

LIGAND FIELD MODEL AND d-d SPECTRA OF d^N METALLOCENE COMPLEXES

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Received September 12, 2000

Accepted December 15, 2000

Dedicated to the memory of Professor Antonín A. Vlček.

Complete ligand field calculations, including spin-orbit coupling, have been carried out for bent d¹ metallocene complexes, [M(Cp)₂L_n] (Cp = η⁵-cyclopentadienyl, n = 1 or 2), in C_{2v} symmetry. Using the strong-field coupling formalism (with exclusion of spin-orbit coupling) the full energy matrices for d², d³, and d⁴ bent metallocenes were constructed in terms of four ligand field splitting parameters and two Racah interelectronic repulsion parameters (only d² energy matrices are presented here). The bonding in the bent d¹ C_{2v} M(Cp)₂ fragment was analyzed from the point of view of the ligand field model. The experimental d-d transition energies of two d¹ metallocene dichlorides, vanadocene and niobocene dichlorides, have been assigned, the values of four one-electron ligand field splitting parameters determined and the effect of spin-orbit coupling estimated. The ground state of both d¹ metallocene dichlorides has shown to be ²A(1a₁⁺), the d-orbital energy order being 1a₁ < b₁ < b₂ < 2a₁ < a₂. Finally, the prediction of d-d spectra for d², d³, and d⁴ bent metallocene complexes is presented.

Keywords: Ligand field theory; Bent metallocene complexes; One-electron d-orbital energies; Spin-orbit coupling; Strong-field energy matrices; d-d Spectra; Vanadocene dichloride; Niobocene dichloride; Sandwich complexes.

Bent d^N metallocene complexes of the [M(Cp)₂L_n] type, where N = 0–4, n = 1–3, Cp = η⁵-C₅H₅ or η⁵-C₅(CH₃)₅, M is a first- or second-row transition metal, and L is an additional ligand with various bonding capabilities, such as π donor, only σ donor or π acceptor, have a remarkable rich chemistry¹. They are noted for two pervasive structural features: first, the two cyclopentadienyl rings are bent back from the parallel (“straight”) geometry found for 3d^N (N = 3–8) [M(Cp)₂] metallocenes, and, second, the L_n ligands

are forced to lie in a common plane bisecting the angle between the normals to the cyclopentadienyl rings. Among a vast variety of bent metallocenes, the halide derivatives have attracted considerable attention because of their catalytic activities in alkene polymerization², potent antitumor³ and potential third-order non-linear optical properties⁴. Consequently, the molecular and electronic structures of bent d^N metallocene complexes have been the subject of a series of experimental and theoretical investigations. For example, with d^1 and d^2 mono- and dihalides, X-ray diffraction studies have been carried out for the determination of crystal and molecular structures⁵, IR and Raman spectroscopies have been used for the ring and skeletal modes assignments⁶, mass spectrometry for the identification of molecular fragmentation patterns^{7a}, EPR spectroscopy for the analysis of hyperfine^{5b,5e,6a,7} and ligand superhyperfine splittings^{7h,8} as well as for obtaining covalency parameters, photoelectron spectroscopy for the location of occupied d-orbital and ligand-orbital energy levels⁹, and ¹H and ¹³C NMR spectroscopy of the paramagnetic d^2 vanadocene monohalides has been used for analyzing the ground-state wave function¹⁰. As far as theoretical investigation is concerned, it is well known that the effect of ligands on electronic properties of transition metal ions in coordination compounds has been studied by two familiar methods: molecular orbital (MO) theory, taking into account both metal and ligand orbitals, and ligand field theory (LFT) invoking only metal d orbitals and expressing ligand fields in terms of parameters which are determined from experimental data. There is no lack of the MO calculations for bent metallocene halide complexes, but, unfortunately, these are most often devoted only to d^0 metallocene dihalides. Only a few d^1 and d^2 metallocene dichlorides have been investigated by extended Hückel^{7b,12a,12b} and Fenske–Hall^{12c} MO calculations. The best known bonding model for bent d^N ($N = 0-4$) metallocenes is due to Lauher and Hoffmann¹³. This model was obtained by bending the straight D_{5h} metallocene molecular system to C_{2v} symmetry, put on a quantitative basis by extended Hückel calculation and complemented by interaction and correlation diagrams using the “molecules-in-molecules” methodology.

To attack some problems of the electronic structure of bent d^N ($N = 1-4$) metallocene complexes and to account for their optical and magnetic properties, it is possible to apply the other approach mentioned above, the LFT, which was successfully applied to a series of d^N ($N = 3-8$) metallocenes $[M(\text{Cp})_2]$ ($M = \text{V, Cr, Mn, Fe, Ru, Co, Ni}$) and some of their sandwich analogues¹⁴. The utility of the LFT for assignment of the low-energy d-d transitions in optical spectra of these transition metal sandwich complexes is now generally accepted^{14f}. Experimental evidence as well as MO calcula-

tions suggest that the classic LFT approach may be applicable to bent d^N metallocene complexes, particularly to those containing simple monoatomic L ligands. Thus, the electronic spectra of permethylated titanocene monohalides^{5e}, vanadocene, niobocene, and molybdenocene dichlorides^{7b,7g,11,12a} were analyzed on the basis that the low-energy bands represented d-d transitions, while the EPR spectra of permethylated titanocene monohalides^{5e,7f} and vanadocene and niobocene dihalides^{7a-7e,7g,7h,8b} were interpreted in terms of d^1 configuration ground states. Hence, if this assumption concerning the ground state levels could be made, it was reasonable to suppose that the excited states of such d^1 and other d^N configurations could also be treated within the framework of the well-tried LFT.

Very recently, the investigations and calculations of ligand field excited states, splitting parameters, multiplet splittings and ligand field interactions for some transition metal and lanthanoid ions in ligand environments of high symmetry were carried out by using a combination of the density functional theory (DFT) and LFT (*e.g.*, refs^{15a-15e}) or the so-called combined LFT/DFT (or CLDT) method (*e.g.*, ref.^{15f}). We believe that the traditional LFT method should be applied to the low-symmetry bent d^N metallocene complexes with the aim to obtain numerical values of the required ligand field parameters and to assign all the experimental d-d transitions as a prerequisite for subsequent application of more sophisticated methods such as DFT/LFT or CLDT.

