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THE MOLECULAR STRUCTURES OF DICYCLOPENTADIENYLVANADIUM, $(C_5H_5)_2V$, AND DICYCLOPENTADIENYLCHROMIUM, $(C_5H_5)_2Cr$, DETERMINED BY GAS PHASE ELECTRON DIFFRACTION

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Summary

The molecular structures of $(C_5H_5)_2V$ and $(C_5H_5)_2Cr$ have been determined by gas phase electron diffraction. The best agreement between calculated and experimental curves is obtained for models with eclipsed C_5H_5 rings (symmetry D_{5h}), but models with staggered rings (symmetry D_{5d}) cannot be definitely ruled out. The M—C and C—C bond distances are 2.169(4) and 1.431(2) Å respectively in $(C_5H_5)_2Cr$, and 2.280(5) and 1.434(3) Å respectively in $(C_5H_5)_2V$. The C—H bonds in $(C_5H_5)_2Cr$ are bent 2.9(1.1)° out of the plane of the carbon atoms towards the metal atom.

The molecular structures of the known di-π-cyclopentadienyl compounds of the first row transition elements are compared in the light of what is known about their electronic structures.

Introduction

We have determined the molecular structures of dicyclopentadienylvanadium (Cp_2V) and dicyclopentadienylchromium (Cp_2Cr) in the gas phase by means of electron diffraction for comparison with the published structures of Cp_2Fe [1, 2], Cp_2Ni [3], and Cp_2Mn [4] in the gas phase and the structure of Cp_2Co [5] in the solid phase.

Experimental and calculation procedure

The samples of Cp_2Cr and Cp_2V were kindly supplied by Professor E.O. Fischer and Dr. F.H. Köhler, and were used without further purification.

The electron scattering patterns were recorded on Balzers Eldigraph KD-G2. The experimental conditions are summarized in Table 1. Attempts to record the scattering pattern of Cp_2V beyond $s = 20$ Å^{-1} by making exposures with nozzle-to-plate distances around 19 cm were not successful, possibly be-

TABLE 1

INFORMATION ABOUT THE INTENSITY DATA

	$(C_5H_5)_2Cr$		$(C_5H_5)_2V$	
Nozzle to plate distance (mm)	498.88	249.02	578.56	328.72
Nozzle temperature (°C)	140-145	140-145	115-125	115-125
Number of plates used	4	3	4	5
s-range (Å^{-1})	1.375-15.250	4.00-30.00	1.500-13.375	2.50-20.50
Increment (Å^{-1})	0.125	0.25	0.125	0.25

cause of the reactivity of the compound. The data were processed and the structures refined using the programs described by Andersen et al. [6] and Seip et al. [7]. The resulting modified molecular intensity points are shown in Figs. 1 and 2.

