Journal of Organometallic Chemistry, 85 (1975) 279—285

ON THE MOLECULAR STRUCTURE OF DICYCLOPENTADIENYL-MAGNESIUM

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(Received September 9th, 1974)

Summary

The molecular structure of $(C_5H_5)_2Mg$ has been determined by gas phase electron diffraction. The best agreement between calculated and experimental intensity curves is obtained for a model with eclipsed (C_5H_5) rings (symmetry D_{5h}), but a model with staggered rings (symmetry D_{5d}) cannot be ruled out. The Mg—C and C—C bond distances are 2.339(4) and 1.423(2) Å respectively. The nature of the metal-to-ring bonding is discussed and it is concluded that $(C_5H_5)_2Mg$ is best regarded as a covalent rather than an ionic compound.

Introduction

The synthesis of Cp_2Mg (Cp = cyclopentadienyl) was first reported by Wilkinson and Cotton [1] and shortly afterwards by Fischer and Hafner [2]. Since crystalline Cp_2Mg is isomorphous with ferrocene, the molecular geometry, at least in the crystalline phase, is that of a sandwich compound with parallel staggered Cp rings and the metal atom in the middle [3].

The chemical and physical properties of the compound (such as the ready reaction with $FeCl_2$ to yield ferrocene and $MgCl_2$, the vigorous reaction with water, and the conductivity of solutions in liquid NH_3) led Wilkinson and coworkers [4] to conclude that the metal-to-ring bonds in Cp_2Mg are weaker and more ionic than in ferrocene. The ionic nature of the compound was later rationalized in terms of the high energies of the 3*d* and to a lesser extent of the $3p$ atomic orbitals of Mg [5], and it was pointed out that the observed sandwich geometry could be the result of electrostatic repulsion between Cp^- rings.

The infrared and Raman spectra of Cp_2Mg in solution and in the solid state have been recorded and assigned by Lippincott and coworkers [6] who pointed out that the spectra are very similar to those of ferrocene and that the intensity of the asymmetric metal—ring stretch band in the infrared spectrum showed that the charge separation is considerably less than that corresponding to the extreme ionic formulation $Cp^-{}_2Mg^{2+}$.

From a combination of calorimetric and mass spectroscopic data Hull and coworkers [7] determined the mean Mg—Cp bond energy as $\bar{B} = 54.5 \pm 12$ kcal mol^{-1}, which while being considerably smaller than in ferrocene, $\bar{B} = 77$ kcal mol^{-1}, is comparable to the bond energy in Cp_2Ni, 53 kcal mol^{-1}.

Recently the He(I) photoelectron spectrum of Cp_2Mg has been reported and assigned on a semiempirical basis [8]. It is interesting to note that the band assigned to ionization from the e_{1g} molecular orbital, which is a combination of the e_1 π orbitals on the Cp rings with the $3p_x$ and $3p_y$ atomic orbitals of Mg, occurs at 0.9 eV higher energy than the band assigned to the e_{1u} molecular orbital, in which the e_1 π orbitals of the rings can only be combined with $3d_{xz}$ and $3d_{yz}$ orbitals on Mg. Hence it would appear that the metal $3p$ atomic orbitals are more effective in the formation of metal-to-ring bonds than is often assumed.

We now report the determination of the molecular structure of Cp_2Mg in the gas phase by means of electron diffraction. After a preliminary account had appeared [9], Bünder and Weiss informed us about the result of a study by X-ray crystallography [10]. Their results are in good agreement with ours.

Experimental and calculation procedure

Cp_2Mg was synthesized from cyclopentadiene and metallic magnesium at 550° and purified by sublimation [11].

The electron scattering pattern was recorded on Balzers Eldiograph KD-G2. The sample reservoir and nozzle were maintained at about 125° (corresponding to a vapor pressure of about 25 mm Hg [12]). Exposures were made with nozzle to photographic plate distances of about 58 and 19 cm. The optical densities of five plates from the first set were recorded at $\Delta s = 0.125$ $Å^{-1}$ intervals, the optical densities of three plates from the last set were recorded at $\Delta s = 0.250$ $Å^{-1}$ intervals. The data were processed as described by Andersen et al. [13].

Every other modified molecular intensity point obtained from the 58 cm plates is shown in Fig. 1A, the modified molecular intensity points obtained from the 19 cm plates are shown in Fig. 1B.

Theoretical curves were calculated from

$$I^{MgC}(s) = \sum_{i \neq j} \frac{|f_i(s)| \cdot |f_j(s)|}{|f_{Mg}(s)| \cdot |f_C(s)|} \cos[\eta_i(s) - \eta_j(s)] \frac{\sin(R_{ij}s)}{R_{ij}} \exp(-\tfrac{1}{2} l_{ij}{}^2 s^2)$$

The sum extends over all atoms 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.

