Journal of Organometallic Chemistry, 102 (1975) 339—343

JAHN—TELLER EFFECTS IN METALLOCENES AND RELATED SPECIES

C. GLIDEWELL
Chemistry Department, University of St. Andrews, Fife KY16 9ST (Great Britain)
(Received July 3rd, 1975)

Summary

The Jahn—Teller effect is invoked to rationalise the observed structures of $(C_5H_5)_2M$ for M = Be, Sn and Pb, and of the slipped dicarbollide complexes $(C_2B_9H_{11})_2M^{-z}$ (M = Ni^{II}, Cu^{II}, Cu^{III} and Au^{III}).

Introduction

The *d*-block metallocenes, $(\eta^5\text{-}C_5H_5)_2M$, whose structures have been determined (M = Mn [1], Fe [2,3,4], Ni [5,6], Ru [4] and Os [7]) all have five-fold axial symmetry with the metal atom equidistant from the two rings. In addition those with M = V [8], Cr [9] or Co [10] appear to be isostructural with ferrocene [2]. By contrast, the *p*-block analogues are less symmetrical: $(\eta^5\text{-}C_5H_5)_2Be$ has five-fold symmetry, but the beryllium atom is not equidistant from the two rings [11], while in $(\eta^5\text{-}C_5H_5)_2Sn$ and $(\eta^5\text{-}C_5H_5)_2Pb$ the ring centres subtend angles at the metal atom of ca. 125° and 135° respectively [12]. It is the purpose of this communication to analyse such structures in terms of the second-order Jahn—Teller effect [13].

Results and discussion

The basis of this approach is the symmetry of an idealised molecule and its energy levels. A molecule is considered to have a certain initial geometry, here taken as axially symmetric with both rings equidistant from the metal atom: suppose the symmetry species of the HOMO and LUMO in this geometry are Γ_0 and Γ_1 respectively; then if the electronic excitation energy $E_1 - E_0$ is not too great, the molecule may distort spontaneously along a vibrational coordinate q whose symmetry species is contained in the direct product $\Gamma_0 \times \Gamma_1$. This may be justified by reference [13] to the form of the force constant f_q for the vibration along q:

$$f_q = \tfrac{1}{2}\langle\Psi_0\left|\frac{\partial^2 U}{\partial q^2}\right|\Psi_0\rangle - \sum_k \frac{[\langle\Psi_0\left|\frac{\partial U}{\partial q}\right|\Psi_k\rangle]^2}{E_k - E_0}$$

TABLE 1

SYMMETRY CLASSES OF RING AND METAL ORBITALS IN D_5 METALLOCENES

	D_{5h}	D_{5d}	D_5
I. Ring orbitals			
(a) Radial	$A_1' + E_1' + A_2'' + E_1''$ (bonding) $E_2' + E_2''$ (antibonding)	$A_{1g} + E_{1g} + A_{2u} + E_{1u}$ (bonding) $E_{2g} + E_{2u}$ (antibonding)	$A_1 + A_2 + 2E_1$ (bonding) $2E_2$ (antibonding)
(b) Tangential ($\parallel C_5$)	$A_1' + E_1' + A_2'' + E_1''$ (bonding) $E_2' + E_2''$ (antibonding)	$A_{1g} + E_{1g} + A_{2u} + E_{1u}$ (bonding) $E_{2g} + E_{2u}$ (antibonding)	$A_1 + A_2 + 2E_1$ (bonding) $2E_2$ (antibonding)
(c) Tangential ($\perp rC_5$)	$E_2' + E_2''$ (bonding) $A_2' + E_1' + A_1'' + E_1''$ (antibonding)	$E_{2g} + E_{2u}$ (bonding) $A_{2g} + E_{1g} + A_{1u} + E_{1u}$ (antibonding)	$2E_2$ (bonding) $A_1 + A_2 + 2E_1$ (antibonding)
II. Metal orbitals			
ns	A_1'	A_{1g}	A_1
np	$E_1' + A_2''$	$A_{2u} + E_{1u}$	$A_2 + E_1$
nd	$A_1' + E_2' + E_1''$	$A_{1g} + E_{1g} + E_{2g}$	$A_1 + E_1 + E_2$

where Ψ_0 and Ψ_k are ground and excited state wave-functions, having energies E_0 and E_k respectively and U represents the total potential energy of the system. If the approximation be made that only the lowest excited state of the system is considered, then f_q becomes:

$$f_q = \tfrac{1}{2}\langle\Psi_0\left|\frac{\partial^2 U}{\partial q^2}\right|\Psi_0\rangle - \frac{[\langle\Psi_0\left|\frac{\partial U}{\partial q}\right|\Psi_1\rangle]^2}{E_1 - E_0}$$