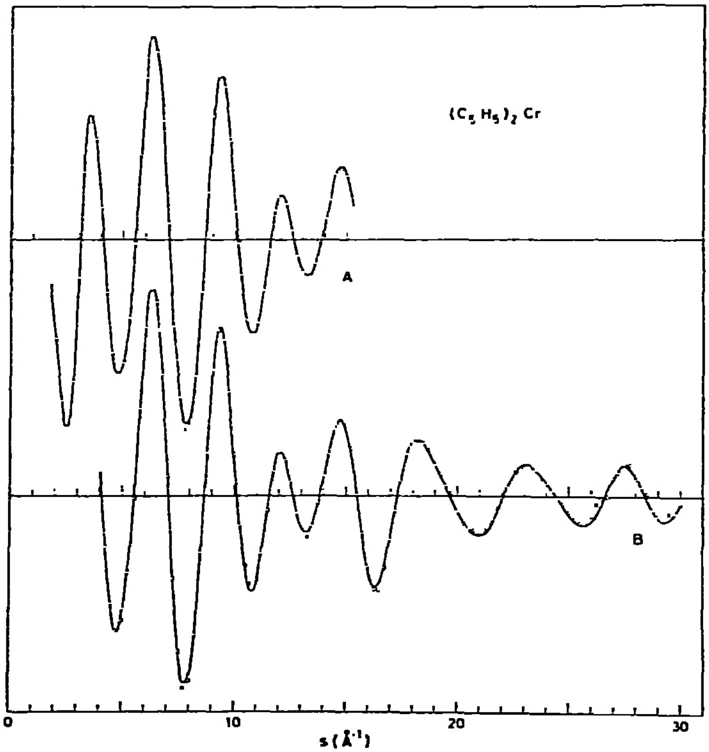

Fig. 1. o: Experimental modified molecular intensity points for $(C_5H_5)_2Cr$ from s = 1.50 to s = 15.25 Å^{-1} (A) and from s = 4.00 to s = 30.00 Å^{-1} (B). In A only every other experimental point is shown. Full lines: theoretical intensity curves calculated for best model of D_{5h} symmetry.

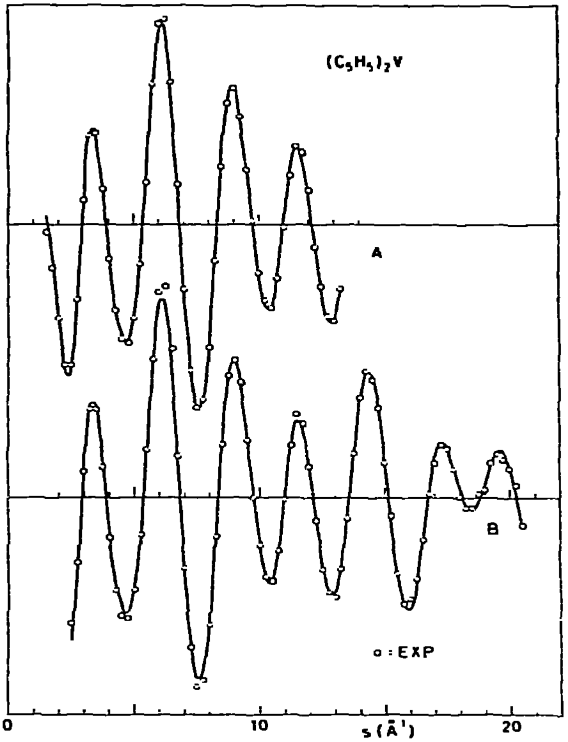

Fig. 2. o: Experimental modified molecular intensity points for $(C_5H_5)_2V$ from $s = 1.50$ to 13.25 Å^{-1} (A) and from $s = 2.50$ to 20.5 Å^{-1} (B). In A only every other experimental point is shown. Full lines: theoretical intensity curves calculated for best model of D_{5h} symmetry.

Theoretical intensity curves were calculated from:

$$I^{MC}(s) = \sum_{i \neq j} \frac{|f_i(s)| \cdot |f_j(s)|}{|f_M(s)| \cdot |f_C(s)|} \cos[\eta_i(s) - \eta_j(s)]$$

$$\frac{\sin(R_{ij}s)}{R_{ij}} \exp(-\tfrac{1}{2} l_{ij}^2 s^2)$$

The sum extends over all atom pairs in the molecule. R_{ij} is the internuclear distance, l_{ij} the root mean square amplitude of vibration. $f_j(s) = |f_j(s)| \exp[i\eta_j(s)]$ is the complex atomic scattering factor of atom j. M = metal atom (Cr or V).

Brunvoll [8] has modified the molecular force field of ferrocene [9] to reproduce the IR active frequencies of Cp_2Cr and Cp_2V respectively listed by Fritz [10] and calculated root mean square amplitudes of vibration, l, and perpendicular amplitude correction coefficents, K, for molecular models with eclipsed and staggered Cp rings. The amplitudes and K-values obtained by calculations on eclipsed models are listed in Table 2 and Table 3 for all distances except H · · · H distances.