Thus, in order to develop the LFT for bent d^N metallocene complexes, complete C_{2v} ligand field energies including spin-orbit coupling for d^1 configuration and full strong-field energy matrices (with spin-orbit coupling exclusion) for d^2 , d^3 and d^4 configurations have been calculated. Using these results, the C_{2v} bent metallocene fragment has been analyzed, the available d-d spectra of two d^1 dihalides assigned and the acquired values of one-electron LF splitting parameters discussed. Finally, general predictions of d-d transitions have been made for those many d-electron bent metallocenes for which the available spectra are of poor quality or even lacking.

THEORETICAL

If the conformation of the two η^5 -bonded cyclopentadienyl rings is eclipsed, $[M(Cp)_2L_n]$ ($n = 1$ or 2) molecules have C_{2v} symmetry, whereas the staggered rings have C_s symmetry. Both eclipsed and staggered conformations have been found in the solid state⁵ and the energy difference between them appears trivial. Moreover, NMR results¹⁶ indicate that the cyclo-

pentadienyl rings possess an internal rotation degree of freedom. To make maximum use of symmetry, we base our ligand field model on the highest possible symmetry, C_{2v} , and adopt the coordinate system shown in Fig. 1 (*i.e.*, the system consistent with that of Lauher and Hoffmann¹³).

The problem to be solved is the effect of the C_{2v} ligand field produced by two η^5 -bonded cyclopentadienyl rings and one or two additional ligands on the central transition metal d^N ($N = 1-4$) ion. The ligand field calculation for a given d^N configuration consists in the construction of the perturbation matrices of elements

$$H'_{mm} = \langle \Psi_m | \hat{H}' | \Psi_n \rangle, \quad (1)$$

where

$$\hat{H}' = \sum_{i=1}^N \hat{V}_{LF}(i) + \sum_{i < j}^N e^2 / (4\pi\epsilon_0 r_{ij}) + \sum_{i=1}^N \xi(r_i) \hat{L}_i \cdot \hat{S}_i. \quad (2)$$

Here the first term represents the potential of d electrons of the central metal ion in the ligand field, the second term the interelectronic Coulombic repulsion, and the last spin-orbit couplings. The i and j symbols refer to the i -th and j -th d electrons. The Ψ_m and Ψ_n are appropriate linear combinations of antisymmetrized determinantal functions. In making up the latter symmetry-related wavefunctions, we have employed the strong-field coupling scheme which is much more convenient in the case of metallocene compounds than the weak-field coupling alternative^{14f}. An ac-

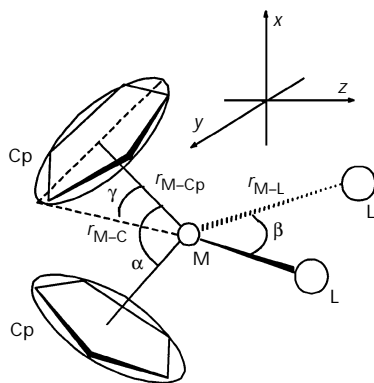


FIG. 1
Bent metallocene $[M(Cp)_2L_2]$ complex

count of the basic ligand field approach applied to d^N metallocenes has been given formerly^{14b}. Very recently, the clear and instructive explanation of the one- and many-electron ligand field methodology presented in a highly didactic style has been given by Lever and Solomon¹⁷.

One-Electron C_{2v} Ligand Field Theory (d^1 Configuration)

Construction of the \hat{V}_{LF} . The one-electron ligand field potential experienced by single d electron in the ligand field can be expanded as follows

$$\hat{V}_{LF} = \sum_K \sum_Q A_K^Q Y_K^Q(\theta, \phi) (r_{<}^K / r_{>}^{K+1}), \quad (3)$$

where the A_K^Q are expansion coefficients, the $Y_K^Q(\theta, \phi)$ are spherical harmonics, and $(r_{<}^K / r_{>}^{K+1})$ is lesser (greater) of the two distances, r , the distance of the d electron from the central metal ion nucleus, and $r_{M-ligand}$, the metal ion–ligand distance. For d electrons, $K = 0, 2, 4$. Since \hat{V}_{LF} represents the ligand field, it must be invariant to all the symmetry operations, \hat{O}_R , of the respective point symmetry group. In the case of the C_{2v} group, the invariance requirement is fulfilled when $|Q| = 0, 2, 4$ ($\hat{O}_R = \hat{C}_2$) and $A_2^2 = A_2^{-2}$, $A_4^2 = A_4^{-2}$, $A_4^4 = A_4^{-4}$ ($\hat{O}_R = \hat{\sigma}_v(xz), \hat{\sigma}_v(yz)$). Therefore, the effective and exact one-electron potential for the C_{2v} ligand field is

$$\begin{aligned} \hat{V}_{LF} = & A_0^0 Y_0^0 (1/r_{>}) + A_2^0 Y_2^0 (r_{<}^2 / r_{>}^3) + A_2^2 (Y_2^2 + Y_2^{-2})(r_{<}^2 / r_{>}^3) + \\ & + A_4^0 Y_4^0 (r_{<}^4 / r_{>}^5) + A_4^2 (Y_4^2 + Y_4^{-2})(r_{<}^4 / r_{>}^5) + A_4^4 (Y_4^4 + Y_4^{-4})(r_{<}^4 / r_{>}^5). \end{aligned} \quad (4)$$

In calculating the A_K^Q coefficients, the ligands are usually approximated by point charges. In the case of “straight” ($D_{\infty h}$) $[M(Cp)_2]$ metallocenes, such an approximation was realized by replacing each cyclopentadienyl ring by a circular line circumscribing the C_5 pentagon and bearing the uniformly spread unit charge^{14b,19}. The same approximation has been adopted in the present case. The partial A_K^Q coefficients for the C_{2v} $[M(Cp)_2L_2]$ complex fragmented into the $M(Cp)_2$ and ML_2 moieties are listed in Table I. The resulting A_K^Q coefficients for the reunified $[M(Cp)_2L_2]$ entity are obtained by summing the partial ones

$$A_K^Q ([M(Cp)_2L_2]) = A_K^Q (M(Cp)_2) + A_K^Q (ML_2). \quad (5)$$

The corresponding coefficients for a $[M(Cp)_2L]$ complex can be obtained by using the following simple relations

$$A_K^Q(\text{ML}) = (1/2)A_K^Q(\text{ML}_2; \beta = 0^\circ) \quad (6a)$$

$$A_K^Q([\text{M}(\text{Cp})_2\text{L}]) = A_K^Q(\text{M}(\text{Cp})_2) + A_K^Q(\text{ML}) . \quad (6b)$$

