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## The Molecular Structure of $C_2F_4Fe(CO)_4$ by Gas-Phase Electron Diffraction

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The molecular structure of tetrafluoroethyleneiron tetracarbonyl has been studied by gas-phase electron diffraction. Data reduced by standard techniques are consistent with a distorted octahedral complex of iron with  $C_{2v}$  symmetry; the carbon atoms of the non-planar  $C_2F_4$  unit occupy two adjacent equatorial sites.  $Fe-C(C_2F_4) = 1.989 \pm 0.010$ ,  $Fe-C(O)_{eq.} = 1.846 \pm 0.010$ ,  $Fe-C(O)_{ax.} = 1.823 \pm 0.010$ ,  $C-C = 1.530 \pm 0.015$ ,  $C-F = 1.336 \pm 0.005$ ,  $C-O = 1.138 \pm 0.003$  Å. The F-C-F angle is  $111.3 \pm 1.1^\circ$ , and the supplement to the angle C-C-(midpoint of vicinal F atoms) is  $41.6 \pm 1.1^\circ$ . The angle between equatorial carbonyl groups is  $104.2 \pm 1.4^\circ$  and the axial carbonyl groups are essentially linear. The results suggest that the  $C_2F_4$  unit resembles a fragment of perfluorocyclopropane rather than perfluoroethylene, and that the complexing with iron is  $\sigma$ , rather than  $\pi$ , in character.

### Introduction

Structurally, olefin complexes of transition metals are of interest because of their unusual bonding, which appears to be neither entirely  $\pi$  nor entirely  $\sigma$  in character (see e.g. Cotton & Wilkinson, 1966). The direct determination of molecular structures by the method of gas-phase electron diffraction has helped to establish the nature of the bonding. Typical of  $\pi$ -complexes is ferrocene, where the ten equal, rather long 2.06 Å Fe-C distances (Bohn & Haaland, 1966; Haaland & Nilsson, 1968) involve only 18 available electrons, insufficient for ten normal  $\sigma$ -bonds. At the other extreme,  $\sigma$ -complexes are typified by  $CH_3Mn(CO)_5$  (Seip & Seip, 1970), where the Mn-CH<sub>3</sub> bond may be considered as a normal two-electron  $\sigma$ -bond. The intermediate character of the bonding in olefin complexes is supported by the electron-diffraction study (Davis & Speed, 1970) of ethylene iron tetracarbonyl,  $C_2H_4Fe(CO)_4$ , which shows that the Fe-C ('olefin') distances are equivalent and again rather long (2.12 Å), as in ferrocene. However the carbon-carbon bond length of  $1.46 \pm 0.03$  Å is considerably greater than that found in ethylene itself,

$r_g = 1.337 \pm 0.002$  Å (Bartell, Roth, Hollowell, Kuchitsu & Young Jr, 1965; Kuchitsu, 1966); in fact it is nearer that in cyclopropane,  $r_g = 1.511 \pm 0.002$  Å (Bastiansen, Fritsch & Hedberg, 1964). Similar lengthenings of such carbon-carbon bonds have been observed in X-ray crystallographic studies, particularly of tetracyanoethylene (TCNE) complexes; Stalick & Ibers (1970) point out that the lengthening is accompanied by a bending back of the  $CX_2$  planes of the olefin,  $C_2X_4$ , away from the metal atom; they also suggest that the lengthening and the bending back are quantitatively correlated. In TCNE complexes the deviation of the  $CX_2$  plane from the original olefin plane is typically  $30^\circ$ ; it is typically  $40^\circ$  for  $CCl_2$  groups in chloro-olefin platinum complexes (McAdam, Francis & Ibers, 1971). It seems possible, from the discussion of Stalick & Ibers, that the extent of the distortion from olefinic geometry may be used as a measure of the degree of  $\sigma$ -complexing with the metal, and if the sparse data they report for  $C_2H_4$  complexes are also considered, the results suggest that the distortion, and thus the degree of  $\sigma$ -complexing, may be greatest for electronegative substituents, X. The study of  $C_2F_4Fe(CO)_4$ , described here, extends these in-

vestigations to a gas-phase olefin complex; because fluorine scatters electrons much more strongly than hydrogen, this study should give more information about any distortion from olefin geometry than is available from the study of  $C_2H_4Fe(CO)_4$ . Furthermore, the presence of electronegative fluorine offers the possibility of a large distortion and a considerable degree of  $\sigma$ -complexing, if the trends discussed above are followed.