The molecular structures were refined as least squares calculations on the intensity data under the constraints of a geometrically consistent r_α structure,

TABLE 2

INTERNUCLEAR DISTANCES (*R*), ROOT MEAN SQUARE VIBRATIONAL AMPLITUDES (*l*) DETERMINED FROM ELECTRON DIFFRACTION (ED) AND CALCULATED FROM A MOLECULAR FORCE FIELD (FF) [8], AND PERPENDICULAR AMPLITUDE CORRECTION COEFFICIENTS (*K*) [8] FOR $(C_5H_5)_2Cr$. ESTIMATED STANDARD DEVIATIONS ARE GIVEN IN PARENTHESES IN UNITS OF THE LAST DIGIT. DISTANCES ARE LISTED AS r_a

	R (Å)	*l*(ED) (Å)	*l*(FF) (Å)	*K* (Å)
C—H	1.108(7)	0.051(9)	0.077	0.0200
C—C	1.431(2)	0.049(2)	0.047	0.0060
Cr—C	2.169(4)	0.078(2)	0.086	0.0025
$Cr \cdots H$	2.889(14)	0.143(14)	0.132	0.0078
$C_1 \cdots C_3$	2.315(3)	0.052(4)	0.064	0.0073
$C_1 \cdots C_6$	3.579(7)	0.263(35)	0.160	0.0024
$C_1 \cdots C_7$	3.857(7)	0.227(17)	0.136	0.0018
$C_1 \cdots C_8$	4.268(7)	0.169(12)	0.093	0.0008
$C_1 \cdots H_2$	2.254(7)	0.125(44)	0.101	0.0126
$C_1 \cdots H_3$	3.370(8)	0.111(14)	0.099	0.0113
$C_1 \cdots H_6$	3.702(21)	0.194[a]	0.194	0.0069
$C_1 \cdots H_7$	4.191(19)	0.186[a]	0.186	0.0053
$C_1 \cdots H_8$	4.881(16)	0.161[a]	0.161	0.0038
h[b]	1.798(4)			
$\angle C_5,H$	2.9(1.1)°			

[a] Assumed value. [b] Perpendicular distance from the metal atom to the Cp rings.

TABLE 3

INTERNUCLEAR DISTANCES (*R*), ROOT MEAN SQUARE VIBRATIONAL AMPLITUDES (*l*) DETERMINED FROM ELECTRON DIFFRACTION (ED) AND CALCULATED FROM A MOLECULAR FORCE FIELD (FF) [8], AND PERPENDICULAR AMPLITUDE CORRECTION COEFFICIENTS (*K*) [8] FOR $(C_5H_5)_2V$. ESTIMATED STANDARD DEVIATIONS ARE GIVEN IN PARENTHESES IN UNITS OF THE LAST DIGIT. DISTANCES ARE LISTED AS r_a

	R (Å)	*l*(ED) (Å)	*l*(FF) (Å)	*K* (Å)
C—H	1.133(14)	0.073(23)	0.077	0.0199
C—C	1.434(3)	0.032(7)	0.047	0.0057
V—C	2.280(5)	0.058(10)	0.086	0.0022
$V \cdots H$	3.047(20)	0.130(22)	0.129	0.0072
$C_1 \cdots C_3$	2.318(5)	0.065(18)	0.063	0.0069
$C_1 \cdots C_6$	3.848(11)	0.196(38)	0.155	0.0021
$C_1 \cdots C_7$	4.103(10)	0.218(26)	0.132	0.0016
$C_1 \cdots C_8$	4.490(8)	0.188(21)	0.091	0.0008
$C_1 \cdots H_2$	2.282(13)	0.099[a]	0.099	0.0122
$C_1 \cdots H_3$	3.402(15)	0.098[a]	0.098	0.0109
$C_1 \cdots H_6$	4.039(28)	0.190[a]	0.190	0.0060
$C_1 \cdots H_7$	4.499(25)	0.182[a]	0.182	0.0047
$C_1 \cdots H_8$	5.157(22)	0.157[a]	0.157	0.0035
h[b]	1.928(6)			
$\angle C_5,H$	−1.5(1.6)°			

[a] Assumed value. [b] Perpendicular distance from the metal atom to the Cp rings.

with a non-diagonal weight matrix and a separately refined scale factor for the intensity data obtained for each nozzle-to-plate distance. The standard deviations obtained were expanded to take into account an estimated uncertainty of 0.1 % in the electron wavelength.