One-electron d orbital energies (spin-orbit coupling neglected). In the C_{2v} ligand field, the d orbital set of five $|m_l\rangle$ functions splits into five sublevels. Their symmetry-adapted linear combinations $|\varphi_i\rangle$, $i = 1-5$, Eqs (7) form basis set for the perturbation calculation involving the \hat{V}_{LF} (Eq. (4)).

$$\begin{aligned} |\varphi_1\rangle &= |a_1(d_{z^2})\rangle = |0\rangle \\ |\varphi_2\rangle &= |a_1(d_{x^2-y^2})\rangle = 2^{-1/2}(|2\rangle + |-2\rangle) \\ |\varphi_3\rangle &= |a_2(d_{xy})\rangle = -i 2^{-1/2}(|2\rangle - |-2\rangle) \\ |\varphi_4\rangle &= |b_1(d_{xz})\rangle = -2^{-1/2}(|1\rangle - |-1\rangle) \\ |\varphi_5\rangle &= |b_2(d_{yz})\rangle = i 2^{-1/2}(|1\rangle + |-1\rangle). \end{aligned} \quad (7)$$

The solutions, *i.e.*, the one-electron d-orbital ligand field energies E_i are the roots of a 5×5 secular determinant

$$|H_{ij} - \Delta E_i \delta_{ij}| = 0, \quad i = 1-5, \quad j = 1 \text{ or } 2, \quad (8)$$

where

$$H_{ij} = \langle \varphi_i | \hat{V}_{\text{LF}} | \varphi_j \rangle. \quad (9)$$

TABLE I

The A_K^Q coefficients for C_{2v} fragments of the $[\text{M}(\text{Cp})_2\text{L}_2]$ complex^a

Coefficient	MCp ₂	ML ₂
A_0^0	$-4(\pi)^{1/2}q$	$-4(\pi)^{1/2}q$
A_2^0	$(\pi/5)^{1/2}(3a-2)(3c-1)q$	$2(\pi/5)^{1/2}(3b-2)q$
A_2^2	$-(3\pi/10)^{1/2}a(3c-1)q$	$2(3\pi/10)^{1/2}bq$
A_4^0	$-(\pi^{1/2}/48)(8-40a+35a^2)(3-30c+35c^2)q$	$-(\pi^{1/2}/6)(8-40b+35b^2)q$
A_4^2	$[(10\pi)^{1/2}/48]a(7a-6)(3-30c+35c^2)q$	$-[(10\pi)^{1/2}/6]b(7b-6)q$
A_4^4	$-[(35\pi/2)^{1/2}/48]a^2(3-30c+35c^2)q$	$-[(70\pi)^{1/2}/12]b^2q$

^a $a = \sin^2(\alpha/2)$; $b = \sin^2(\beta/2)$; $c = \cos^2 \gamma$; q is unit charge.

If the \hat{V}_{LF} (Eq. (4)) is introduced into Eq. (9), the calculation itself reduces to the enumeration of the integrals

$$\int_0^\pi \int_0^{2\pi} Y_l^{m_l}(\theta, \phi) Y_K^Q(\theta, \phi) Y_l^{m_l}(\theta, \phi) \sin\theta \, d\theta \, d\phi = \langle Y_{\phi_i} | Y_K^Q | Y_{\phi_j} \rangle, \quad (10)$$

the values of which are listed in Table II.

When the values of integrals (Eq. (10)) from Table II and the expressions for the A_K^Q coefficients are introduced into the H_{ij} (Eq. (9)), then, taking into account Eq. (11),

$$\int_0^\infty R_{n,2}(r) (r_{<}^K / r_{>}^{K+1}) R_{n,2}(r) r^2 \, dr = \langle r_{<}^K | r_{>}^{K+1} \rangle, \quad (11)$$

it is advantageous to define the following one-electron ligand field splitting parameters

$$\begin{aligned} Ds &= (1/7)(3c - 1) \langle r_{<}^2 / r_{>}^3 \rangle_{\text{Cp}} (e^2 / 4\pi\epsilon_0) \\ Dt &= -(1/84)(35c^2 - 30c + 3) \langle r_{<}^2 / r_{>}^3 \rangle_{\text{Cp}} (e^2 / 4\pi\epsilon_0) \\ Dq &= (2/21) \langle r_{<}^4 / r_{>}^5 \rangle_{\text{L}} (e^2 / 4\pi\epsilon_0) \\ Dr &= (2/7) \langle r_{<}^2 / r_{>}^3 \rangle_{\text{L}} (e^2 / 4\pi\epsilon_0) \\ E_0 &= 2(\langle 1/r_{>} \rangle_{\text{Cp}} + \langle 1/r_{>} \rangle_{\text{L}}) (e^2 / 4\pi\epsilon_0), \end{aligned} \quad (12)$$

TABLE II
Values of the $\langle Y_{\phi_i} | Y_K^Q | Y_{\phi_j} \rangle$ integrals

<i>i</i>	<i>j</i>	Y_K^Q					
		Y_0^0	Y_2^0	$Y_2^2 + Y_2^{-2}$	Y_4^0	$Y_4^2 + Y_4^{-2}$	$Y_4^4 + Y_4^{-4}$
1	1	$(2\pi^{1/2})^{-1}$	$(1/7)(5/\pi)^{1/2}$	0	$3/(7\pi^{1/2})$	0	0
1	2	0	0	$-(1/7)(10/\pi)^{1/2}$	0	$(1/7)(15/2\pi)^{1/2}$	0
2	2	$(2\pi^{1/2})^{-1}$	$-(1/7)(5/\pi)^{1/2}$	0	$(14\pi^{1/2})^{-1}$	0	$(5/14\pi)^{1/2}$
3	3	$(2\pi^{1/2})^{-1}$	$-(1/7)(5/\pi)^{1/2}$	0	$(14\pi^{1/2})^{-1}$	0	$-(5/14\pi)^{1/2}$
4	4	$(2\pi^{1/2})^{-1}$	$(1/14)(5/\pi)^{1/2}$	$(1/7)(15/2\pi)^{1/2}$	$-2/(7\pi^{1/2})$	$(1/7)(10/\pi)^{1/2}$	0
5	5	$(2\pi^{1/2})^{-1}$	$(1/14)(5/\pi)^{1/2}$	$-(1/7)(15/2\pi)^{1/2}$	$-2/(7\pi^{1/2})$	$-(1/7)(10/\pi)^{1/2}$	0

where $c = \cos^2 \gamma$ (see Fig. 1). It should be stressed that these ligand field parameters are best treated phenomenologically. The E_0 parameter is related to the spherically symmetrical part of the \hat{V}_{LF} , which only destabilizes all the split d levels to the same extent and contributes nothing to the splitting. For the limit $R_C = R_L = R$, one obtains $\langle 1/r_>_{\text{Cp}} = \langle 1/r_>_{\text{L}} = \langle 1/r_>$ and hence

$$E_0(C_{2v}) = 4\langle 1/r_> (e^2/4\pi\epsilon_0) = E_0(T_d) = (2/3)E_0(O_h). \quad (13)$$