### Procedure

A sample of  $(C_2F_4)Fe(CO)_4$  was prepared by the method of Fields, Germain, Haszeldine & Wiggins (1970). Both this sample and a sample provided by R. Fields were used for the electron-diffraction experiment. Both samples were redistilled ( $25^\circ C$ , 4 mmHg) prior to use.

The diffraction experiment was performed in the Balzers KDG2 instrument at UMIST, with experimental conditions as summarized in Table 1. Optical density data were collected on a Joyce-Loebl automated microdensitometer, and processed by the standard Manchester procedure (Beagley, Monaghan & Hewitt, 1971). Table 1 also gives the tally of data collected, and the weights assigned for full matrix least-squares refinement of the structural parameters. The molecular model (Fig. 1) was constrained to  $C_{2v}$  symmetry, with the ethylenic carbon atoms, two of the carbonyl groups, and the iron atom lying in an equatorial plane. The remaining two carbonyl groups were assumed to occupy axial positions completing irregular octahedral coordination around iron, but the angle  $C_{ax}FeC_{ax}$  was allowed to depart from  $180^\circ$ . All  $C\equiv O$  distances were assumed equal, with all  $FeCO$  angles =  $180^\circ$ . However,  $Fe-C(O)_{ax}$  and  $Fe-C(O)_{eq.}$  were allowed to have unequal lengths. The fluorine atoms were assumed equidistant from the iron atom, but the

six atoms of the  $C_2F_4$  group were not constrained to one plane. Ten independent variables then serve to fix the geometry (see below).

### Results

The final radial distribution curve (Fig. 2) is readily interpreted in terms of the above molecular model. All the peaks are multiple. That at  $1-1.5 \text{ \AA}$  contains C-O, C-F and C-C. That near  $2 \text{ \AA}$  contains the three types of Fe-C distance and also vicinal  $F \cdots F$  at  $\sim 2.2 \text{ \AA}$ . The small peak near  $2.5 \text{ \AA}$  is an important one, containing predominantly  $F \cdots F(cis)$  and  $C(eq.) \cdots C(ax.)$ . Assigning  $F \cdots F(cis)$  to this peak implies a non-planar  $C_2F_4$  group. Assigning  $F \cdots F(cis)$  elsewhere led to an unsatisfactory fit in dependent regions of the radial distribution curve, and poor agreement between observed and calculated intensities. The major peak near  $3 \text{ \AA}$  contains the second neighbour distances to iron,  $Fe \cdots F$ ,  $Fe \cdots O(ax.)$  and  $Fe \cdots O(eq.)$ , as well as lesser contributors. The remaining four resolved peaks contain the multitude of longer distances between carbon, oxygen, and fluorine atoms. There are thus only eight resolved peaks, although ten independent geometrical parameters must be determined for the model

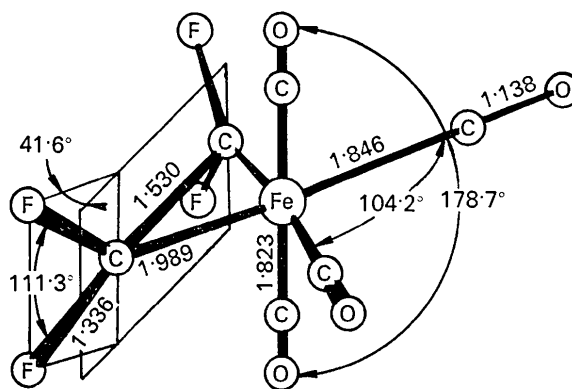


Fig. 1. The molecular structure of  $C_2F_4Fe(CO)_4$ .

Table 1. *Experimental conditions and weighting scheme*

Plates	Ilford N60		
Wavelength	$0.05657 \pm 0.00003 \text{ \AA}$		
Sample temp.	$30^\circ C$		
Nozzle temp.	$33^\circ C$		
Camera distance (cm)	100	50	25
Number of plates used	2	2	1
Total number of diameters scanned	8	7	16
$s$ -minimum ( $\text{\AA}^{-1}$ )	1.000	2.50	6.50
$s$ -maximum ( $\text{\AA}^{-1}$ )	8.225	14.00	25.00
$s$ -interval ( $\text{\AA}^{-1}$ )	0.025	0.05	0.10
Weighting parameters:			
$L_1$ ( $\text{\AA}^{-1}$ ) <sup>2</sup>	3.0	3.0	11.5
$L_2$ ( $\text{\AA}^{-1}$ )	7.5	13.0	18.0
$P_1$ ( $\text{\AA}$ )	1.0	0.5	0.1
$P_2$ ( $\text{\AA}$ )	1.0	0.5	0.1

