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# THE MOLECULAR STRUCTURE OF DECAMETHYLFERROCENE STUDIED BY GAS PHASE ELECTRON DIFFRACTION. DETERMINATION OF EQUILIBRIUM CONFORMATION AND BARRIER TO INTERNAL ROTATION OF THE LIGAND RINGS

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## Summary

The molecular structure of decamethylferrocene, ($\eta$-$C_5Me_5$)$_2$Fe, has been determined by gas phase electron diffraction. The Fe—C and C(Cp)—C(Cp) bond distances, 2.064(3) and 1.439(2) Å, respectively, are indistinguishable from those in ferrocene, $Cp_2Fe$. But, while the equilibrium conformation of gaseous $Cp_2Fe$ is eclipsed ($D_{5h}$), the equilibrium conformation of $(C_5Me_5)_2Fe$ is staggered ($D_{5d}$) with a barrier to internal rotation of the ligand rings $V_5$ = 1.0(0.3) kcal mol$^{-1}$. And while the C—H bonds in $Cp_2Fe$ are bent about 4° out of the plane of the $C_5$ ring towards the metal atom, the C(Cp)—C(Me) bonds in $(C_5Me_5)_2Fe$ are bent 3.4(0.5)° out of the plane in the opposite direction.

## Introduction

We have determined the molecular structure of decamethylferrocene ($\eta$-$C_5Me_5$)$_2$Fe in the gas phase for comparison with the structure of ferrocene, $Cp_2Fe$ (Cp = cyclopentadienyl) [1].

## Experimental and structure analysis

$(C_5Me_5)_2Fe$ was prepared as described by King [2]. The electron scattering pattern was recorded on the Oslo electron-diffraction unit [3] with a nozzle

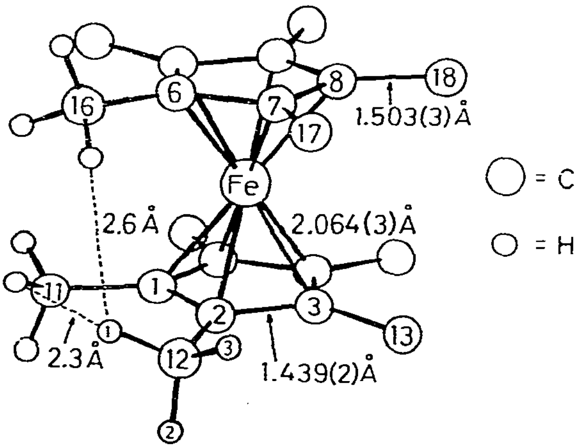

Fig. 1. Molecular model of $(C_5Me_5)_2Fe$. Symmetry $D_{5d}$ (staggered ligand rings). Most of the hydrogen atoms have been omitted for clarity.

temperature of 180 ± 5°C and nozzle-to-plate distances of about 48 and 20 cm. The optical densities of six plates from each set were processed using the programs described by Andersen et al. [4]. Backgrounds were subtracted from the total scattered intensities after multiplication with the modifying function $s/f_{Fe}(s) \cdot f_C(s)$ [4]. The background was calculated as a seventh degree polynominal of $s$ for the 50 cm plates and as an eight degree polynominal for the 20 cm plates. The coefficients were determined by a least-squares procedure using theoretical modified molecular intensity data [5]. The modified experimental molecular intensity data obtained by averaging the intensity values for each nozzle-to-plate distance ranged from $s = 2.00$ to 19.50 $Å^{-1}$ and from $s = 8.00$ to 44.00 $Å^{-1}$.

The structure analysis was based on the following assumptions: (i) The equilibrium molecular structure has either $D_{5d}$ symmetry (i.e. staggered $C_5Me_5$ rings as shown in Fig. 1) or $D_{5h}$ symmetry (eclipsed ligand rings). (ii) The C(Cp)—$CH_3$ fragments have $C_{3v}$ symmetry and the methyl groups are oriented in such a way that one C—H bond is *anti* the Fe—C(Cp) bond as indicated in Fig. 1. This is the orientation found for six of the ten methyl groups in crystalline $(C_5Me_2)_2Fe$ [6,7] and for all methyl groups in *sym*-octamethylferrocene [6].

For both $D_{5d}$ and $D_{5h}$ molecular models the equilibrium geometry is then determined by six independent parameters, e.g. the bond distances C(1)—C(2), C(1)—C(11), C—H and Fe—C, the valence angle ∠C—C—H and the angle between the C(1)—C(2) bond and the $C_5$ ring plane which we denote by $\angle C_5$, C—C and define as positive when the bonds are bent towards the metal atom.