Inasmuch as the definitions of the Ds and Dt parameters are identical to those for $(D_{\infty h}) [M(\text{Cp})_2]$ metallocenes^{19a}, an acceptable basis results for comparing bent metallocene complexes to parallel ("straight") ones. The Dq parameter is quite analogous to that for octahedral complexes^{18d} and for the $Dq(C_{2v})$ it holds

$$Dq(C_{2v}) = (4/7)Dq(O_h) = (9/7)Dq(T_d), \quad (14)$$

so that a comparison between $[M(\text{Cp})_2L_n]$ and octahedral $[ML_6]^{2-}$ or tetrahedral $[ML_4]$ species is possible.

With the four one-electron ligand field splitting parameters, Ds , Dt , Dq and Dr , the roots of the secular determinant (8) or the one-electron d-orbital energies for a $[M(\text{Cp})_2L_n]$ complexes are (note that formally $E_i = \Delta E_i - E_0$)

$$E_1(1a_1) = (1/2)\{H_{11} + H_{22} - [(H_{11} - H_{22})^2 + 4H_{12}^2]^{1/2}\}$$

$$E_2(2a_1) = (1/2)\{H_{11} + H_{22} + [(H_{11} - H_{22})^2 + 4H_{12}^2]^{1/2}\}$$

$$H_{11} = -(3a - 2)Ds - (3/4)(8 - 40a + 35a^2)Dt + (3/4)(8 - 40b + 35b^2)Dq - (3b - 2)Dr$$

$$H_{22} = (3a - 2)Ds - (1/4)(4 - 20a + 35a^2)Dt + (1/4)(4 - 20b + 35b^2)Dq + (3b - 2)Dr$$

$$H_{12} = \sqrt{3}[-aDs + (5/4)a(7a - 6)Dt + (5/4)b(7b - 6)Dq + bDr] \quad (15)$$

$$E_3(a_2) = H_{33} = (3a - 2)Ds + (5a - 1)Dt - (5b - 1)Dq + (3b - 2)Dr$$

$$E_4(b_1) = H_{44} = Ds + (4 - 35a + 35a^2)Dt - (4 - 5b)Dq - (3b - 1)Dr$$

$$E_5(b_2) = H_{55} = -(3a - 1)Ds + (4 - 5a)Dt - (4 - 35b + 35b^2)Dq + Dr,$$

where $a = \sin^2(\alpha/2)$ and $b = \sin^2(\beta/2)$ (see Fig. 1). The two a_1 orbitals are denoted as $1a_1$ and $2a_1$ in accordance with the convention established by

Lauher and Hoffmann¹³. The correctness of the one-electron energies (Eqs (15)) can be verified in several ways:

(i) The equation $\sum_{i=1}^5 E_i = 0$ holds (the centre-of-gravity conservation rule);

(ii) For $Dq = Dr = 0$ (i.e., $R_L \rightarrow \infty$) and $\alpha = 180^\circ$, one obtains

$$\begin{aligned} E_3(a_2) &= E_4(b_1) = Ds + 4Dt \equiv E(\pi) \\ E_2(2a_1) &= 2Ds - 6Dt \equiv E(\sigma) \\ E_1(1a_1) &= E_5(b_2) = -2Ds - Dt \equiv E(\delta) \end{aligned}$$

and then one-electron d-orbital energies for $(D_{\infty h})$ [M(Cp)₂] metallocenes^{19a};

(iii) When $\gamma = 0^\circ$, ring centroid = R_L , and $\sin^2(\alpha/2) = \sin^2(\beta/2) = 2/3$, the [M(Cp)₂L₂] complex transforms into a tetrahedral one [ML₄]. If the equalities $Ds = Dr$ and $Dq = -Dt$ are used, Eq. (15) for one-electron d-orbital energies for a tetrahedral [ML₄] complex^{18d} becomes

$$\begin{aligned} E_2(2a_1) &= E_4(b_1) = E_5(b_2) = (28/9)Dq(C_{2v}) = 4Dq(T_d) \equiv E(t_2) \\ E_1(1a_1) &= E_3(a_2) = -(14/3)Dq(C_{2v}) = -6Dq(T_d) \equiv E(e). \end{aligned}$$

It should be noted that the one-electron d-orbital energy for a [M(Cp)₂L] (C_{2v}) complex can be simply derived from Eqs (15) by setting $\beta = 0^\circ$ into appropriate coefficients at Dq and Dr and then dividing the residual Dq and Dr coefficients by two, for example

$$H_{11} = -(3a - 2)Ds - (3/4)(8 - 40a + 35a^2)Dt + 3Dq + Dr.$$

It is evident that d-orbital splitting in C_{2v} [M(Cp)₂L_n] complexes depends not only on the four ligand field splitting parameters, but also on the molecular structure parameters (two angles α and β for $n = 2$ and the single angle α for $n = 1$).