Radial distribution curves were calculated by Fourier inversion of experimental and calculated intensity curves after multiplication with the artificial damping function $\exp(-ks^2)$. The experimental intensity functions were then spliced to each other and to the theoretical curve calculated for the best model below $s = 1.375$ Å^{-1}.

Structure refinement

A molecular model of Cp_2Cr in which the two Cp rings are eclipsed is shown in Fig. 3. A molecular model with staggered rings is obtained by rotating one ring 36° about the fivefold symmetry axis. The symmetry of the eclipsed model is D_{5h}, the symmetry of the staggered model D_{5d}. In either case the structure is determined by four independent parameters, i.e. the C—H, C—C, and M—C bond distances and the angle between the C—H bonds and the plane of the carbon atoms in the ring. This angle is denoted by $\angle C_5$, H and defined as positive when the C—H bonds are bent towards the metal atom.

The values obtained for the four structure parameters and ten vibrational amplitudes of Cp_2Cr by refinement on the eclipsed model are listed in Table 2. The amplitudes that were not refined were fixed at their calculated values. The generalized R-factor [7] was $R_3 = 11.49$.

Refinement of a staggered model did not give as good agreement between experimental and calculated intensities, the generalized R-factor obtained being $R_3 = 11.95$. None of the parameter values obtained [except of course for the three amplitudes $l(C_1 \cdots C_6)$, $l(C_1 \cdots C_7)$ and $l(C_1 \cdots C_8)$] differed from those obtained by refinement of an eclipsed model by more than one standard deviation. In particular $\angle C_5,H = 3.3(1.3)°$.

The values obtained for the four structure parameters and eight vibrational amplitudes of Cp_2V by refinement of an eclipsed model are listed in Table 3.

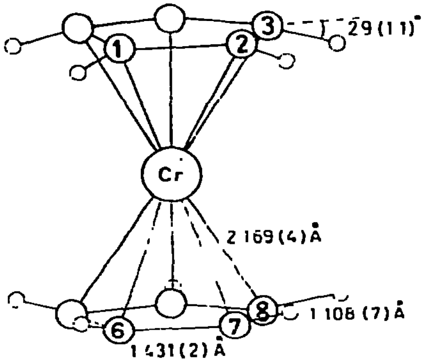

Fig. 3. Molecular model of $(C_5H_5)_2Cr$ with eclipsed rings, symmetry D_{5h}.

Attempts to refine $l(C_1 \cdots H_2)$ and $l(C_1 \cdots H_3)$ led to divergence. The generalized R-factor was $R_3 = 12.92$.

For Cp_2V too refinement of a staggered model yielded poorer agreement between experimental and calculated intensities, the generalized R-factor being $R_3 = 13.22$. The value obtained for $\angle C_5,H$, $-7.4(1.6)^\circ$, was very different from the value obtained by refinement of an eclipsed model, $-1.5(1.6)^\circ$. None of the other parameter values [except again for $l(C_1 \cdots C_6)$, $l(C_1 \cdots C_7)$ and $l(C_1 \cdots C_8)$] differed from those obtained by refinement of an eclipsed model by more than one standard deviation.

Discussion

The electronic structure of ferrocene is now well understood [11]. The last three molecular orbital calculations [12-14] agree that the highest filled molecular orbitals (i.e. those orbitals from which electrons are most easily removed or excited) are the e_{2g} and a_{1g} orbitals, and that the lowest empty (virtual) orbital is e_{1g}. The a_{1g} and e_{2g} orbitals are predominantly $3d$ orbitals on the Fe atom; if the z-axis is assumed to lie along the fivefold symmetry axis of the molecule $a_{1g} \approx 3d_{z^2}$ and $e_{2g} \approx 3d_{xy}$ and $3d_{x^2-y^2}$. The a_{1g} and e_{2g} orbitals are close in energy and are probably weakly bonding between the metal atom and the two rings. The lowest empty orbital, e_{1g}, is the antibonding combination of the Fe $3d_{xz}$ and $3d_{yz}$ orbitals with the e_{1g} π-orbitals of the ring, their energy is several eV above that of the filled a_{1g} and e_{2g} orbitals. The picture presented by the molecular orbital calculations is consistent with the electronic absorption spectra and photoelectron spectra [14].

