Journal of Organometallic Chemistry, 107 (1976) 273—279

DYNAMIC JAHN—TELLER EFFECT AND AVERAGE STRUCTURE OF DICYCLOPENTADIENYLCOBALT, $(C_5H_5)_2Co$, STUDIED BY GAS PHASE ELECTRON DIFFRACTION

ARNE ALMENNINGEN, ELLEN GARD, ARNE HAALAND *,

Department of Chemistry, The University of Oslo, Blindern, Oslo 3 (Norway)

and JON BRUNVOLL

Institute of Theoretical Chemistry, Technical University of Norway, N-7034 Trondheim (Norway)

(Received September 9th, 1975)

Summary

The molecular structure of $(C_5H_5)_2Co$ has been determined by gas phase electron diffraction. The best agreement between calculated and experimental intensity curves is obtained with 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 mean Co—C and C—C bond distances are 2.119(3) Å and 1.429(2) Å respectively. The average angle between the C—H bonds and the C_5 ring is 2.1(0.8)°. The value obtained for the C—C vibrational amplitude, l(C—C) = 0.055(1) Å, is significantly larger than the amplitude calculated from a molecular force field and the corresponding amplitudes in $(C_5H_5)_2Fe$ and $(C_5H_5)_2Ni$ determined by electron diffraction, and confirms the presence of a dynamic Jahn—Teller effect of the magnitude calculated from ESR data. The average structure is compared with those of the metallocenes of the other first row transition elements.

Introduction

We have determined the molecular structure of dicyclopentadienylcobalt (Cp_2Co) in the gas phase by electron diffraction for comparison with the structures of the known metallocenes of the other first row transition elements Cp_2V [1], Cp_2Cr [1], Cp_2Mn [2], Cp_2Fe [3,4] and Cp_2Ni [5]. Among these metallocenes Cp_2Cr and Cp_2Co have orbitally degenerate ground electronic states, $^3E_{2g}$ and $^2E_{1g}$ respectively [6], and would be expected to exhibit Jahn—Teller dis-

---

* To whom correspondence should be addressed.

tortions. Cp_2Co has been carefully investigated by ESR spectroscopy by Ammeter and coworkers [7,8,9]. For an E_{1g} electronic state it follows from group theoretical arguments that to the first order only e_{2g} distortions are Jahn—Teller active. None of the e_{2g} normal modes of a metallocene involves displacement of the metal atom, and the distortions are therefore confined to the Cp rings. Among the e_{2g} normal modes there are asymmetric C—C stretching vibrations and in-plane and out-of-plane CCC deformation modes. Ammeter and coworkers have calculated the Jahn—Teller energy and distortion for the C—C stretching mode [9]. They conclude that the effect is dynamic, the calculated elongations/shortenings of individual bonds being about 0.03 Å.

The molecular structure of Cp_2Co in the crystalline phase has recently been determined by X-ray diffraction by Bünder and Weiss [10]. The Cp rings were found to be parallel and staggered and the effective molecular symmetry was D_{5d}.

While the present investigation was in progress we were informed about the results of another gas phase electron diffraction investigation of Cp_2Co by Hedberg et al. [11].

Experimental and calculation procedures

A sample of Cp_2Co was kindly supplied by Dr. M.L.H. Green, Oxford, and was used without further purification. The electron scattering pattern was