An approximate molecular force field for decamethylferrocene was constructed by combination of the force field of ferrocene [8] and a typical force field for the group C—$CH_3$ [9]. The force field was then adjusted to reproduce the infrared and Raman active frequencies listed by Duggan and Hendrickson [10]. Root mean square vibrational amplitudes, $l$, and perpendicular amplitude correction coefficients, $K$, were calculated for models of $D_{5d}$ and $D_{5h}$ sym-

TABLE 1

INTERATOMIC DISTANCES, $r_a$, ROOT MEAN SQUARE VIBRATIONAL AMPLITUDES, $l$, AND PERPENDICULAR AMPLITUDE CORRECTION COEFFICIENTS, $K$, FOR $(C_5Me_5)_2Fe$ (Estimated standard deviations in parentheses in units of the last digit)

| | $r_a$ (Å) | $l$(ED) (Å) | $l$(FF) (Å) | $K$ (Å) | | $r_a$ (Å) | $l_{fw}$(ED) (Å) | $l_{fw}$(FF) (Å) | $K_{fw}$ (Å) |
|---|---|---|---|---|---|---|---|---|---|
| Fe—C(1) | 2.064(3) | 0.066(2) | 0.086 | 0.002 | C(1)···C(6) | 2.41 | 0.146 | 0.146 | 0.002 |
| C(1)—C(2) | 1.439(2) | 0.048 ass | 0.048 | 0.004 | C(1)···C(7) | 3.87 | 0.109 $^{b}$ | 0.117 | 0.002 |
| C(1)—C(11) | 1.503(3) | 0.053 ass | 0.053 | 0.012 | C(1)···C(8) | 4.13 | 0.096 $^{a}$ | 0.103 | 0.002 |
| C(11)—H(11) | 1.115(4) | 0.077(4) | 0.079 | 0.072 | C(1)···C(16) | 3.89 | 0.141 $^{b}$ | 0.149 | 0.003 |
| Fe···C(11) | 3.230 | 0.103(2) | 0.094 | 0.003 | C(1)···C(17) | 4.75 | 0.133 | 0.133 | 0.003 |
| Fe···H(1) | 3.507 | 0.218 ass | 0.218 | 0.023 | C(1)···C(18) | 5.21 | 0.125 $^{c}$ | 0.124 | 0.003 |
| Fe···H(2) | 4.125 | 0.116(7) $^{a}$ | 0.123 | 0.023 | C(11)···C(16) | 3.88 | 0.168 $^{b}$ | 0.176 | 0.004 |
| C(1)···C(3) | 2.326 | 0.055(2) | 0.066 | 0.004 | C(11)···C(17) | 5.62 | 0.146 | 0.146 | 0.003 |
| C(1)···C(12) | 2.615 | 0.072(2) | 0.077 | 0.007 | C(11)···C(18) | 6.46 | 0.128 | 0.128 | 0.003 |
| C(1)···C(13) | 3.775 | 0.072(2) $^{b}$ | 0.080 | 0.005 | | | | | |
| C(11)···C(12) | 3.192 | 0.136(2) | 0.126 | 0.008 | | | | | |
| C(11)···C(13) | 5.164 | 0.097(3) $^{c}$ | 0.095 | 0.005 | | | | | |

$\angle C_5$, C—C = −3.4 (0.5)°; $\angle$C—C—H = 112.4 (0.8)°; $V_5 = V_{ecl} - V_{stag} = 1.0_5(0.3_0)$ kcal mol$^{-1}$
$h^d$ 1.662(2) Å

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[a] ED: from least squares refinements on the electron diffraction data. FF: calculated from an approximate molecular force field. fw: framework value, see text. For numbering of the atoms consult Fig. 1. (*a*), (*b*), (*c*) denotes groups of amplitudes given the same shift from their calculated values. (*d*) perpendicular distance from Fe to the center of the Cp ring.

metry. The most important amplitudes and correction coefficients obtained for distances within a Fe($C_5Me_5$) fragment by calculations on a $D_{5d}$ model are listed in Table 1.

After initial refinements of $D_{5d}$ and $D_{5h}$ models, we introduced a dynamic model simulating restricted internal rotation of the $C_5Me_5$ rings which was found to be in better agreement with the experimental intensity data than either of the two rigid models.

If the dihedral angle $\phi$ is defined as zero when the ligand rings are eclipsed, $\phi = 36°$ corresponds to a staggered conformation, and all possible conformations are included when $\phi$ varies from 0 to 72° or from —36 to 36°.

(iii) It was assumed that the barrier to internal rotation can be represented by:

$$V(\phi) = \frac{V_5}{2}(1 + \cos(5\phi))$$

when $V_5 = V_{ecl} - V_{stag}$. Hence $V_5 > 0$ corresponds to a staggered and $V_5 < 0$ to an eclipsed equilibrium conformation.