Photoelectron spectra show that the dicyclopentadienyl compounds of the other first row transition metals have the following ground state electronic structures in the gas phase [15, 16]:

Cp_2V	a_{1g}^1	e_{2g}^2	
Cp_2Cr	a_{1g}^1	e_{2g}^3	
Cp_2Mn	a_{1g}^1	e_{2g}^2	e_{1g}^2
Cp_2Fe	a_{1g}^2	e_{2g}^4	
Cp_2Co	a_{1g}^2	e_{2g}^4	e_{1g}^1
Cp_2Ni	a_{1g}^2	e_{2g}^4	e_{1g}^2

These configurations suggest that the strongest metal to ligand bonds, and hence the shortest M—C bond distance, should be found in ferrocene.

If it is assumed that the loss of an electron from the a_{1g} or e_{2g} orbitals weakens the M—Cp bond to the same extent as the introduction of an electron into the antibonding e_{1g} orbital, we can define the "electron imbalance" of each complex as the number of holes in the a_{1g} and e_{2g} orbitals plus the number of electrons in the e_{1g} orbital, and it would follow that the metal to ring bonding should decrease in strength with increasing "electron imbalance". The numbers thus obtained are:

Cp_2Fe	0
Cp_2Co	1
Cp_2Cr	2
Cp_2Ni	2
Cp_2V	3
Cp_2Mn	5

TABLE 4

ELECTRONIC STRUCTURE, M—C BOND DISTANCES AND ROOT MEAN SQUARE VIBRATIONAL AMPLITUDES FOR THE KNOWN DI-π-CYCLOPENTADIENYL COMPOUNDS OF THE FIRST ROW TRANSITION ELEMENTS

Compounds	Electron configuration	Electron imbalance	R(M—C) (Å)	l(M—C) (Å)	Method
$(C_5H_5)_2Fe$	$a_{1g}^2\ e_{2g}^4$	0	2.064(3)	0.062(1)	ED [2]
$(C_5H_5)_2Co$	$a_{1g}^2\ e_{2g}^4\ e_{1g}^1$	1	2.096(8)		X [5]
$(C_5H_5)_2Cr$	$a_{1g}^1\ e_{2g}^3$	2	2.169(4)	0.078(2)	ED
$(C_5H_5)_2Ni$	$a_{1g}^2\ e_{2g}^4\ e_{1g}^2$	2	2.196(4)	0.084(3)	ED [3]
$(C_5H_5)_2V$	$a_{1g}^1\ e_{2g}^2$	3	2.280(5)	0 058(10)	ED
$(C_5H_5)_2Mn$	$a_{1g}^1\ e_{2g}^2\ e_{1g}^2$	5	2.383(3)	0.135(2)	ED [4]

The M—C bond distances, *R*, and M—C root mean square vibrational amplitudes, *l*, in these molecules except Cp_2Co obtained by gas phase electron diffraction are listed in Table 4. The M—C bond distance of Cp_2Co has been taken from an X-ray study by Bünder and Weiss [5]. It is probable that the value obtained by electron diffraction would be about 0.01 Å greater.

It is seen that the M—C bond distance increases regularly with electron imbalance. The M—C bond distance in Cp_2Ni is somewhat greater than in Cp_2Cr (the difference is greater than the combined uncertainty), indicating that the e_{1g} orbital is more antibonding than the a_{1g} and e_{2g} orbitals are bonding.

It is further seen that the M—C vibrational amplitudes increases with increasing electron imbalance except for Cp_2V where it is very inaccurately determined, probably because of the lack of scattering data at angles larger than $s = 20$ Å^{-1}.