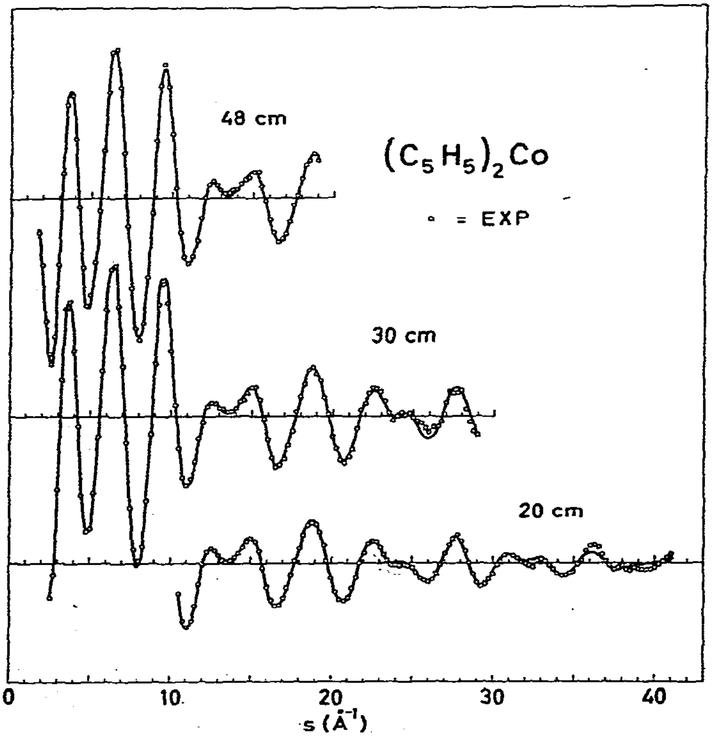

Fig. 1. o: Experimental modified molecular intensity points for $(C_5H_5)_2Co$ from $s = 1.75$ Å^{-1} to 19.00 Å (top curve), from $s = 2.50$ Å^{-1} to 29.00 Å^{-1} (middle curve), and from $s = 10.50$ Å^{-1} to 41.00 Å^{-1}. In the top curve only every second experimental point is shown. Full lines: theoretical intensity curves calculated for best model of D_{5h} symmetry.

TABLE 1

INTERNUCLEAR DISTANCES (*R*), ROOT MEAN SQUARE VIBRATIONAL AMPLITUDES (*l*) DETERMINED BY ELECTRON DIFFRACTION (ED), AND CALCULATED FROM A MOLECULAR FORCE FIELD (FF), AND PERPENDICULAR AMPLITUDE CORRECTION COEFFICIENTS (*K*) FOR $(C_5H_5)_2Co$ (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	1.111(8)	0.084(1)	0.077	0.0200
C—C	1.429(2)	0.055(1)	0.047	0.0059
Co—C	2.119(3)	0.082(1)	0.085	0.0023
Co···H	2.867(9)	0.143(11)	0.125	0.0077
C(1)···C(3)	2.312(3)	0.055(2)	0.064	0.0071
C(1)···C(6)	3.473(5)	0.16(5)	0.156	0.0024
C(1)···C(7)	3.753(5)	0.18(3)	0.133	0.0018
C(1)···C(8)	4.164(5)	0.21(2)	0.091	0.0009
C(1)···H(2)	2.245(7)	0.21(4)	0.100	0.0123
C(1)···H(3)	3.375(8)	0.097(10)	0.098	0.0110
C(1)···H(6)	3.560(15)	0.25(21)	0.190	0.0068
C(1)···H(7)	4.112(13)	0.117(13)	0.180	0.0052
C(1)···H(8)	4.808(12)	0.19(2)	0.154	0.0038
h [a]	1.739(2)			
$\angle C_5$, H [b]	2.1(0.8) °			

[a] Perpendicular distance from the metal atom to the Cp rings. [b] For definition see text.

recorded on the Oslo electron diffraction unit [12] with nozzle to photographic plate distances of about 48, 30 and 20 cm. The optical densities of 6 plates from the first set, 4 plates from the second and 5 plates from the third were processed using the programs described by Andersen et al. [13]. The resulting modified molecular intensity points are shown in Fig. 1.

The molecular force field of ferrocene [14] was modified to reproduce the IR active frequencies listed by Fritz [15] and root mean square amplitudes of vibration, *l*, and perpendicular amplitude correction coefficients, *K*, were calculated for molecular models with eclipsed and staggered Cp rings. The amplitudes and *K* values for all distances except H···H distances by calculations on an eclipsed model are listed in Table 1.

The molecular structure was refined by least squares calculations on the intensity data under the constraints of a geometrically consistent r_α structure using programs written by Seip [13,16]. Theoretical modified molecular intensity curves were calculated from eq. 11 in reference [13]. The final refinements were carried out with a non-diagnoal weight matrix with 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.

The radial distribution curves shown in Fig. 2 were calculated by Fourier inversion of experimental and calculated intensity curves after multiplication with the artificial damping function $\exp(-\frac{1}{2}ks^2)$. The experimental curves were then spliced to each other and to the theoretical curve calculated for the best model below $s = 1.625$ Å^{-1}.