Weighting takes the form:

$$s < L_1: w = \exp[-P_1(L_1 - s)]$$

$$L_1 \leq s \leq L_2: w = 1$$

$$s > L_2: w = \exp[-P_2(s - L_2)]$$

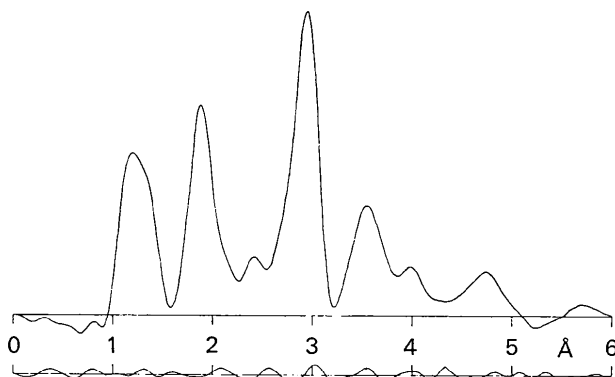


Fig. 2. Experimental radial distribution curve and difference curve (refinement I; damping constant,  $0.003 \text{ \AA}^2$ ).

Table 2. Independent parameters and e.s.d.'s

Distances in Å; angles in degrees; e.s.d. given below parameter values.

	Refinement I		Refinement II		Refinement III	
	Value	Amplitude	Value	Amplitude	Value	Amplitude
Fe-C(C <sub>2</sub> F <sub>4</sub> )	1.989	0.044	1.995	0.050	1.977	0.049
Fe-C(O) (mean)	0.010	0.011	0.015	0.015	0.007	0.011
	1.835		1.836		1.833	
	0.006		0.009		0.006	
Fe-C(O) (eq.-ax.)	0.023		0.017		0.023	
	0.016		0.017		0.016	
C-C	1.530	0.050*	1.542	0.050*	1.516	0.0469*
	0.016		0.016		0.013	
C-F	1.336	0.047	1.338	0.045	1.336	0.044
	0.005	0.009	0.005	0.008	0.004	0.009
O(ax.)...O(eq.)	4.189	0.196	4.178	0.232	4.141	0.2451*
	0.042	0.052	0.041	0.045	0.034	
∠F-C-F	111.3		111.7		109.9	
	1.2		1.3		0.5	
∠F out of plane†	41.6		43.2		43.3	
	1.1		1.2		0.6	
∠C <sub>eq</sub> FeC <sub>eq</sub>	104.2		106.6		106.6	
	1.4		1.4		0.7	
C-O	1.138	0.024*	1.138	0.024*	1.136	0.024*
	0.003		0.003		0.003	

\* Assumed

† Defined as the supplement to the angle (vic. F midpoint)-C-C

Table 3. Dependent parameters and e.s.d.'s

Distances in Å; angles in degrees.