One-electron d-orbital energies including spin-orbit coupling. Now, the Hamiltonian (5) comprises only one-electron operators and hence becomes

$$\hat{H}' = \hat{V}_{LF} + \xi(r)\hat{I} \cdot \hat{S}. \quad (16)$$

With d¹ electron configuration, we have 10 spinorbitals $|m_l, m_s\rangle$ or $|m_l^\pm\rangle$. To obtain one-electron d-orbital energies including spin-orbit coupling we need to solve the relevant 10×10 energy matrix with elements $\langle m_l, m_s | \hat{V}_{LF} + \xi(r)\hat{I} \cdot \hat{S} | m_l', m_s' \rangle$. Instead of the orbital $|\varphi_i\rangle$ functions (7), the following $|\chi_i\rangle$ functions (17), so phased as to yield only real matrix elements, are used for the perturbation calculation

$$\begin{aligned}
 |\chi_1\rangle &= |a_1(d_{z^2})\rangle = |0\rangle = |d_{z^2}\rangle \equiv |\varphi_1\rangle \\
 |\chi_2\rangle &= |a_1(d_{x^2-y^2})\rangle = 2^{-1/2}(|2\rangle + |-2\rangle) = |d_{x^2-y^2}\rangle \equiv |\varphi_2\rangle \\
 |\chi_3\rangle &= |a_2(d_{xy})\rangle = 2^{-1/2}(|2\rangle - |-2\rangle) = i|d_{xy}\rangle \equiv i|\varphi_3\rangle \\
 |\chi_4\rangle &= |b_1(d_{xz})\rangle = 2^{-1/2}(|1\rangle - |-1\rangle) = -i|d_{xz}\rangle \equiv -i|\varphi_4\rangle \\
 |\chi_5\rangle &= |b_2(d_{yz})\rangle = 2^{-1/2}(|1\rangle + |-1\rangle) = -i|d_{yz}\rangle \equiv -i|\varphi_5\rangle.
 \end{aligned} \tag{17}$$

It should be stated that both basis sets (7) and (17) yield identical results when applied to the \hat{V}_{LF} .

The elements $\langle m_l, m_s | \xi(r) \hat{l} \cdot \hat{s} | m'_l, m'_s \rangle$ were constructed by direct applying the spin-orbit coupling operator with $\hat{l} \cdot \hat{s} = \hat{l}_z \cdot \hat{s}_z + (1/2)\hat{l}_+ \cdot \hat{s}_- + (1/2)\hat{l}_- \cdot \hat{s}_+$ and $\hat{l}_\pm = \hat{l}_x \pm i\hat{l}_y$, $\hat{s}_\pm = \hat{s}_x \pm i\hat{s}_y$ to $|\chi_i^{m_s, l}\rangle$. In the C_{2v} ligand field, the 10×10 energy matrix induced by the basis set of 10 spinorbitals reduces to the two 5×5 matrices (18), both leading to the identical eigenvalues.

$$\begin{array}{ccccc}
 \langle \chi_1^- | & \langle \chi_2^- | & \langle (-\chi_3)^- | & \langle (-\chi_4)^+ | & \langle \chi_5^+ | \\
 \langle \chi_1^+ | & \langle \chi_2^+ | & \langle \chi_3^+ | & \langle \chi_4^- | & \langle \chi_5^- | \\
 \left| \begin{array}{ccccc}
 H_{11} & H_{12} & 0 & (\sqrt{3}/2)\zeta_{nd} & (\sqrt{3}/2)\zeta_{nd} \\
 & H_{22} & \zeta_{nd} & -(1/2)\zeta_{nd} & (1/2)\zeta_{nd} \\
 & & H_{33} & (1/2)\zeta_{nd} & -(1/2)\zeta_{nd} \\
 & & & H_{44} & -(1/2)\zeta_{nd} \\
 & & & & H_{55}
 \end{array} \right| & \begin{array}{cc}
 \langle \chi_1^+ | & \langle \chi_1^- | \\
 \langle \chi_2^+ | & \langle \chi_2^- | \\
 \langle \chi_3^+ | & \langle (-\chi_3)^- | \\
 \langle \chi_4^- | & \langle (-\chi_4)^+ | \\
 \langle \chi_5^- | & \langle \chi_5^+ |
 \end{array}
 \end{array} \tag{18}$$

Here $\zeta_{nd} = \langle R_{nd}(r) | \xi(r) | R_{nd}(r) \rangle \hbar^2$ and for H_{ii} ($i = 1-5$) and H_{12} , the relations (15) hold again.

Many-Electron C_{2v} Ligand Field Theory for d^N Systems ($N = 2-4$) (Spin-Orbit Coupling Neglected)

Strong-field coupling formalism. As mentioned above, the strong-field approach appears to be more convenient for metallocene compounds than the weak-field one. For the assignment and interpretation of the d-d transitions in the electronic spectra of metallocene complexes, the strong-field treatment neglecting spin-orbit coupling is usually sufficient^{14d,14f}.

The perturbation Hamiltonian (5) for a d^N electron system without spin-orbit effects becomes

$$\hat{H}' = \sum_{i=1}^N \hat{V}_{\text{LF}}(\mathbf{i}) + \sum_{i < j}^N e^2 / (4\pi\epsilon_0 r_{ij}) \quad (19)$$

and, in the strong-field coupling scheme,

$$\sum_{i=1}^N \hat{V}_{\text{LF}}(\mathbf{i}) > \sum_{i < j}^N e^2 / (4\pi\epsilon_0 r_{ij}),$$

in matrix elements

$$\hat{H}'_{mn} = \langle \Psi_m | \sum_{i=1}^N \hat{V}_{\text{LF}}(\mathbf{i}) + \sum_{i < j}^N e^2 / (4\pi\epsilon_0 r_{ij}) | \Psi_n \rangle, \quad (20)$$

Ψ_m, Ψ_n (Eq. (21)) are now some of all the possible N -electron strong-field functions constructed from symmetry-adapted linear combinations of antisymmetrized products (Slater determinants) $|\phi_u\rangle$ of spinorbitals corresponding to a particular electron orbital configuration $\gamma_1^{n_1} \gamma_2^{n_2} \dots \gamma_5^{n_5}$ (where $n_1 + n_2 + \dots + n_5 = N$).

$$\Psi_m = \sum_u c_u \phi_u \quad (21)$$

The two-, three-, and four-electron strong-field functions $\Psi_m = |(\gamma_1^{n_1} \gamma_2^{n_2} \dots \gamma_5^{n_5})^{2S+1} \Gamma, M_S\rangle$ obtained by means of standard procedures¹⁸ are listed in Table III. Using these many-electron functions, the matrix elements of the operator (19) were calculated. The elements of the interelectronic Coulombic repulsion operator were calculated from tabulated^{18a,18d,20} integrals $\langle ab|1/r_{12}|cd\rangle$, where a, b, c, d are some of the functions ϕ_i (7).