Both terms in f_q are positive, but depending on their relative magnitudes f_q may be: (1) positive, in which case the system executes small amplitude vibrations; (2) approximately zero, when the vibrational amplitudes are large; and (3) negative (especially when $E_1 - E_0$ is small), in which case the system distorts along a coordinate q such that Γ_q is contained in $\Gamma_0 \times \Gamma_1$, which is the condition necessary for $\langle\Psi_0|\partial U/\partial q|\Psi_1\rangle$ to be non-zero.

There seems to have been no calculation which orders all the orbital energy levels in metallocenes, but a simple ordering based largely on symmetry ground is adequate for the present purpose. For the axial systems the appropriate molecular point groups, assuming the molecule to be normally rigid, are D_{5h} (as found for M = Fe [4], Ni [5], Ru [4] and Os [7]), D_{5d} (in $(C_5H_5)_2Be$ the rings are staggered [11]) or D_5. Taking a basis set of carbon $2p$ orbitals for the ring bonding, these may be factorised into three groups: (1) those radial to a ring; (2) those tangential to a ring and parallel to the C_5 axis; and (3) those tangential to a ring and normal to the C_5 axis: no symmetry operation of the molecule can interconvert these groups. The transformation properties of these orbital groups, and their bonding character, are noted for D_{5h}, D_{5d}, and D_5 in Table 1.

It is reasonable to suppose that the inter-carbon orbital interactions decrease in the order: radial > tangential ($\perp r C_5$) > tangential ($\parallel C_5$), and that the metal orbitals, taken as $2s + 2p$ for Be, $5s + 5p + 5d$ for Sn, and $6s + 6p + 6d$ for Pb, interact most strongly with the parallel tangential set of ring orbitals. On this basis, plausible configurations for $(C_5H_5)_2M$, linear at M, are for M = Be:

in D_{5h}

$(1a_1')^2(1a_2'')^2(1e_2')^4(1e_2'')^4(2a_1')^2(2a_2'')^2(1e_1')^4(1e_1'')^4(2e_1')^4(2e_1'')^4(2e_1')^0(3e_1'')^0$ ...

and in D_{5d}

$(1a_{1g})^2(1a_{2u})^2(1e_{2u})^4(1e_{2g})^4(2a_{1g})^2(2a_{2u})^2(1e_{1u})^4(1e_{1g})^4(2e_{1u})^4(2e_{1g})^4(3e_{1u})^0(3e_{1g})^0$ ...

while for M = Sn and Pb, the configurations are:

in D_{5h}

$(1a_1')^2(1a_2'')^2(1e_2')^4(1e_2'')^4(2a_1')^2(2a_2'')^2(1e_1')^4(1e_1'')^4(2e_1')^4(2e_1'')^4(3e_1')^2(2e_2')^0$ ...

and in D_{5d}

$(1a_{1g})^2(1a_{2u})^2(1e_{2u})^4(1e_{2g})^4(2a_{1g})^2(2a_{2u})^2(1e_{1u})^4(1e_{1g})^4(2e_{1u})^4(2e_{1g})^4(3e_{1u})^2(2e_{2g})^0$ ...

with configurations in D_5 following from these.

If the first electronic excitation energy is less than ca. 4 eV, as seems likely

[14], then the beryllium compound will distort along a vibrational coordinate q whose symmetry species is contained for D_{5h} in the direct product: $E'_1 \times E''_1 = A''_1 + A''_2 + E''_2$; and for D_{5d} in $E_{1u} \times E_{1g} = A_{1u} + A_{2u} + E_{2u}$. Of the vibrations of a metallocene in either of these point groups, those of symmetry A''_2 in D_{5h} or A_{2u} in D_{5d} generate the observed distortion. Similarly for the tin and lead compounds, the symmetry species of the distortion is contained for D_{5h} in the product: $E'_1 \times E'_2 = E'_1 + E'_2$; and for D_{5d} in $E_{1u} \times E_{2g} = E_{1u} + E_{2u}$. Vibrations of symmetry types E'_1 in D_{5h} and E_{1u} in D_{5d} generate the observed distortions.