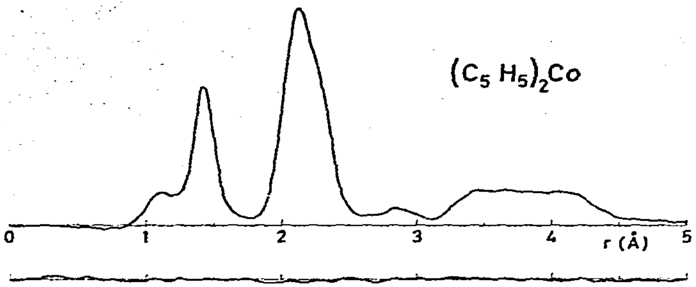

Fig. 2. Upper curve: experimental radial distribution curve for $(C_5H_5)_2Co$. Lower curve: difference between the experimental curve and a theoretical radial distribution curve calculated for best model of D_{5h} symmetry. Artificial damping constant $k = 0.001$ Å^2.

Results and discussion

Structure refinement. A molecular model of Cp_2Co 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 Co—C bond distances and the angle between the C—H bonds and the plane of the ring carbon atoms. This angle is denoted by $\angle C_5$, H and is defined as positive when the C—H bonds are bent towards the metal atom.

The values obtained for the four structure parameters and the root mean square vibrational amplitudes of all distances except H···H distances by least squares refinement of an eclipsed model are listed in Table 1. The H···H amplitudes were fixed at their calculated values. The generalized R factor [16] was $R_3 = 11.23$.

Refinement of a staggered model did not yield quite as good agreement between calculated and experimental intensities, the generalized R factor obtained being $R_3 = 11.58$. None of the parameter values obtained [except of course for the amplitudes of atom pairs on different rings, $l(C\cdots C')$ and $l(C\cdots H')$] differed

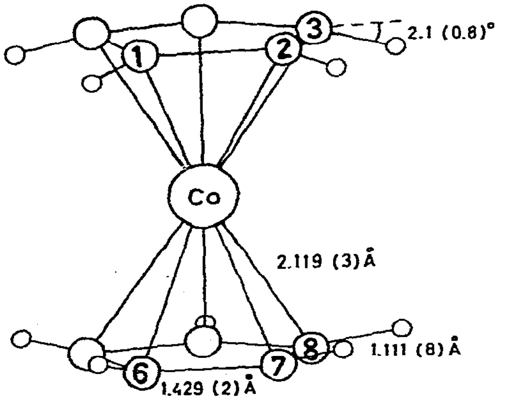

Fig. 3. Molecular model of $(C_5H_5)_2Co$ with eclipsed rings, symmetry D_{5h}.

TABLE 2

ELECTRON CONFIGURATION [6,17] AND GAS PHASE MOLECULAR STRUCTURE 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)	Ref.
$(C_5H_5)_2Fe$	${}^1A_{1g}(a_{1g}{}^2, e_{2g}{}^4)$	0	2.064(3)	0.062(1)	3, 4
$(C_5H_5)_2Co$	${}^2E_{1g}(a_{1g}{}^2, e_{2g}{}^4, e_{1g}{}^1)$	1	2.119(3)	0.082(1)	this work
$(C_5H_5)_2Cr$	${}^3E_{2g}(a_{1g}{}^1, e_{2g}{}^3)$	2	2.169(4)	0.078(2)	1
$(C_5H_5)_2Ni$	${}^3A_{2g}(a_{1g}{}^2, e_{2g}{}^4, e_{1g}{}^2)$	2	2.196(4)	0.084(3)	5
$(C_5H_5)_2V$	${}^4A_{2g}(a_{1g}{}^1, e_{2g}{}^1)$	3	2.280(5)	0.058(10)	1
$(C_5H_5)_2Mn$	${}^6A_{1g}(a_{1g}{}^1, e_{2g}{}^2, e_{1g}{}^2)$	5	2.383(3)	0.135(2)	2

by more than one standard deviation. In particular $\angle C_5, H = 3.0(1.3)^\circ$. We therefore base our discussion on the parameter values listed in Table 2.