	Refinement I			Refinement II			Refinement III		
	Value	Amplitude	and its e.s.d.	Value	Amplitude	and its e.s.d.	Value	Amplitude	and its e.s.d.
Fe...F	2.905	0.077	0.010	2.898	0.086	0.011	2.891	0.103	0.013
Fe...O(eq.)	2.984	0.055*		2.978	0.055*		2.974	0.0503*	
Fe...O(ax.)	2.961	0.054*		2.962	0.054*		2.954	0.0525*	
C(C <sub>2</sub> F <sub>4</sub> )...F	2.419	0.027	0.038	2.420	0.018	0.056	2.403	0.0867*	
C(C <sub>2</sub> F <sub>4</sub> )...C(eq.) (syn)	3.050	0.179*		3.027	0.179*		3.017	0.1053*	
C(C <sub>2</sub> F <sub>4</sub> )...C(eq.) (anti)	3.709	0.179*		3.705	0.179*		3.685	0.1053*	
C(C <sub>2</sub> F <sub>4</sub> )...O(eq.) (syn)	3.999	0.153*		3.970	0.153*		3.961	0.1284*	
C(C <sub>2</sub> F <sub>4</sub> )...O(eq.) (anti)	4.816	0.160	0.058	4.810	0.151	0.062	4.788	0.1284*	
C(C <sub>2</sub> F <sub>4</sub> )...C(ax.)	2.712	0.103*		2.719	0.103*		2.731	0.1490*	
C(C <sub>2</sub> F <sub>4</sub> )...O(ax.)	3.583	0.171*		3.591	0.171*		3.610	0.1795*	
F...F(vic.)	2.205	0.056*		2.214	0.056*		2.188	0.0585*	
F...F(cis)	2.658	0.053	0.016	2.637	0.050	0.017	2.632	0.1306*	
F...F(trans)	3.454	0.060*		3.443	0.060*		3.423	0.0873*	
F...C(eq.) (syn)	3.643	0.067	0.012	3.634	0.070	0.012	3.628	0.076	0.011
F...C(eq.) (anti)	4.585	0.116	0.019	4.583	0.124	0.020	4.577	0.134	0.016
F...O(eq.) (syn)	4.433	0.277	0.067	4.416	0.249	0.047	4.410	0.1710*	
F...O(eq.) (anti)	5.671	0.159	0.011	5.666	0.161	0.011	5.660	0.160	0.015
F...C(ax.) (syn)	2.799	0.127	0.061	2.810	0.132	0.070	2.845	0.125	0.025
F...C(ax.) (anti)	3.984	0.097	0.019	3.998	0.106	0.014	4.008	0.090	0.012
F...O(ax.) (syn)	3.290	0.174	0.020	3.300	0.199	0.026	3.351	0.191	0.022
F...O(ax.) (anti)	4.887	0.194	0.024	4.901	0.184	0.018	4.916	0.160	0.016
C(eq.)...C(eq.)	2.914	0.179*		2.950	0.179*		2.951	0.1053*	
C(eq.)...O(eq.)	3.876	0.153*		3.913	0.153*		3.912	0.1284*	
C(eq.)...C(ax.)	2.586	0.275	0.111	2.585	0.342	0.133	2.562	0.1490*	
C(eq.)...O(ax.)	3.479	0.175	0.054	3.475	0.203	0.038	3.446	0.1795*	
O(eq.)...O(eq.)	4.710	0.171*		4.756	0.171*		4.753	0.1718*	
O(eq.)...C(ax.)	3.486	0.171*		3.478	0.171*		3.451	0.1818*	
C(ax.)...C(ax.)	3.645	0.150*		3.636	0.150*		3.622	0.0649*	
C(ax.)...O(ax.)	4.783	0.057*		4.765	0.057*		4.749	0.0663*	
O(ax.)...O(ax.)	5.921	0.374*		5.890	0.374*		5.872	0.0677*	
Fe-C(O)eq.	1.846†	0.045*		1.845	0.045*		1.845	0.0484*	
Fe-C(O)ax.	1.823†	0.045*		1.828	0.045*		1.822	0.0506*	
∠CCF	115.0			114.2			114.7		
∠C <sub>ax</sub> FeC <sub>ax</sub>	178.7			178.8			176.0		
∑wΔ <sup>2</sup>	0.214 × 10 <sup>4</sup>			0.216 × 10 <sup>4</sup>			0.253 × 10 <sup>4</sup>		

\* Assumed

† E.s.d. are 0.010 Å

described above. The choice of the ten independent parameters is as in Table 2. The excess of parameters over peaks leads to correlation between parameters, which particularly affects Fe-C(O) (eq.-ax.) and Fe-C( $C_2F_4$ ). The two 'olefinic' carbon atoms contribute only a small percentage of the total scattering; consequently the C-C bond length is not too well determined.