Ferrocene is eclipsed in the gas phase, the barrier to internal rotation of the rings being 0.9(0.3) kcal mol^{-1} [1, 2]. The angle between the C—H bonds and the C_5 ring, which is defined as positive when the bonds are bent towards the metal atom, is 3.7(0.9)° after correction for shrinkage [17]. It would seem reasonable to assume that as the metal-to-ring bond weakens, and hence the ring-to-ring distance increases, the barrier to internal rotation of the rings should decrease and the rings approach planarity.

The electron diffraction data of ferrocene were recorded at 140°. At this temperature the thermal energy is comparable to the barrier height and the concentration of staggered molecules in the gas jet at any instant is about a third of the concentration of eclipsed molecules. Least squares refinements of staggered and eclipsed models with a diagonal weight matrix gave signigicantly better agreement for the eclipsed model, the *R*-factor ratio being 1.21. If in the other molecules under discussion the rotational barrier is lower, the relative concentration of staggered molecules in the gas jet would increase, and the fit obtained by refinement on staggered models should approach that obtained by refinement on eclipsed models. In fact the *R*-factor ratios obtained are: Cp_2Fe, $R = 1.21$; Cp_2Cr, $R = 1.04$; Cp_2V, $R = 1.02$; Cp_2Mn, $R = 1.01$.

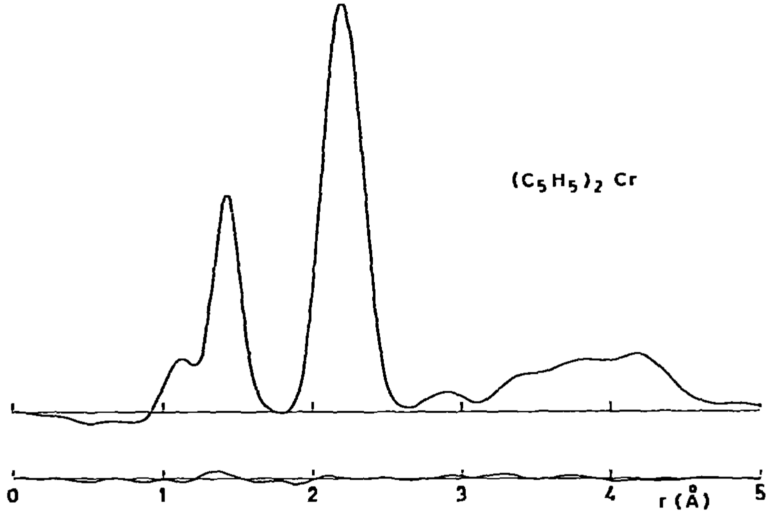

Fig. 4. Upper curve: experimental radial distribution curve for $(C_5H_5)_2Cr$. Lower curve: difference between the experimental curve and theoretical radial distribution curve calculated for best model of D_{5h} symmetry. $k = 0.0025$ Å^2.

Like Cp_2Fe, Cp_2Mn was refined with diagonal weight matrix only [4].

In the investigation of Cp_2Ni no R-factors were listed, but it was stated that eclipsed and staggered models gave equally good fit [3].

The angle $\angle C_5,H$ decreases from 3.7(0.9)° in ferrocene to 2.9(1.1)° in Cp_2Cr, which still is greater than 0° at the 2 % significance level. But in Cp_2Ni $\angle C_5,H = 0.3(1.5)°$ without shrinkage corrections. If it is assumed that this correction is of the same magnitude as in ferrocene, $\angle C_5,H = -0.6(1.5)°$. In any case it is not significantly different from zero. Neither is the angle in Cp_2V,