The possibility that the rings in the initial structure are in essentially free rotation must also be considered: this appears to be the case for $(C_5H_5)_2Mn$ [1] and $(C_5H_5)_2Ni$ [6], while rotational barriers are small in both $(C_5H_5)_2Fe$ and $(C_5H_5)_2Ru$ [4]. The rigid-molecule point groups D_5, D_{5d} and D_{5h} cannot then be used, and the appropriate group is the nuclear permutation group ${}^2G_{100}$ [15]. However, it is permissible in these circumstances [16] to regard the cyclopentadienide ligands as compound atoms, denoted by L, and to consider the molecule ML_2 in the point group $D_{\infty h}$ in which L has pseudo-atomic orbitals of symmetry types $\sigma + 2\pi + 2\delta$: BeL_2 is then regarded as a 12 valence-electron triatomic and SnL_2 and PbL_2 as 14 valence-electron species. Following Walsh [17], plausible valence-shell configurations are, for linear BeL_2:

$$(1\sigma_g)^2(1\sigma_u)^2(1\pi_u)^4(1\pi_g)^4(2\pi_u)^0(2\sigma_g)^0 \ ...$$

and for linear SnL_2 and PbL_2:

$$(1\sigma_g)^2(1\sigma_u)^2(1\pi_u)^4(1\pi_g)^4(2\pi_u)^2(2\sigma_g)^0 \ ...$$

BeL_2 may therefore be subject to distortion along a vibration whose symmetry species is contained in $\Pi_g \times \Pi_u = \Sigma_u^+ + \Sigma_u^- + \Delta_u$ while SnL_2 and PbL_2 are expected to distort along a vibration whose symmetry species is $\Pi_u \times \Sigma_g = \Pi_u$. The vibrational modes of a linear ML_2 molecule are of symmetries Σ_g^+, Π_u and Σ_u^+ (corresponding to ν_1, ν_2 and ν_3 respectively in Herzberg's numbering [18]). The only possible distorting vibrations, therefore, are Σ_u^+ for BeL_2 and Π_u for SnL_2 and PbL_2, in each example corresponding to the distortion observed experimentally.

Closely related to the metallocenes are the bis-dicarbollide complexes $(C_2B_9H_{11})_2M^{-Z}$. Those containing metal atoms whose formal oxidation states imply six or fewer d electrons are axially symmetric (i.e. M = Cr^{III} (d^3) [19], Co^{III} and Ni^{IV} (d^6) [20,21]); in addition the mixed d^5 complex $C_5H_5Fe^{III}C_2B_9H_{11}$ is also axially symmetric [22]. By contrast, those containing formally d^8 or d^9 metals have slipped structures which while centrosymmetric have the five-fold axes of the individual ligands parallel rather than colinear: these include complexes having M = Cu^{II} (d^9) [23], Ni^{II}, Cu^{III} and Au^{III} (d^8) [24]. Adopting the rigid-molecule approximation in D_{5d} (the dicarbollide ions in these complexes are found always to be staggered), and regarding the ligands as 6 electron donors, the following simplified valence-shell configuration results for a $d^{(6+p)}$ metal:

$$(1a_{1g})^2(1a_{2u})^2(1e_{1u})^4(1e_{1g})^4(2a_{1g})^2(1e_{2g})^4(2e_{1u})^p(2a_{2u})^0 \ ...$$

For a d^8 metal, $p = 2$, and the system may be unstable to a vibration of symmetry species $E_{1u} \times A_{2u} = E_{1g}$. For a d^9 metal, $p = 3$, and the system is unstable to a first-order Jahn—Teller distortion along a non-totally symmetric vibrational coordinate whose symmetry species is contained in $(E_{1u})^2 = A_{1g} + A_{2g} + E_{2g}$. Distortions along vibrations of either E_{1g} or E_{2g} symmetry will generate the observed structures. It is perhaps worth noting here that in an accurate electron diffraction study of the formally d^8 system $(C_5H_5)_2Ni$ [6], the authors found some evidence for the occurrence of a Jahn—Teller distortion (presumably second-order, since the compound has two unpaired electrons in $e_{1u}(D_{5d})$ or $e_1'(D_{5h})$ [25]), but were unable closely to define the nature of the distortion.

