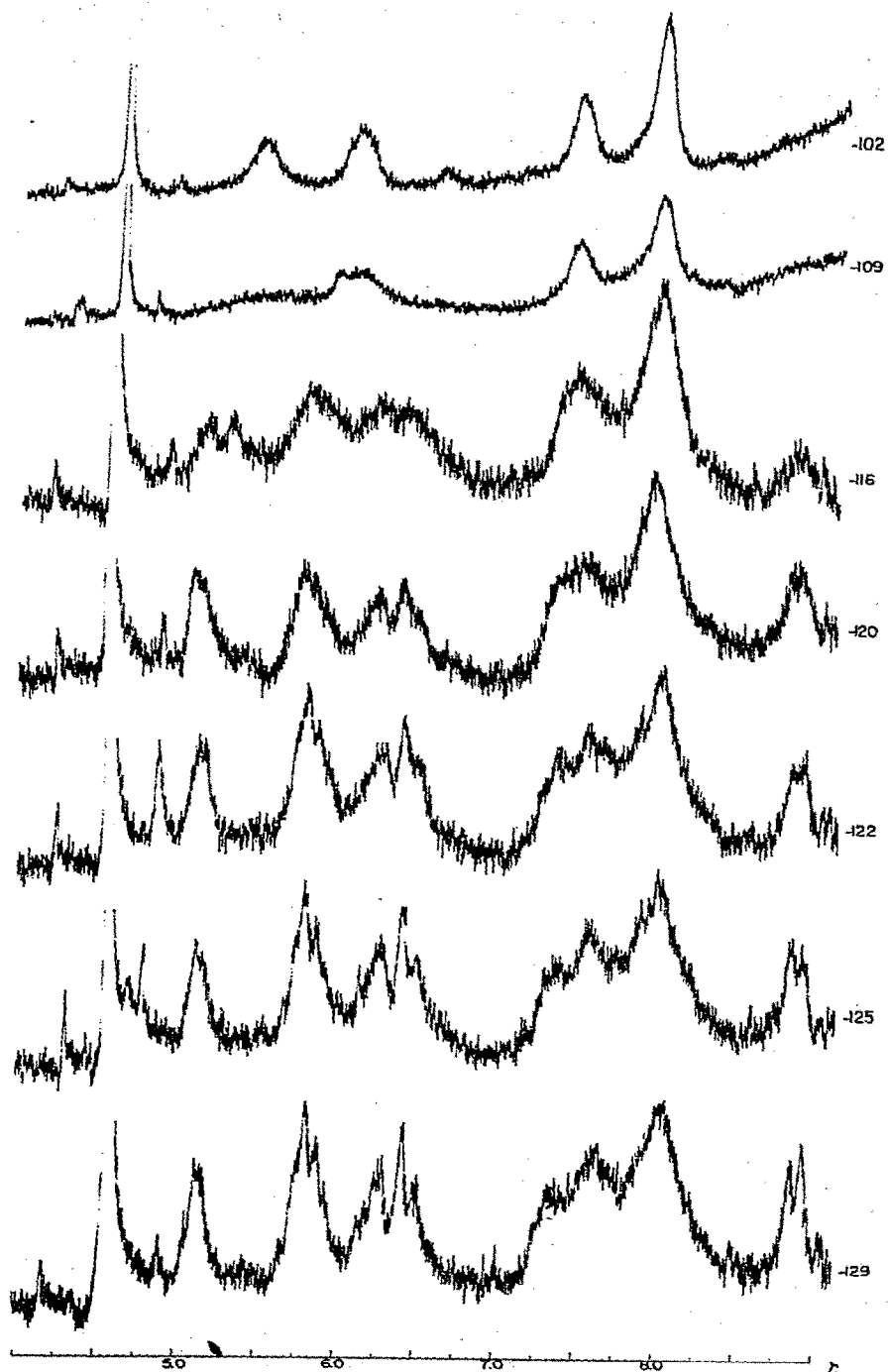


TABLE 6

LEAST-SQUARES PLANES IN THE C<sub>8</sub> RING IN (C<sub>10</sub>H<sub>12</sub>)Fe<sub>2</sub>(CO)<sub>6</sub>, (C<sub>8</sub>H<sub>10</sub>)Fe<sub>2</sub>(CO)<sub>6</sub>, AND (C<sub>8</sub>H<sub>8</sub>)Ru<sub>2</sub>(CO)<sub>6</sub>