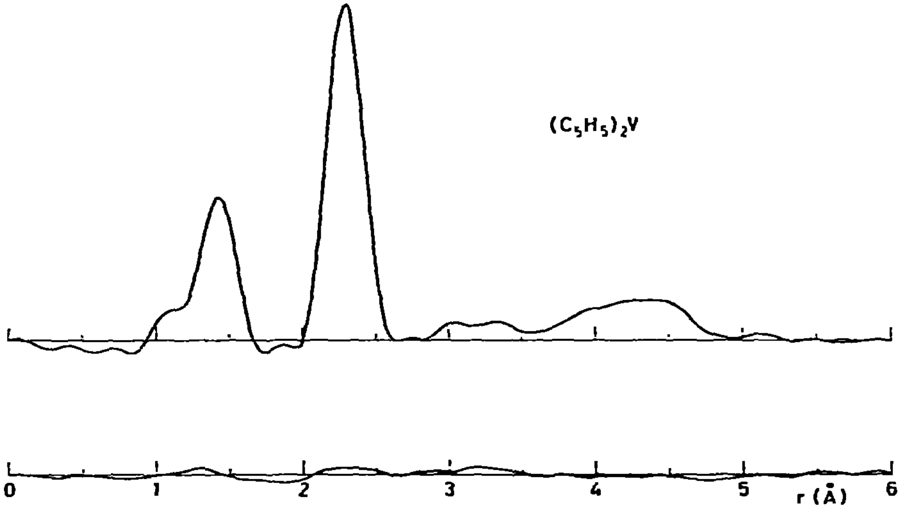

Fig. 5. Upper curve: experimental radial distribution curve for $(C_5H_5)_2V$. Lower curve: difference between the experimental curve and theoretical radial distribution curve calculated for best model of D_{5h} symmetry. $k = 0.0025$ Å^2.

$\angle C_5, H = -1.5(1.6)°$. In Cp_2Mn the M · · · H distance peak in the radial distribution curve overlaps with other peaks, and the value obtained $\angle C_5, H = 6.5(1.4)°$ cannot be regarded with much confidence.

On the whole the available evidence, though not entirely clear cut, indicates that the barrier to rotation of the ligand rings does decrease as the metal to ring distance increases and that the deviation from planarity of the Cp rings decrease as the M—C bonds become weaker. Since Cp_2Co would be expected to show the greatest barrier and greatest deviation from ring planarity after ferrocene, an electron diffraction investigation would clearly be of great interest.

Acknowledgements

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References

1 R.K. Bohn and A. Haaland, J. Organometal. Chem., 5 (1966) 470.
2 A. Haaland and J.E. Nilsson, Acta Chem. Scand., 22 (1968) 2653.
3 L. Hedberg and K. Hedberg, J. Chem. Phys., 53 (1970) 1228.
4 A. Almenningen, A. Haaland and T. Motzfeldt, in Selected Topics in Structure Chemistry, Universitetsforlaget, Oslo, 1967, p. 105.
5 E. Weiss and W. Bünder, private communication; W. Bünder, Doctor's Thesis, Universität Hamburg, 1974.
6 B. Andersen, H.M. Seip, T.G. Strand and R. Stølevik, Acta Chem Scand., 23 (1969) 3224.
7 H.M. Seip, T.G. Strand and R. Stølevik, Chem. Phys. Lett., 3 (1969) 1937.
8 J. Brunvoll, private communication.
9 L. Schäfer, J. Brunvoll and S.J. Cyvin, J. Mol. Struct., 11 (1972) 459.
10 H.P. Fritz, Advan. Organometal. Chem., 1 (1964) 239.
11 M.L.H. Green, Organometallic Compounds, Vol. 2, Methuen, London, 1967, p. 97.
12 M.-M. Coutiere, J. Demuynck and A. Veillard, Theor. Chim. Acta, 27 (1972) 281.
13 E.J. Baerends and P. Ros, Chem. Phys. Lett., 23 (1973) 391.
14 N. Rösch and K.H. Johnson, Chem. Phys. Lett., 24 (1974) 179.
15 S. Evans, M.L.H. Green, B. Jewitt, A.F. Orchard and C.F. Pygall, J. Chem. Soc. Faraday Trans. II, 68 (1972) 1847.
16 S. Evans, M.L.H. Green, B. Jewitt, G.H. King and A.F. Orchard, J. Chem. Soc. Faraday Trans. II, 70 (1974) 356.
17 A. Haaland, J. Lusztyk, J. Brunvoll and K.B. Starowieyski, J. Chem. Soc. Chem. Commun., (1974) 54.