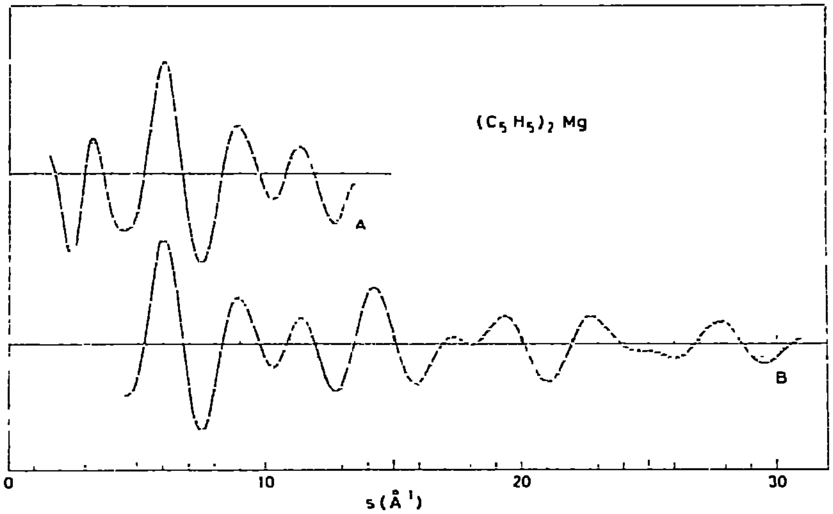

Fig. 1. Experimental modified molecular intensity points from s = 1.25 to 13.50 $Å^{-1}$ (A) and from s = 4.50 to 31.00 $Å^{-1}$ (B). In A only every other experimental point is shown. Full line: theoretical intensity curve calculated for best model of D_{5h} symmetry.

The symmetry force field for Cp_2Fe [14] was modified to reproduce the infrared and Raman spectra of Cp_2Mg [6] and root mean square amplitudes of vibration, *l*, and perpendicular amplitude correction coefficients, *K*, were calculated for models with eclipsed and staggered rings. The amplitudes and *K*

TABLE 1

INTERNUCLEAR DISTANCES (*R*), ROOT MEAN SQUARE VIBRATIONAL AMPLITUDES (*l*) DETERMINED FROM THE ELECTRON DIFFRACTION (ED) DATA AND CALCULATED FROM A MOLECULAR FORCE FIELD (FF), AND PERPENDICULAR AMPLITUDE CORRECTION COEFFICIENTS FOR $(C_5H_5)_2Mg$

Estimated standard deviations are given in parentheses in units of the last digit. The distances are listed as r_a.

	R (Å)	*l* (ED) (Å)	*l* (FF) (Å)	*K* (Å)
C—H	1.116(7)	0.078(7)	0.077	0.0236
C—C	1.423(2)	0.044(1)	0.046	0.0104
Mg—C	2.339(4)	0.103(3)	0.126	0.0031
Mg··· H	3.072(20)	0.179(25)	0.158	0.0086
$C_1 \cdots C_3$	2.301(3)	0.054(3)	0.065	0.0144
$C_1 \cdots C_6$	4.009(8)	0.191(16)	0.252	0.0022
$C_1 \cdots C_7$	4.244(7)	0.255(13)	0.209	0.0020
$C_1 \cdots C_8$	4.613(6)	0.221(11)	0.134	0.0011
$C_1 \cdots H_2$	2.265(6)	0.083(13)	0.101	0.0166
$C_1 \cdots H_3$	3.372(7)	0.120(14)	0.098	0.0163
$C_1 \cdots H_6$	4.176(28)	0.254 [a]	0.254	0.0062
$C_1 \cdots H_7$	4.615(26)	0.236 [a]	0.236	0.0053
$C_1 \cdots H_8$	5.247(23)	0.203 [a]	0.203	0.0042
h	2.008(4)			

$\angle C_5, H = -1.0(1.6)^\circ$

[a] Assumed value.

values obtained by calculations on an eclipsed model are listed in Table 1 for all distances except H···H distances.

The molecular structure was refined by least-squares calculations on the intensity data under the constraints of a geometrically consistent r_α structure, with a non-diagonal weight matrix and a separately refined scale factor for the intensity data obtained for each nozzle-to-plate distance [15]. The standard deviations obtained were expanded to take into account an estimated uncertainty of 0.1 % in the electron wavelength.

Radial distribution curves (Fig. 3) 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 $s = 1.125$ Å^{-1}.