For a d^7 metal, $p = 1$, and behaviour analogous to d^9 is expected. For a d^6 metal, $p = 0$, but no Jahn-Teller distortion is expected since $E(1e_{2g}) - E(2e_{1u})$ is substantial [14]. For d^3 and d^5, first-order Jahn—Teller distortions are anticipated to be small; $1e_{2g}$ is approximately non-bonding and for degeneracies in orbitals not greatly involved in bonding the magnitude of the distortion is generally found to be small, or undetectable by diffraction methods, possible because of a dynamical interchange between several Jahn—Teller extrema [26]. It may also be noted that no accurate structure determinations appear to have been reported for those metallocenes expected to be subject to first-order Jahn—Teller distortions: the formally d^5 system $(C_5H_5)_2Fe^+I_3^-$, for example, exhibits disorder in the crystal, so that no detailed conclusions could be drawn about the structure of $(C_5H_5)_2Fe^+$ [27].

The results discussed above demonstrate that the second-order Jahn—Teller effect is a powerful aid to the understanding of the molecular geometry of metallocenes and their analogues, in that it predicts the nature of any deviation from the idealised geometry without requiring any calculations.

References

1 A. Almenningen, A. Haaland and T. Motzfeld, in P. Andersen, O. Bastiansen and S. Furberg (Eds.), Selected Topics in Structure Chemistry, Universitetsforlaget, Oslo, 1967, p. 105.
2 J.D. Dunitz, L.E. Orgel and A. Rich, Acta Crystallogr., 9 (1956) 373.
3 B.T.M. Willis, Acta Crystallogr. A, 13 (1960) 114.
4 A. Haaland and J.E. Nilsson, Acta Chem. Scand., 22 (1968) 17.
5 I.A. Ronova, D.A. Bochvar, A.L. Chistjakov, Y.T. Struchkov and N.V. Alekseev, J. Organometal. Chem., 18 (1969) 337.
6 L. Hedberg and K. Hedberg, J. Chem. Phys., 53 (1970) 1228.
7 F. Jellinek, Z. Naturforsch., 14b (1959) 737.
8 E. Weiss and E.O. Fischer, Z. Anorg. Allg. Chem., 278 (1955) 219.
9 E. Weiss and E.O. Fischer, Z. Anorg. Allg. Chem., 284 (1956) 69.
10 W. Pfab and E.O. Fischer, Z. Anorg. Allg. Chem., 274 (1953) 317.
11 A. Haaland, Acta Chem. Scand., 22 (1968) 3030.
12 A. Almenningen, A. Haaland and T. Motzfeld, J. Organometal. Chem., 7 (1967) 97.
13 R.F.W. Bader, Mol. Phys., 3 (1960) 137; Can. J. Chem., 40 (1962) 1164.
14 E.M. Shustorovich and M.E. Dyatkina, Dokl. Akad. Nauk. SSSR., 128 (1959) 1234.
15 P.R. Bunker, Mol. Phys., 9 (1965) 247.
16 P.R. Bunker, J. Chem. Phys., 42 (1965) 2991.
17 A.D. Walsh, J. Chem. Soc. (1953) 2266.
18 G. Herzberg, Infra-red and Raman Spectra, D. Van Nostrand, Princeton, N.J., 1945.
19 D. St. Clair, A. Zalkin and D.H. Templeton, Inorg. Chem., 10 (1971) 2587.
20 A. Zalkin, T.E. Hopkins and D.H. Templeton, Inorg. Chem., 6 (1971) 1911.
21 M.R. Churchill and K. Gold, J. Amer. Chem. Soc., 92 (1970) 1180.
22 A. Zalkin, D.H. Templeton and T.E. Hopkins, J. Amer. Chem. Soc., 87 (1965) 8988.
23 R.M. Wing, J. Amer. Chem. Soc., 89 (1967) 5599.
24 R.M. Wing, J. Amer. Chem. Soc., 90 (1968) 4828.
25 G. Wilkinson, P.L. Pauson and F.A. Cotton, J. Amer. Chem. Soc., 76 (1954) 1970.
26 A.D. Liehr, J. Phys. Chem., 67 (1963) 389.
27 T. Bernstein and F.H. Herbstein, Acta Crystallogr. B, 24 (1968) 1640.