The dynamic model represents the gas by a mixture of species with $\phi = 0$, 18, 36 and 54° (or —18°). The mole fraction of each species was calculated from:

$$\chi(\phi) = N\exp(-V(\phi)/RT)$$

where $N$ is a normalizing factor [1b]. (iv) Finally it was assumed that the geometry of the ligand rings and the Fe—C bond distances remain unaltered during internal rotation, i.e. are the same for each value of $\phi$.

For distances between atoms in different rings we calculated framework vibrational amplitudes, $l_{fw}$, and correction coefficients, $K_{fw}$, by omitting the contributions from the normal mode corresponding to internal rotation of the rings. The most important of the values obtained for the staggered model are listed in Table 1. These parameters were also calculated for an eclipsed model, and for the intermediate models $\phi = 18°$ and 54° by interpolation.

The six independent structure parameters, $V_5$, eight of the most important vibrational amplitudes between atoms in the same Fe($C_5Me_5$) fragment, and two scale factors were refined by least-squares calculations on the intensity data with a nondiagonal weight matrix using a program written by Seip [11] and modified by Gundersen [12]. Those amplitudes that could not be refined, were fixed at the values calculated from the approximate molecular force field.

The three longest distances within the Fe($C_5Me_5$) fragment, Fe · · · H(2), C(1) · · · C(13) and C(11) · · · C(13), are found in the range of distances between C atoms in different ligand rings. The vibrational amplitudes of three distances would therefore be sensitive to errors in the calculated $l_{fw}$. In these cases close-lying distances were grouped together as indicated by the letters *a*, *b* and *c* in Table 1, and the vibrational amplitudes given the same shift from the values calculated from the molecular force field. In each of the three instances the resulting shifts are seen to be small.

The refinement converged to the parameters listed in Table 1. The standard deviations have been expanded to include an estimated uncertainty of 0.1% in the electron wavelength. The standard deviations of $V_5$ and $\angle C_5$,C—C have been