Least-squares refinements were performed with a series of experimental molecular intensity curves differing only in the form of the strictly smooth background curves adopted. With the most promising background, the most satisfactory agreement between experimental and calculated molecular intensity curves occurred in a refinement where the ten independent parameters, 17 amplitudes, and the three scale factors, were allowed to vary simultaneously; the residual  $\sum |dI| / \sum I_{mol}^{obs}(s)$  reached 0.058 at convergence. Certain other points of convergence, with other backgrounds and different combinations of refined parameters were rejected because they were accompanied by both a higher residual and some physically unreasonable parameters. The converged independent and dependent geometrical parameters, and the corresponding amplitude values are given, together with their estimated standard deviations, in Tables 2 and 3 (Refinement I). All the e.s.d.'s quoted in the tables include subjective allowances for parameter correlation, data correlation, and systematic errors. Revising the choice of independent parameters, taking Fe-C(O)eq. and Fe-C(O)ax. instead of their mean and difference, led to the same convergence point; however, the mean distance does not suffer from the parameter correlation of its components, so its e.s.d. is lower than the 0.010 Å e.s.d. of the individual Fe-C(O) distances. The unrefined amplitudes of refinement I were fixed at reasonable values, largely those found for corresponding distances in iron pentacarbonyl (Beagley, Cruickshank, Pinder, Robiette & Sheldrick, 1969). Refinement II takes account of shrinkage within the  $Fe(CO)_4$  fragment. The shrinkages proposed by Brunvoll (1967) for iron pentacarbonyl were applied; at convergence, the

residual was 0.059. In refinement II the same thirty parameters as before were varied and the fixed amplitudes were allotted the values used before. In refinement III, which also takes account of shrinkage, a different approach was used; fewer parameters were refined, and the outstanding amplitudes (as well as the shrinkages) were fixed at the values calculated by Brunvoll (1967), and for the  $C_2F_4$  fragment, at the amplitude values found experimentally by Chiang & Bennett (1971) in perfluorocyclopropane. With the number of refined parameters thus reduced to twenty-three, some reduction in parameter correlation was anticipated. At the convergence of refinement III the residual was 0.070. For refinements II and III the values given for non-bonded distances in Tables 2 and 3 are those used in the intensity calculations, and thus have had the shrinkages subtracted.

The observed molecular intensity curves from refinement I are shown in Fig. 3, together with the difference curves,  $I_{mol}^{obs}(s) - I_{mol}^{calc}(s)$ .

### Discussion

As can be seen from Figs. 2 and 3, the  $C_{2v}$  model assumed gives excellent agreement with experiment. The  $^{19}F$  n.m.r. spectrum (a singlet) is also consistent with a model of  $C_{2v}$  symmetry, as is the infrared spectrum in the carbonyl stretching region (Fields *et al.*, 1970).

The residuals and  $\sum w d^2$  values indicate that the results of refinements I and II are to be preferred to those of refinement III, and statistical tests support this conclusion. However, all the refinements show the main results are not critically dependent on the assumptions. The structure is complex and near the limit for complete solution by electron diffraction, so that not too much significance should be attached to some of the fine details. There appears to be little to choose between the reliabilities of refinements I and II, and indeed the results themselves hardly differ when e.s.d.'s are taken into account. Thus the diffraction data are rather intensive to shrinkage, and the following dis-

Table 4. Comparison of  $C_2F_4Fe(CO)_4$  with other molecules

	$C_2F_4Fe(CO)_4$ This work	$C_2H_4Fe(CO)_4$ Davis & Speed (1970)	$(C_2F_5)_2Fe(CO)_4$ Churchill (1967)	$Fe(CO)_5$ Beagley <i>et al.</i> (1969)	$C_2(CN)_4Pt(P\bar{O}_3)_2$ Bombieri <i>et al.</i> (1970)
(a) Fe-C(O)eq.	1.846 Å 0.010	1.84 Å 0.02	1.853 Å (av.) 0.014	1.833 Å 0.002	—
Fe-C(O)ax.	1.823 0.010	1.80 0.02	1.837 (av.) 0.014	1.806 0.003	—
Fe-C(O) (mean)	1.835 0.006	1.82	1.845	1.822 0.001	—
$\angle C_{eq}FeC_{eq}$	104.2° 1.4	105° 2	88.9° 0.6	(120°)	—
(b) Fe-C (organic)	1.989 Å 0.010	2.12 Å 0.02	2.068 Å 0.014	—	—
C-C	1.530 0.015	1.46 0.03	—	—	1.49 Å 0.05
$\angle$ out of plane	41.6 1.1	—	—	—	31.8°

cussion is based on the results of refinement I, in which several e.s.d.'s are found to be lower.

Table 4(a) compares the results for the  $\text{Fe}(\text{CO})_4$  fragment of the molecule with results for related molecules. The weight of evidence from all four molecules suggests that  $\text{Fe}-\text{C}(\text{O})_{\text{eq.}} > \text{Fe}-\text{C}(\text{O})_{\text{ax.}}$ , but it is only in  $\text{Fe}(\text{CO})_5$  that this inequality has been established reliably, owing to the high e.s.d.'s in the other cases.