Structure refinement

A molecular model of Cp_2Mg in which the two Cp rings are eclipsed is shown in Fig. 2. 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, e.g. the C—H, C—C, and Mg—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 by refinement on the eclipsed model are listed in Table 1. The amplitudes that were not refined, were fixed at their calculated values. The generalized R factor [15] was $R_3 = 8.23$.

Refinement of a staggered model did not give as good agreement between experimental and calculated intensities: the generalized R factor being $R_3 = 8.59$. Moreover, the values obtained for $\angle C_5$, H = −11.2(3.6) and $l(\mathrm{Mg} \cdots \mathrm{H}) =$ 0.267(45) Å seem unreasonable. The values obtained for the other parameters are not significantly different from those in Table 1.

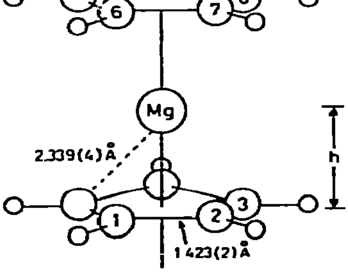

Fig. 2. Molecular model of $(C_5H_5)_2Mg$ with eclipsed rings, symmetry D_{5h}.

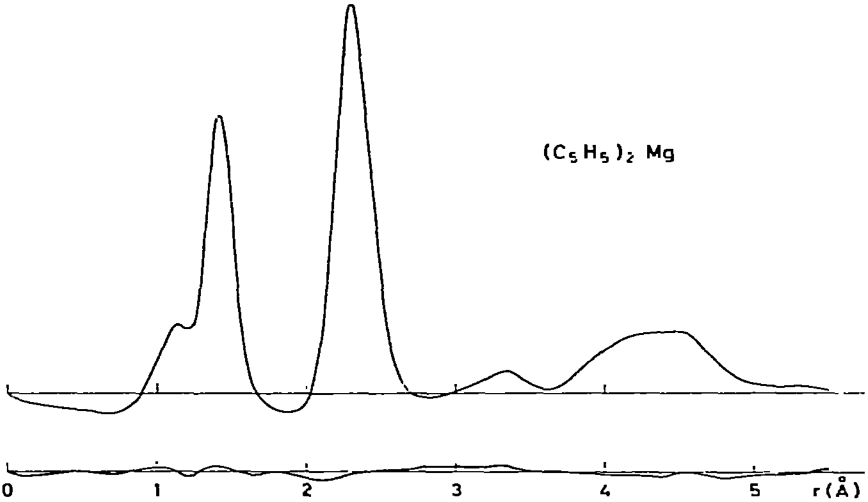

Fig. 3. Upper curve: experimental radial distribution curve for $(C_5H_5)_2Mg$. Lower curve: difference between the experimental curve and theoretical radial distribution function calculated for best model of D_{5h} symmetry.

Discussion

The Mg—C bond distance obtained, 2.339(4), is in agreement with the value obtained by X-ray crystallography [10], 2.304(8) Å, when it is recalled that correction for thermal motion may add a few hundreths of an angstrom to the latter. The Mg—C bond distance in Cp_2Mg is thus considerably shorter than the Mg—C(Cp) distance in $CpMgBr \cdot (C_2H_5)N(CH_2)_2 \cdot N(C_2H_5)_2$, 2.55(5)Å [16]. The difference is hardly surprising, since in the latter compound the Cp ring need only function as a one-electron ligand for the Mg atom to be surrounded by an electron octet.

The mean M—Cp bond energy in Cp_2Mg is comparable to the M—Cp bond energy in Cp_2Ni, but lower than in Cp_2Fe [7]. Comparison of the M—C vibrational amplitudes determined by electron diffraction (Table 2) indicates that metal-to-ring bonding is somewhat weaker in Cp_2Mg than in Cp_2Ni. The same conclusion is reached by considering the symmetric M—Cp stretching frequencies (which are independent of the mass of the metal atom) in the three compounds (Table 2). If the stretching motion is approximated by a three-body model, the force constant of the M—C bonds can be calculated from $\nu_{sym} = (1/2\pi)(f/M)^{1/2}$ where M is the mass of the Cp ring. The resulting force constants indicate that the M—Cp bond is much stronger in Cp_2Fe than in Cp_2Ni, which in turn is slightly stronger than in Cp_2Mg.

The C—C bond distance in Cp_2Mg, 1.423(2), is very similar to the C—C bond distance in $CpBeCH_3$, 1.420(2) [21], or the mean C—C bond distance in $CpAl(CH_3)_2$, 1.422(2) Å [22]. These distances are all significantly shorter than the C—C bond distance in Cp_2Fe, 1.440(2)Å [19]. The bond distance in the latter compound is probably increased as a result of interaction of metal 3*d* electrons with antibonding $e_2(\pi)$ orbitals of the rings.