Strong-field energy matrices (excluding spin-orbit coupling). The dimension of d^2 representation is 25×25 . However, the C_{2v} symmetry of the ligand field and zero matrix elements among ${}^{2S+1}\Gamma$ terms differing both in spin multiplicity and Γ result in reduction to one 1×1 spin-triplet matrix (3A_1); three 3×3 spin-triplet matrices (${}^3A_2, {}^3B_1, {}^3B_2$), three 3×3 spin-singlet matrices (${}^1A_2, {}^1B_1, {}^1B_2$), and one 6×6 spin-singlet matrix (1A_1). Table IV gives the

TABLE III
 General strong-field wave functions $|(Y_i^{n_i} Y_j^{n_j} \dots)^{2S+1} \Gamma, M_\Sigma\rangle$ for d^N configurations ($N = 2, 3, 4$) in C_{2v} symmetry^a

d^2 configuration

(i) $Y_i^1 Y_j^1$ $(Y_i Y_j)^3 \Gamma, 1) = |Y_i^+ Y_j^+|$
 $(Y_i Y_j)^3 \Gamma, 0) = 2^{-1/2}(|Y_i^+ Y_j^-| + |Y_i^- Y_j^+|)$
 $(Y_i Y_j)^3 \Gamma, -1) = |Y_i^- Y_j^-|$

(ii) Y_i^2 $(Y_i^2)^1 \Gamma, 0) = |Y_i^+ Y_i^-|$

d^3 configuration

(i) $Y_i^1 Y_j^1 Y_k^1$ $(Y_i Y_j Y_k)^4 \Gamma, 3/2) = |Y_i^+ Y_j^+ Y_k^+|$
 $(Y_i Y_j Y_k)^4 \Gamma, 1/2) = 3^{-1/2}(|Y_i^+ Y_j^+ Y_k^-| + |Y_i^+ Y_j^- Y_k^+| + |Y_i^- Y_j^+ Y_k^+|)$
 $(Y_i Y_j Y_k)^4 \Gamma, -1/2) = 3^{-1/2}(|Y_i^+ Y_j^- Y_k^-| + |Y_i^- Y_j^+ Y_k^-| + |Y_i^- Y_j^- Y_k^+|)$
 $(Y_i Y_j Y_k)^4 \Gamma, -3/2) = |Y_i^- Y_j^- Y_k^-|$
 $(Y_i Y_j Y_k)^2 \Gamma, 1/2) = 6^{-1/2}(|Y_i^+ Y_j^+ Y_k^-| + |Y_i^+ Y_j^- Y_k^+| - 2|Y_i^- Y_j^+ Y_k^+|)$
 $(Y_i Y_j Y_k)^2 \Gamma, -1/2) = 6^{-1/2}(2|Y_i^+ Y_j^- Y_k^-| - |Y_i^- Y_j^+ Y_k^-| - |Y_i^- Y_j^- Y_k^+|)$
 $(Y_i Y_j Y_k)^2 \Gamma, 1/2) = 2^{-1/2}(|Y_i^+ Y_j^+ Y_k^-| - |Y_i^- Y_j^- Y_k^+|)$
 $(Y_i Y_j Y_k)^2 \Gamma, -1/2) = 2^{-1/2}(|Y_i^+ Y_j^- Y_k^-| - |Y_i^- Y_j^+ Y_k^+|)$

(ii) $Y_i^2 Y_j^1$ $(Y_i^2 Y_j)^2 \Gamma, 1/2) = |Y_i^+ Y_i^- Y_j^+|$
 $(Y_i^2 Y_j)^2 \Gamma, 1/2) = |Y_i^+ Y_i^- Y_j^-|$

d^4 configuration

(i) $Y_i^1 Y_j^1 Y_k^1 Y_l^1$ $(Y_i Y_j Y_k Y_l)^5 \Gamma, 2) = |Y_i^+ Y_j^+ Y_k^+ Y_l^+|$
 $(Y_i Y_j Y_k Y_l)^5 \Gamma, 1) = (1/2)(|Y_i^+ Y_j^+ Y_k^+ Y_l^-| + |Y_i^+ Y_j^+ Y_k^- Y_l^+| + |Y_i^+ Y_j^- Y_k^+ Y_l^+| + |Y_i^- Y_j^+ Y_k^+ Y_l^+|)$
 $(Y_i Y_j Y_k Y_l)^5 \Gamma, 0) = 6^{-1/2}(|Y_i^+ Y_j^+ Y_k^+ Y_l^-| + |Y_i^+ Y_j^+ Y_k^- Y_l^+| + |Y_i^+ Y_j^- Y_k^+ Y_l^+| + |Y_i^- Y_j^+ Y_k^+ Y_l^+| + |Y_i^- Y_j^+ Y_k^- Y_l^+| + |Y_i^- Y_j^- Y_k^+ Y_l^+|)$
 $(Y_i Y_j Y_k Y_l)^5 \Gamma, -1) = (1/2)(|Y_i^+ Y_j^- Y_k^+ Y_l^-| + |Y_i^- Y_j^+ Y_k^+ Y_l^-| + |Y_i^- Y_j^- Y_k^+ Y_l^+| + |Y_i^- Y_j^+ Y_k^- Y_l^+|)$
 $(Y_i Y_j Y_k Y_l)^5 \Gamma, -2) = |Y_i^- Y_j^- Y_k^- Y_l^-|$
 $(Y_i Y_j Y_k Y_l)^3 \Gamma, 1) = (1/2)(|Y_i^+ Y_j^+ Y_k^+ Y_l^-| + |Y_i^+ Y_j^+ Y_k^- Y_l^+| - |Y_i^+ Y_j^- Y_k^+ Y_l^+| - |Y_i^- Y_j^+ Y_k^+ Y_l^+|)$
 $(Y_i Y_j Y_k Y_l)^3 \Gamma, 0) = 2^{-1/2}(|Y_i^+ Y_j^+ Y_k^+ Y_l^-| - |Y_i^- Y_j^- Y_k^+ Y_l^+|)$
 $(Y_i Y_j Y_k Y_l)^3 \Gamma, -1) = (1/2)(|Y_i^+ Y_j^- Y_k^+ Y_l^-| + |Y_i^- Y_j^+ Y_k^+ Y_l^-| - |Y_i^- Y_j^- Y_k^+ Y_l^+| - |Y_i^- Y_j^+ Y_k^- Y_l^+|)$
 $(Y_i Y_j Y_k Y_l)^3 \Gamma, 1) = 2^{-1/2}(|Y_i^+ Y_j^+ Y_k^+ Y_l^-| - |Y_i^- Y_j^- Y_k^+ Y_l^+|)$
 $(Y_i Y_j Y_k Y_l)^3 \Gamma, 0) = (1/2)(|Y_i^+ Y_j^+ Y_k^+ Y_l^-| + |Y_i^+ Y_j^+ Y_k^- Y_l^+| - |Y_i^- Y_j^- Y_k^+ Y_l^+| - |Y_i^- Y_j^+ Y_k^- Y_l^+|)$
 $(Y_i Y_j Y_k Y_l)^3 \Gamma, -1) = 2^{-1/2}(|Y_i^+ Y_j^- Y_k^+ Y_l^-| - |Y_i^- Y_j^+ Y_k^+ Y_l^-|)$
 $(Y_i Y_j Y_k Y_l)^3 \Gamma, 1) = 2^{-1/2}(|Y_i^+ Y_j^+ Y_k^+ Y_l^-| - |Y_i^- Y_j^- Y_k^+ Y_l^+|)$
 $(Y_i Y_j Y_k Y_l)^3 \Gamma, 0) = (1/2)(|Y_i^+ Y_j^+ Y_k^+ Y_l^-| - |Y_i^+ Y_j^+ Y_k^- Y_l^+| - |Y_i^- Y_j^- Y_k^+ Y_l^+| + |Y_i^- Y_j^+ Y_k^- Y_l^+|)$
 $(Y_i Y_j Y_k Y_l)^3 \Gamma, -1) = 2^{-1/2}(|Y_i^+ Y_j^+ Y_k^+ Y_l^-| - |Y_i^- Y_j^- Y_k^+ Y_l^+|)$
 $(Y_i Y_j Y_k Y_l)^1 \Gamma, 0) = (1/2)(|Y_i^+ Y_j^+ Y_k^+ Y_l^-| - |Y_i^+ Y_j^+ Y_k^- Y_l^+| + |Y_i^- Y_j^- Y_k^+ Y_l^+| - |Y_i^- Y_j^+ Y_k^- Y_l^+|)$
 $(Y_i Y_j Y_k Y_l)^1 \Gamma, 0) = 12^{-1/2}(|Y_i^+ Y_j^+ Y_k^+ Y_l^-| + |Y_i^+ Y_j^+ Y_k^- Y_l^+| - 2|Y_i^- Y_j^- Y_k^+ Y_l^+| + |Y_i^- Y_j^+ Y_k^- Y_l^+| + |Y_i^- Y_j^+ Y_k^- Y_l^-| - 2|Y_i^- Y_j^- Y_k^+ Y_l^+|)$