Equations of Planes <sup>a</sup>				
	A	B	C	D
<b>(C<sub>10</sub>H<sub>12</sub>)Fe<sub>2</sub>(CO)<sub>6</sub></b>				
Plane I <sup>b</sup>	1.868	- 7.361	6.786	0.792
Plane II	-3.074	- 8.087	5.565	0.1209
Plane III	-7.593	- 2.027	2.685	0.5032
Plane IV	-0.893	- 9.922	5.043	-0.7501
<b>(C<sub>8</sub>H<sub>10</sub>)Fe<sub>2</sub>(CO)<sub>6</sub></b>				
Plane I <sup>b</sup>	7.502	3.812	9.085	-6.469
Plane II	0.417	0.481	14.236	-6.030
Plane III	-4.216	- 4.262	11.231	-2.316
<b>(C<sub>8</sub>H<sub>8</sub>)Ru<sub>2</sub>(CO)<sub>6</sub></b>				
Plane I <sup>b</sup>	-2.273	-13.230	5.801	-0.085
Plane II	2.876	- 8.227	7.642	-2.641
Plane III	8.055	- 1.907	3.779	-3.001
<b>Deviations from least-squares planes (Å)</b>				
Atom	(C <sub>10</sub> H <sub>12</sub> )Fe <sub>2</sub> (CO) <sub>6</sub>	(C <sub>8</sub> H <sub>10</sub> )Fe <sub>2</sub> (CO) <sub>6</sub>	(C <sub>8</sub> H <sub>8</sub> )Ru <sub>2</sub> (CO) <sub>6</sub>	
<b>Plane I</b>				
C(3)	-0.011	0.023	-0.014	
C(4)	-0.053	-0.095	-0.050	
C(5)	0.151	0.146	0.145	
C(6)	-0.163	-0.116	-0.153	
C(7)	0.077	0.042	0.072	
<b>Plane III</b>				
C(1)	0.062	0.194	0.014	
C(2)	-0.034	-0.104	-0.007	
C(7)	0.034	0.105	0.007	
C(8)	-0.062	-0.196	-0.014	
<b>Plane IV</b>				
C(1)	-0.050	—	—	
C(8)	0.050	—	—	
C(9)	-0.050	—	—	
C(10)	0.050	—	—	
<b>Angles between least-squares planes (°)</b>				
	(C <sub>10</sub> H <sub>12</sub> )Fe <sub>2</sub> (CO) <sub>6</sub>	(C <sub>8</sub> H <sub>10</sub> )Fe <sub>2</sub> (CO) <sub>6</sub>	(C <sub>8</sub> H <sub>8</sub> )Ru <sub>2</sub> (CO) <sub>6</sub>	
Plane I-Plane II	41.2	44.7	39.3	
Plane I-Plane III	84.3	86.6	83.9	
Plane I-Plane IV	32.8	—	—	
Plane II-Plane III	45.2	43.6	46.9	
Plane II-Plane IV	—	—	—	
Plane III-Plane IV	59.6	—	—	

<sup>a</sup> Equations have the form Ax + By + Cz + D = 0 where x, y, z are fractional triclinic (or monoclinic) coordinates.<sup>b</sup> Planes I, II, III, IV are identified in Fig. 2.

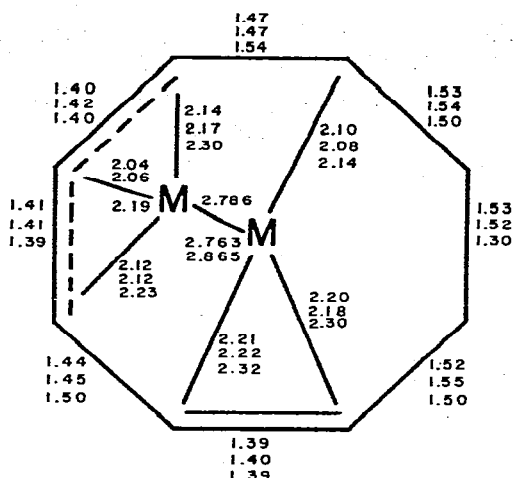


Fig. 4. Schematic drawing of the  $C_8$  ring bonded to an  $M-M$  moiety for  $(C_{10}H_{12})Fe_2(CO)_6$ ,  $(C_8H_{10})Fe_2(CO)_6$ , and  $(C_8H_8)Ru_2(CO)_6$ . Bond distances for the compounds are listed in the above order from top to bottom. The standard deviations on the bond lengths are ca.  $0.02\text{\AA}$ .

found previously for  $(C_8H_{10})Fe_2(CO)_6$  and  $(C_8H_8)Ru_2(CO)_6$ . Here the respective angles are  $45^\circ$ ,  $87^\circ$ , and  $44^\circ$  for the Fe complex and  $39^\circ$ ,  $84^\circ$ , and  $47^\circ$  for the Ru complex. Additional information is given in Table 6.