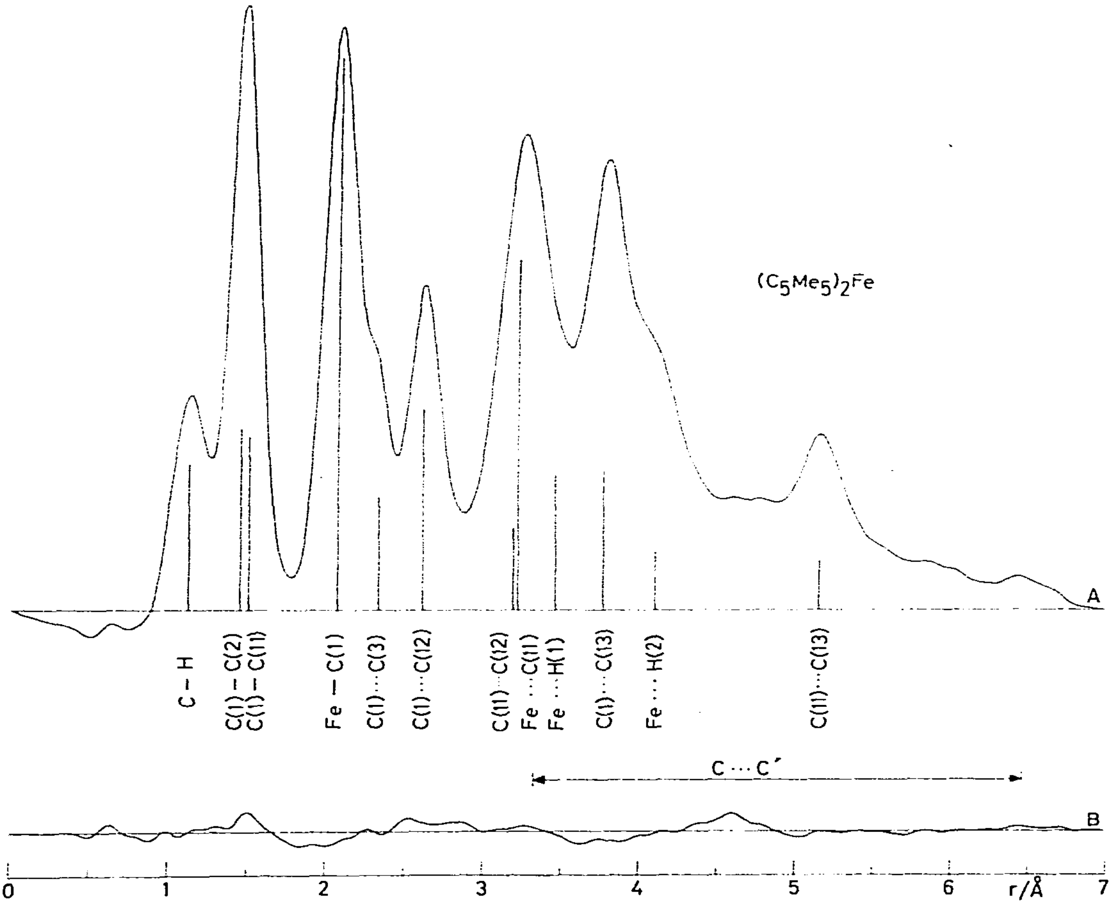

Fig. 2. A. Experimental radial distribution curve for $(C_5Me_5)_2Fe$. Artificial damping constant $k$ 0.0016 Å$^2$. B. Difference between the experimental curve and a theoretical RD curve calculated for the best model.

doubled in order to include the uncertainty introduced by assumptions (i) to (iv) and the approximate nature of the force field.

A radial distribution curve calculated by Fourier inversion of the experimental intensity data is shown in Fig. 2 along with the difference between this curve and a theoretical curve calculated for the best model.

## Discussion

In Table 2 we compare the most important structure parameters of $(C_5Me_5)_2Fe$ and $Cp_2Fe$ obtained by gas phase electron diffraction (ED) and those obtained for $(C_5Me_5)_2Fe$ by X-ray crystallography [7].

The Fe—C and C(Cp)—C(Cp) bond distances found in the two compounds by ED are indistinguishable, while the bond distances found by X-ray crystallography are 0.01 to 0.02 Å shorter. We believe the difference to be due to systematic errors introduced into the X-ray study by librational motion and the

TABLE 2

STRUCTURE PARAMETERS OF $Cp_2Fe$ AND $(C_5Me_5)_2Fe$

| | $Cp_2Fe$ (ED) | $(C_5Me_5)_2Fe$ (ED) | $(C_5Me_5)_2Fe$ (X) |
|---|---|---|---|
| Fe—C(Cp) (Å) | 2.064(3) | 2.064(3) | 2.050(2) |
| C(Cp—C(Cp) (Å) | 1.440(2) | 1.439(2) | 1.419(2) |
| C(Cp)—C(Me) (Å) | — | 1.503(3) | 1.502(3) |
| $\angle C_5$, C—X [a] | 3.7(0.9)° | −3.4(0.5)° | −2.4(0.6)° |
| Equilibrium conformation | $D_{5h}$(ecl) | $D_{5d}$(stag) | ($D_{5d}$(stag)) |
| $V_5$ [b] (kcal $mol^{-1}$) | −0.9(0.3) | $1.0_5(0.3_0)$ | — |
| Reference | 1 | this work | 7 |

[a] This angle is defined as positive when the C—X bonds are bent towards the metal atom. [b] $V_5 = V_{ecl} - V_{stag}$.

asymmetric distribution of the valence electrons in the ligand rings [13].

The C(Cp)—C(Me) bond distance in $(C_5Me_5)_2Fe$ is close to a standard $sp^2$—$sp^3$ C—C bond distance.

The equilibrium conformation of gaseous $(C_5Me_5)_2Fe$ is staggered ($D_{5d}$), while the equilibrium conformation of $Cp_2Fe$ is eclipsed ($D_{5h}$). In both molecules the barrier to internal rotation is about 1 kcal $mol^{-1}$. This means that introduction of the ten methyl groups increases the energy of the eclipsed conformation relative to the staggered by about 2 kcal $mol^{-1}$. This may reasonably be assumed to be the result of Van der Waals interactions between the methyl groups. The shortest inter-ring H · · · H distance in staggered $(C_5Me_5)_2Fe$, indicated by a stippled line in Fig. 1, is 2.6 Å.

The staggered equilibrium conformation of $(C_5Me_5)_2Fe$ is retained in the crystalline phase and there is no indication of disorder.

While the C—H bonds in $Cp_2Fe$ are bent about 4° out of the plane of the $C_5$ ring towards the metal atom, the C(Cp)—C(Me) bonds in $(C_5Me_5)_2Fe$ are bent about 3° out of the plane away from Fe. Again it seems reasonable to assume the difference to be due to Van der Waals interaction between the methyl groups; between groups on different rings or on the same ring. The shortest H · · · H intra-ring distance, indicated by a dashed line in Fig. 1, is 2.3 Å. This distance increases when the C(Cp)—C(Me) bond is bent away from Fe; the greatest separation would occur if the C—C bonds were bent so far down that H(1) was in the $C_5$ plane.

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