TABLE III
(Continued)

d^4 configuration

$$\begin{aligned}
 \text{(ii) } \gamma_i^2 \gamma_j \gamma_k^1 & \quad (\gamma_i^2 \gamma_j \gamma_k)^3 \Gamma, 1) = |\gamma_i^+ \gamma_i^- \gamma_j^+ \gamma_k^+| \\
 & \quad (\gamma_i^2 \gamma_j \gamma_k)^3 \Gamma, 0) = 2^{-1/2} (|\gamma_i^+ \gamma_i^- \gamma_j^+ \gamma_k^-| + |\gamma_i^+ \gamma_i^- \gamma_j^- \gamma_k^+|) \\
 & \quad (\gamma_i^2 \gamma_j \gamma_k)^3 \Gamma, -1) = |\gamma_i^+ \gamma_i^- \gamma_j^- \gamma_k^-| \\
 & \quad (\gamma_i^2 \gamma_j \gamma_k)^1 \Gamma, 0) = 2^{-1/2} (|\gamma_i^+ \gamma_i^- \gamma_j^+ \gamma_k^-| - |\gamma_i^+ \gamma_i^- \gamma_j^- \gamma_k^+|) \\
 \text{(iii) } \gamma_i^2 \gamma_j^2 & \quad (\gamma_i^2 \gamma_j^2)^1 \Gamma, 0) = |\gamma_i^+ \gamma_i^- \gamma_j^+ \gamma_j^-|
 \end{aligned}$$

^a One-electron $|\gamma\rangle$ functions are defined in Eq. (7) or (17).

TABLE IV
Simplified designation for d^2 strong-field terms $|(\gamma_i^{n_i} \gamma_j^{n_j})^{2S+1} \Gamma, M_S\rangle$

Γ	$\gamma_i^{n_i} \gamma_j^{n_j}$	Designation		Γ	$\gamma_i^{n_i} \gamma_j^{n_j}$	Designation	
		$^3\Gamma$	$^1\Gamma$			$^3\Gamma$	$^1\Gamma$
A_1	$a_1(z^2)^1 a_1(x^2 - y^2)^1$	1	2	B_1	$a_2^1 b_2^1$	14	17
	$a_1(z^2)^2$		3		$a_1(z^2)^1 b_1^1$	15	18
	$a_1(x^2 - y^2)^2$		4		$a_1(x^2 - y^2)^1 b_1^1$	16	19
	a_2^2		5				
	b_1^2		6	B_2	$a_2^1 b_1^1$	20	23
	b_2^2		7		$a_1(z^2)^1 b_2^1$	21	24
				$a_1(x^2 - y^2)^1 b_2^1$	22	25	
A_2	$b_1^1 b_2^1$	8	11				
	$a_1(z^2)^1 a_2^1$	9	12				
	$a_1(x^2 - y^2)^1 a_2^1$	10	13				

simplified designation of the relevant strong-field terms $(\gamma_i^{n_i}, \gamma_j^{n_j})^{2S+1}\Gamma, M_S$ for $d^2 [M(\text{Cp})_2L_n]$. The full strong-field energy matrices for this $d^2 C_{2v}$ system are presented in Table V, where the Coulombic repulsions are expressed in terms of the Racah parameters, B and C .

Similarly, the 50×50 dimension of d^3 representation reduces to one 1×1 spin-quadruplet matrix (4A_1), three 3×3 spin-quadruplet matrices (4A_2 , 4B_1 , 4B_2), and four 10×10 spin-doublet matrices (2A_1 , 2A_2 , 2B_1 , 2B_2).