The data used in the parallel electron diffraction investigation by Hedberg and coworkers [11] were less extensive than ours, and vibrational corrections were not included in the refinement. Only a limited number of vibrational amplitudes were refined along with the four structure parameters. The values obtained are, however, in excellent agreement with ours:

R(C—H) = 1.095(16) Å
R(C—C) = 1.430(3) Å
R(Co—C) = 2.113(3) Å
$\angle C_5, H = 3.7(3.3)^\circ$

l(C—H) = 0.088(15) Å
l(C—C) = 0.056(3) Å
l(Co—C) = 0.082(4) Å
l(Co···H) = 0.137(29) Å
$l(C_1 \cdots C_3)$ = 0.059(5) Å

The numbers in parentheses are two standard deviations and include estimates of systematic errors. That the Co—C bond distance obtained by Hedberg et al. is 0.006 Å shorter than ours may perhaps be ascribed to the neglect of shrinkage corrections.

Dynamic Jahn—Teller effect. Our structure refinement has been carried out on highly symmetrical models, and the existence of Jahn—Teller distortions have not been considered. The superposition of a dynamic Jahn—Teller effect on the normal vibrations of the molecule would lead to effective amplitudes, l-values, that are larger than those calculated from the molecular force-field or those found in similar but Jahn—Teller inactive compounds. Thus when the elongations/shortenings of individual C—C bonds calculated by Ammeter et al. [9] are superposed on the C—C amplitude calculated from the molecular force-field, the effective l-value should be: $l_{eff} = (0.030^2 + 0.047^2)^{1/2}$ Å = 0.056 Å; in excellent agreement with the observed values. The fact that identical l-values have been obtained in two independent electron diffraction investigations and that both are significantly larger than the C—C amplitudes found in Cp_2Fe, 0.046(1) Å [3] and Cp_2Ni, $0.044(1_5)$ Å [5] leaves no doubt that the effect is real[*].

Before comparing the average structure of Cp_2Co with the structures of the

---

[*] We are not aware of any study of the Jahn—Teller effect in Cp_2Cr, but the C—C amplitude obtained, l(C—C) = 0.049(2) Å [1], indicates that the effect is smaller than in Cp_2Co.

metallocenes of the other first row transition elements, we wish to point out that an e_{2g} CCC out-of-plane deformation distortion would increase the effective Co—C vibrational amplitude and that e_{2g} C—C stretch, e_{2g} CCC in-plane and CCC out-of-plane distortions all would increase the vibrational amplitudes between atom pairs in different rings, thus obscuring the effect of ring libration.

Comparison with the metallocenes of the other first row transition elements. The electron configuration of the metallocenes of the first row transition elements as well as the population in the highest molecular orbitals (a_{1g}, e_{2g} and e_{1g}) [6,17] are listed in Table 2. The a_{1g} and e_{2g} orbitals are probably weakly bonding, the e_{1g} orbital antibonding between the metal atom and the Cp rings. We have already defined 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 pointed out that the M—C bond distance increases with increasing electron imbalance [1]. We have also discussed the effect of increasing electron imbalance and the concommittant weakening of the M—C bond on the vibrational amplitude l(M—C), on $\angle C_5$, H and on the barrier to rotation of the Cp rings.

The values obtained for the M—C bond distance and for $\angle C_5$, H in Cp_2Co conforms to expectations. However, the Co—C vibrational amplitude which is expected to be intermediate between the M—C amplitudes of Cp_2Fe and Cp_2Ni, turns out to be indistinguishable from the latter. The reason may be a dynamic Jahn—Teller effect involving an e_{2g} CCC out-of-plane deformation.

Hedberg et al. [11] who only refined a mean C···C′ amplitude, found that eclipsed and staggered models gave essentially equally good agreement between calculated and observed intensity curves and concluded that the barrier to internal rotation was too low to allow the equilibrium conformation to be determined.

We have refined all six C···C′ and C···H′ amplitudes. A somewhat better agreement was obtained with the eclipsed model indicating that the equilibrium conformation of the molecule is eclipsed. But the generalized R-factor ratio is only $R = R_{stag}/R_{ecl} = 1.03$ and a staggered equilibrium conformation cannot be ruled out.

The equilibrium conformation of Cp_2Fe in the gas phase is eclipsed and the barrier to internal rotation is 0.9(0.3) kcal mol^{-1} [3]. Since among the metallocenes in Table 2 Cp_2Co appears to have the strongest M—Cp bonds after ferrocene, we had hoped that the rotational barrier would be high enough to allow the equilibrium structure to be determined [1]. This expectation has not been fulfilled, perhaps because of the additional motion introduced by the dynamic Jahn—Teller effect.