TABLE 2

MEAN M—Cp BOND ENERGIES ($\bar{B}$), SYMMETRIC M—Cp STRETCHING FREQUENCIES (ν_{sym}), CORRESPONDING M—Cp FORCE CONSTANTS (f_{sym}) AND ROOT MEAN SQUARE VIBRATIONAL AMPLITUDES (l) FOR Cp_2Fe, Cp_2Ni AND Cp_2Mg

	Cp_2Fe	Cp_2Ni	Cp_2Mg
$\bar{B}$ (kcal mol^{-1})	77 ± 12 [a]	53 ± 12 [a]	54 ± 12 [a]
ν_{sym} (cm^{-1})	301 [b]	207 [c]	191 [d]
f_{sym} (mdyn Å^{-1})	3.47	1.64	1.40
l (Å)	0.052(1) [e]	0.084(3) [f]	0.103(3)

[a] Ref. 7. [b] Ref. 17. [c] Ref. 18. [d] Ref. 6. [e] Ref. 19. [f] Ref. 20.

In contrast to Cp_2Fe [19] and Cp_2Cr [9] no significant bending of the C—H bonds out of the plane of the C atoms is detected.

That a better fit is obtained by refinement on an eclipsed than on a staggered model indicates that the equilibrium conformation of Cp_2Mg in the gas phase, like that of Cp_2Fe [19], is eclipsed, but the barrier to internal rotation of the ring is lower than the thermal energy available (0.8 kcal mol^{-1}) so that a considerable fraction of the molecules at a given instant is in or near the staggered conformation. This view is supported by the magnitude of the relative vibrational amplitudes of C atoms in different rings, $l(C_1 \cdots C_6)$, $l(C_1 \cdots C_7)$ and $l(C_1 \cdots C_8)$. In any case it is clear that the staggered conformation adopted in the crystalline environment is determined by packing forces. The heat of sublimation of Cp_2Mg is 15.9 kcal mol^{-1} [12].

In order to obtain insight into the nature of the bonding and the charge distribution, we have performed a series of CNDO/2 molecular orbital calculations [23] on Cp_2Mg using the structure parameters in Table 1. Calculations on eclipsed and staggered models resulted in very small rotation barriers, but favored a staggered equilibrium conformation rather than an eclipsed one. Calculations with an (*sp*) basis [23] indicate that the staggered conformation is more stable than the eclipsed conformation by about 50 cal mol^{-1}, calculations with an (*spd*) basis reduced the difference to about 30 cal mol^{-1}.

The calculations with (*sp*) basis gave a charge of +0.74 electron units on the metal atom, which is considerably less than the charge on the metal atom in Cp_2Fe obtained by ab initio molecular orbital calculations, +1.23 [24]. Inclusion of 3*d* orbitals on Mg in the basis would almost certainly reduce the positive charge on the metal atom: CNDO calculations with an (*spd*) basis, which certainly overestimates the effect of the 3*d* orbitals, resulted in a charge of —0.13. The calculations therefore offer no support for the formulation of Cp_2Mg as an ionic compound, $Cp^-{}_2Mg^{2+}$.

Examination of the molecular orbitals obtained shows that both the 3*s* and 3*p* orbitals on Mg combine with the pertinent π orbitals of the Cp rings [8]:

a_{1g}: $0.20\, s + 0.98\, a_{1g}\, (\pi)$

a_{1u}: $0.17\, p_z + 0.98\, a_{1u}\, (\pi)$

e_{1u}: $0.36\, p_x + 0.93\, e_{1u}\, (\pi)$

e_{1g}: $e_{1g}\, (\pi)$

The energies obtained were in qualitative agreement with the He(I) photoelectron spectra.

In conclusion, we believe that Cp_2Mg is best regarded as a covalent molecule, the bonding between metal and ring being effected mainly by combination of the $3p_x$ and $3p_y$ orbitals on Mg with the e_{1u} π orbitals of the rings. The strength of the M—Cp bond thus formed is comparable or slightly weaker than in Cp_2Ni, though considerably weaker than in ferrocene. The charge separation is probably not greater in Cp_2Mg than in Cp_2Ni or Cp_2Fe.

Acknowledgements

We are grateful to siv. ing. Ragnhild Seip for help in recording the electron scattering data, and to PAN Institute of Low Temperature and Structural Research (Wroclaw), and to the Norwegian Research Council for Science and the Humanities for financial support.

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