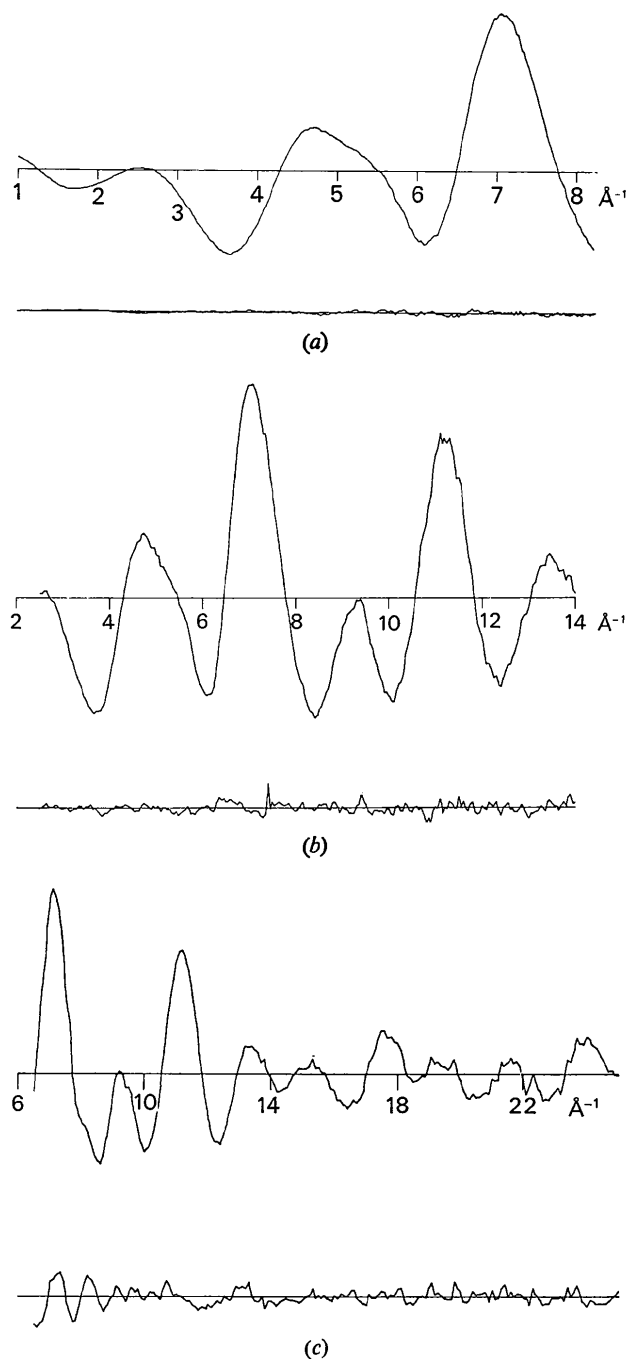


Fig. 3. Experimental molecular intensity curves and difference curve (refinement I) for various camera distances: (a) 100 cm; (b) 50 cm; (c) 25 cm.

Indeed the difference  $\text{Fe}-\text{C}(\text{O})$  ( $\text{eq}-\text{ax}$ ) in  $\text{C}_2\text{F}_4\text{Fe}(\text{CO})_4$ , which is  $0.023 \pm 0.016 \text{ \AA}$  cannot be considered significant. The results in the table also suggest that  $\text{Fe}-\text{C}(\text{O})$  (mean) is greater in the fluorinated molecules. Table 4(b) compares, for a series of molecules, features associated with the bonding between a metal and the organic fragment. Fluorination clearly shortens, and thus strengthens, the  $\text{Fe}-\text{C}$  (organic) bond length, while the  $\text{C}-\text{C}$  bond is probably lengthened, and thus weakened;  $\text{C}-\text{C}$  is decidedly longer than the double-bond length of  $\sim 1.34 \text{ \AA}$ . In addition, the  $\text{C}_2\text{F}_4$  fragment is considerably distorted from planarity. As suspected in the introduction, the trends in distortion from olefinic geometry established by Stalick & Ibers (1970) clearly extrapolate to include  $\text{C}_2\text{F}_4\text{Fe}(\text{CO})_4$ . In butatriene complexes of iron (Bright & Mills, 1971, 1972) the originally linear butatriene chain is bent in a manner corresponding to the out-of-plane distortions in the ethylenic complexes; the nature of the bonding in all these complexes appears somewhat similar.