Investigations of 1,1′-dimethylmanganocene, $(C_5H_4CH_3)_2Mn$, have shown the compound to be in equilibrium between a high spin and a low spin electronic state in the gas phase and in hydrocarbon solutions [6,18,19]. The high spin state, $^6A_{1g}$ (a_{1g}^1, e_{2g}^2, e_{1g}^2), is analogous to the ground state of unsubstituted Cp_2Mn, and the Mn—C bond distance in this state should therefore be about 2.38 Å. But the low spin state, $^2E_{2g}$(a_{1g}^2, e_{2g}^3), has an electron imbalance equal to one, and the structure should be similar to that of Cp_2Co, i.e. R(M—C) = 2.12 Å. A gas phase electron diffraction investigation of $(C_5H_4CH_3)_2Mn$ has been initiated.

The M—C bond distances in Table 2 should not be regarded as standard

M—C(Cp) bond distances. As pointed out by Bünder and Weiss [10] in the case of cobaltocene, the exchange of one Cp ring for one or more ligands resulting in a different number of electrons in the valence shell of the metal atom is expected to alter the distance between the metal atom and the remaining Cp ring. In particular complexes with a noble gas electron configuration about the metal (like Cp_2Fe) are expected to exhibit shorter M—C(Cp) distances than the open shell species in Table 2. Thus the Mn—C(Cp) distance in $CpMn(CO)_3$ is 2.165(25) Å [20], and the Ni—C distance in CpNiNO determined by microwave spectroscopy 2.112 Å [21].

Acknowledgements

We are grateful to Professor K. Hedberg for communicating the results of their work on Cp_2Co, to Dr. M.L.H. Green for the sample, and to the Norwegian Reserach Council for Science and the Humanities for financial support.

References

1 E. Gard, A. Haaland, D.P. Novak and R. Seip, J. Organometal. Chem., 88 (1975) 181.
2 A. Almenningen, A. Haaland and T. Motzfeldt, in Selected Topics in Structure Chemistry, Universitetsforlaget, Oslo, 1967, p. 105.
3 A. Haaland and J.E. Nilsson, Acta Chem. Scand., 22 (1968) 2653.
4 A. Haaland, J. Lusztyk, D.P. Novak, J. Brunvoll and K.B. Starowieyski, J. Chem. Soc., Chem. Commun., (1974) 54.
5 L. Hedberg and K. Hedberg, J. Chem. Phys., 53 (1970) 1228.
6 S. Evans, M.L.H. Green, B. Jewitt, G.H. King and A.F. Orchard, J. Chem. Soc. Faraday Trans. II, 70 (1974) 356.
7 J.H. Ammeter and J.D. Swalen, J. Chem. Phys., 57 (1972) 678.
8 J.H. Ammeter and J.M. Brom, Chem. Phys. Lett., 27 (1974) 380.
9 J.H. Ammeter, N. Oswald and R. Bucher, Helv. Chim. Acta, 58 (1975) 671.
10 W. Bünder and E. Weiss, J. Organometal. Chem., 92 (1975) 65.
11 A.K. Hedberg, L. Hedberg and K. Hedberg, J. Chem. Phys., in press.
12 O. Bastiansen, O. Hassel and E. Risberg, Acta Chem. Scand., 9 (1955) 232.
13 B. Andersen, H.M. Seip, T.G. Strand and R. Stølevik, Acta Chem. Scand., 23 (1969) 3224.
14 L. Schäfer, J. Brunvoll and S.J. Cyvin, J. Mol. Struct., 11 (1972) 459.
15 H.P. Fritz, Advan. Organometal. Chem., 1 (1964) 239.
16 H.M. Seip, T.G. Strand and R. Stølevik, Chem. Phys. Lett., 3 (1969) 1937.
17 S. Evans, M.L.H. Green, B. Jewitt, A.F. Orchard and C.F. Pygall, J. Chem. Soc. Faraday Trans. II, 68 (1972) 1847.
18 M.E. Schwitzer, R. Wang, M.F. Rettig and A.H. Maki, J. Amer. Chem. Soc., 96 (1974) 7669.
19 J.H. Ammeter, R. Bucher and N. Oswald, J. Amer. Chem. Soc., 96 (1974) 7833.
20 A.F. Bernd and R.E. Marsh, Acta Cryst., 16 (1963) 118.
21 A.P. Cox, private communication.