In the present structure the four-membered ring (plane IV) joins the  $C_8$  ring in an *exo* fashion. The angle between planes III and IV is  $60^\circ$ . As indicated by the smallness of the deviations from least-squares plane IV in Table 6, the four-membered ring is essentially planar. This is in contrast to the normal preference of the cyclobutane ring for a folded conformation<sup>16</sup>. The cyclobutane ring conformation in this and related compounds will be discussed more fully in a forthcoming paper<sup>17</sup>.

In view of the close similarity of the structure of  $(C_{10}H_{12})Fe_2(CO)_6$  to those of  $(C_8H_8)Ru_2(CO)_6$  and  $(C_8H_{10})Fe_2(CO)_6$ , both of which have been shown to be fluxional<sup>4,5</sup>,  $(C_{10}H_{12})Fe_2(CO)_6$  would certainly be expected to exhibit comparable fluxional character. Our previous examination of the PMR spectrum as a function of temperature<sup>11</sup> extended only to about  $-70^\circ$ . Down to this temperature no marked changes in the appearance of the spectrum were observed. It was therefore tentatively suggested that the molecule might have a crosswise structure, similar to that of  $(C_7H_8)Fe_2(CO)_6$ <sup>8</sup>, with a permanent plane of symmetry. When the actual structure of the molecule in the crystal became known, it was apparent that examination of the PMR spectrum at still lower temperatures was required. This more complete study gave the results shown in Fig. 3.

It is clear that the previous study<sup>11</sup> of the PMR spectrum had, by sheer bad luck, stopped just short of the temperature range ( $< -70^\circ$ ) in which pronounced collapse of certain spectral features takes place. The more extensive study now reported shows qualitatively that  $(C_{10}H_{12})Fe_2(CO)_6$  is fluxional. It also suggests, by comparison with the published spectra<sup>5</sup> of  $(C_8H_{10})Fe_2(CO)_6$ , that a comparable rearrangement process is involved. The most obvious difference between the fluxionality of  $(C_8H_{10})Fe_2(CO)_6$  and  $(C_{10}H_{12})Fe_2(CO)_6$  is in the lower activation energy for the latter, which leads to a difference of roughly  $40^\circ$  in the temperatures at which comparable degrees of spectrum collapse are observed in the two cases.

No more detailed analysis of the PMR spectra will be attempted here since further studies including both  $^{13}\text{C}$  spectra and the PMR spectra of deuterated species are underway. The results of these investigations may permit us to determine in detail the rearrangement pathway and evaluate kinetic activation parameters.

## REFERENCES

- 1 R. B. King, *Inorg. Chem.*, 2 (1963) 807.
- 2 G. F. Emerson, J. E. Mahler, R. Pettit and R. Collins, *J. Amer. Chem. Soc.*, 86 (1964) 3590.
- 3 C. E. Keller, G. F. Emerson and R. Pettit, *J. Amer. Chem. Soc.*, 87 (1965) 1388.
- 4 F. A. Cotton, A. Davison, T. J. Marks and A. Musco, *J. Amer. Chem. Soc.*, 91 (1969) 6598.
- 5 F. A. Cotton and T. J. Marks, *J. Organometal. Chem.*, 19 (1969) 237.
- 6 F. A. Cotton and W. T. Edwards, *J. Amer. Chem. Soc.*, 90 (1968) 5412.
- 7 F. A. Cotton and W. T. Edwards, *J. Amer. Chem. Soc.*, 91 (1969) 843.
- 8 F. A. Cotton, B. G. DeBoer and T. J. Marks, *J. Amer. Chem. Soc.*, 93 (1971) 5069.
- 9 H. Maltz and G. Deganello, *J. Organometal. Chem.*, 27 (1971) 383.
- 10 J. A. Elix and M. V. Sargent, *J. Amer. Chem. Soc.*, 91 (1969) 4734.
- 11 F. A. Cotton and G. Deganello, *J. Organometal. Chem.*, 38 (1972) 147; *J. Amer. Chem. Soc.*, 94 (1972) 2142.
- 12 J. A. Ibers, *International Tables for X-ray Crystallography*, Vol. 3, The Kynoch Press, Birmingham, 1962, Table 3.3.1A.
- 13 R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys.*, 42 (1965) 3175.
- 14 J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, 17 (1964) 781.
- 15 D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 53 (1970) 1891.
- 16 H. Booth in J. W. Emsley, J. Feeney and L. H. Sutcliffe (Eds.), *Progress in N.M.R. Spectroscopy*, Vol. 4, Pergamon Press, 1969; J. S. Wright and L. Salem, *J. Amer. Chem. Soc.*, 94 (1972) 322.
- 17 F. A. Cotton, B. A. Frenz and J. Troup, *J. Amer. Chem. Soc.*, in press.
- 18 D. J. Ciappenelli, F. A. Cotton and L. Kruczynski, *J. Organometal. Chem.*, 42 (1972) 159.