As to the nature of the bonding between iron and the  $\text{C}_2\text{F}_4$  fragment, the comparisons in Table 5 are helpful. The dimensions of the  $\text{C}_2\text{F}_4$  fragment fall neatly between those of perfluorocyclopropane and perfluorocyclohexane, suggesting that the bonding in the complex resembles that of a  $\sigma$ -bonded ring compound rather than a  $\pi$ -complex. The above discussion suggests that the effect of replacing hydrogen by fluorine is to strengthen the iron-to-olefin bonding and to increase the degree of  $\sigma$ -complexing. [Evans & Russell (1971) conclude from crystallographic studies that in rhodium complexes  $\pi$ -complexing is increased.] The bonding between iron and olefin seems to be strengthened at the expense of a lengthening, and weakening, of the  $\text{Fe}-\text{C}(\text{O})$  bonds.

Table 5. Comparison of  $\text{C}_2\text{F}_4$  fragment with other molecules

	$(\text{C}_2\text{F}_4)\text{Fe}(\text{CO})_4$ This work	$\text{C}_2\text{F}_4$ Bauer (1972)	Cyclo- $\text{C}_3\text{F}_6$ Chiang & Bernett (1973)	Cyclo- $\text{C}_6\text{F}_{12}$ Hjortaa & Strømme (1968)
C-C	1.530 Å 0.015	1.311 Å	1.505 Å 0.003	1.551 Å 0.003
C-F	1.336 0.005	1.319	1.314 0.001	1.337 0.002
$\angle \text{F}-\text{C}-\text{F}$	111.3° 1.1	112.4°	112.2° 1.0	109.1° 0.3

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## Structure et Configuration Absolue de la Ferrocéno-2,3 Méthyl-5 (*exo*) Cyclohexène-2 One-1 Lévogyre

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The structure of (–)-2,3-ferroceno-5-*exo*-methylcyclohex-2-en-1-one has been determined from three-dimensional X-ray diffractometer data. This compound crystallizes in the orthorhombic system with cell constants  $a = 9.97$ ,  $b = 19.5$ ,  $c = 6.54$  Å, space group  $P2_12_12_1$ . The structure was solved by a direct method of phase determination and was refined by block-diagonal least-squares methods. The final reliability index is 0.063. The absolute configuration is  $2R_p$   $5S_c$ .

### Introduction

Les ferrocénocyclohexénones homopontées  $\alpha$  et  $\beta$  méthylées et les alcools qui en dérivent posent des problèmes d'ordre stéréochimique. Ceux-ci ont déjà fait l'objet d'une publication récente (Gautheron & Broussier, 1971) et ce mémoire étudie plus spécialement la famille des cétones. L'accès aux cétones est possible par cyclisation homoannulaire des acides  $\gamma$ -ferrocényl- $\beta$ -méthylbutyrique et  $\gamma$ -ferrocényl- $\alpha$ -méthylbutyrique; elles présentent deux éléments d'asymétrie: un carbone asymétrique dans le cycle orthocondensé et une asymétrie métalloccénique qui dépend du sens de l'enroulement du cycle. La structure d'une cétone optiquement active sera donc parfaitement connue si l'on sait déterminer la configura-

tion respective de ces deux asymétries. Or, si l'on connaît l'une des chiralités et la nature *endo* ou *exo* du substituant, on peut en déduire la structure exacte de l'énantiomère étudié. Le premier problème qui se pose est donc la détermination de la nature *endo* ou *exo* du substituant méthyle porté par le cycle orthocondensé. Il peut être résolu en série racémique.

La cyclisation des acides  $\gamma$ -ferrocényl  $\beta$  ou  $\alpha$ -méthylbutyrique racémiques (composés 1 ou 2 de la Fig. 1) conduit, dans chaque cas, à deux cétones diastéréoisomères racémiques, respectivement les composés ( $\pm$  5) et ( $\pm$  6) pour l'acide  $\alpha$ -méthylé, et les composés ( $\pm$  3) et ( $\pm$  4) pour l'acide  $\beta$ -méthylé.

La structure de ces cétones peut être établie par l'ensemble des transformations de la Fig. 1: la réduction par  $LiAlH_4$  des deux cétones ( $\pm$  5) et ( $\pm$  6) conduit