TABLE V
Strong-field energy matrices for $d^2 [M(\text{Cp})_2L_2]$ complexes

3A_1 :	$H_{11}+H_{22}-8B$	$ 1\rangle$					
1A_1 :	$H_{11}+H_{22}-2C$	$\sqrt{2}H_{12}$	$\sqrt{2}H_{12}$	0	$\sqrt{6}B$	$-\sqrt{6}B$	$ 2\rangle$
		$2H_{11}+4B+3C$	$4B+C$	$4B+C$	$B+C$	$B+C$	$ 3\rangle$
			$2H_{22}+4B+3C$	C	$3B+C$	$3B+C$	$ 4\rangle$
				$2H_{33}+4B+3C$	$3B+C$	$3B+C$	$ 5\rangle$
					$2H_{44}+4B+3C$	$3B+C$	$ 6\rangle$
						$2H_{55}+4B+3C$	$ 7\rangle$
3A_2 :	$H_{44}+H_{55}-5B$	0	$6B$				$ 8\rangle$
		$H_{11}+H_{33}-8B$	H_{12}				$ 9\rangle$
			$H_{22}+H_{33}+4B$				$ 10\rangle$
1A_2 :	$H_{44}+H_{55}+B+2C$	$2\sqrt{3}B$	0				$ 11\rangle$
		$H_{11}+H_{33}+2C$	H_{12}				$ 12\rangle$
			$H_{22}+H_{33}+4B+2C$				$ 13\rangle$
3B_1 :	$H_{33}+H_{55}-5B$	$-3\sqrt{3}B$	$3B$				$ 14\rangle$
		$H_{11}+H_{44}+B$	$H_{12}-3\sqrt{3}B$				$ 15\rangle$
			$H_{22}+H_{44}-5B$				$ 16\rangle$
1B_1 :	$H_{33}+H_{55}+B+2C$	$-\sqrt{3}B$	$-3B$				$ 17\rangle$
		$H_{11}+H_{44}+3B+2C$	$H_{12}-\sqrt{3}B$				$ 18\rangle$
			$H_{22}+H_{44}+B+2C$				$ 19\rangle$
3B_2 :	$H_{33}+H_{44}-5B$	$-3\sqrt{3}B$	$-3B$				$ 20\rangle$
		$H_{11}+H_{55}+B$	$H_{12}+3\sqrt{3}B$				$ 21\rangle$
			$H_{22}+H_{55}-5B$				$ 22\rangle$
1B_2 :	$H_{33}+H_{44}+B+2C$	$-\sqrt{3}B$	$3B$				$ 23\rangle$
		$H_{11}+H_{55}+3B+2C$	$H_{12}+\sqrt{3}B$				$ 24\rangle$
			$H_{22}+H_{55}+B+2C$				$ 25\rangle$

Finally, the 100×100 dimension of d^4 representation reduces to three 1×1 spin-quintuplet matrices (5A_2 , 5B_1 , 5B_2), one 2×2 spin-quintuplet matrix (5A_1), one 9×9 spin-triplet matrix (3A_1), three 11×11 spin-singlet matrices (1A_2 , 1B_1 , 1B_2), three 12×12 spin-triplet matrices (3A_2 , 3B_1 , 3B_2), and one 17×17 spin-singlet matrix (1A_1).

Because of large numbers of the d^3 and d^4 strong-field energy matrices and large dimensions of several matrices, these are not presented here but are available from the first author on request. The formal correctness of all the d^2 , d^3 , and d^4 strong-field energy matrices was verified by

(i) transforming d^2 functions from O_h symmetry^{18d} or d^3 functions from $D_{\infty h}$ symmetry^{14b} to the C_{2v} one and

(ii) comparing results of numerical calculations carried out under zero ligand field strength ($Ds = Dt = Dq = Dr = 0$) with d^2 , d^3 , and d^4 free ion energies.

EXPERIMENTAL

All reactions and manipulations were performed under dry, oxygen-free argon atmosphere using standard Schlenk and glovebox techniques. Vanadium tetrachloride and dicyclopentadiene were purchased from Fluka, whereas niobocene dichloride and solvents ($CHCl_3$, CH_2Cl_2) were obtained from Sigma-Aldrich. Vanadocene dichloride was prepared and purified by procedures described in the literature^{21a,21b}, niobocene dichloride was purified by repeated vacuum sublimation. Their purity was checked by elemental analysis, IR and EPR spectroscopy. Solvents ($CHCl_3$, CH_2Cl_2) were purified by standard methods and freshly distilled prior to use.

Electronic absorption spectra ($10\,000$ – $35\,000\text{ cm}^{-1}$ region) of vanadocene dichloride ($CHCl_3$) and niobocene dichloride (CH_2Cl_2) were recorded on a V-550 JASCO spectrometer as 10^{-3} to 10^{-2} M solutions using 2.5 cm sealed cells. The measured absorption spectra were fit as sums of Gaussian curves using the program Microcal Origin^{21c}. The ν_{\max} and ϵ_{\max} values obtained by Gaussian analysis of the absorption curves are listed in Table VI.

RESULTS AND DISCUSSION

With the bent d^N metallocene derivatives, the LFT has not yet been employed. In this section, three topics relating to these organometallics will be dealt with within the ligand field model developed above: (i) the d^1 bent $M(Cp)_2$ fragment; (ii) the d-d spectra of two d^1 metallocene dichlorides both with the exclusion and inclusion of spin-orbit coupling; and (iii) the qualitative prediction of the d-d spectra for two-, three-, and four-electron bent metallocenes.

d¹ M(Cp)₂ Fragment

In view of the fact that the electronic structure of the *d¹* model bent fragment [Ti(Cp)₂]⁺ as a function of the angle between the normals to the cyclopentadienyl rings has been studied by using the extended Hückel calculation¹³, it is desirable to inquire into the same problem from the point of view of the LFT as well.

As a hypothetical *d¹* M(Cp)₂ fragment of *C_{2v}* symmetry may arise from a parent *d¹* [M(Cp)₂L_{*n*}] complex by removing L_{*n*} ligands to infinity (*R_L* = ∞; then *Dq* = *Dr* = 0), it is no problem to establish the variation of the fragment d-orbital energies as a function of the bending angle α. It is sufficient to introduce the above condition for the *Dq* and *Dr* parameters into Eqs (15). In addition, if we define the ratio *Ds/Dt* = *k* and express the orbital energies relatively in *Dt* units, the trends of the d-orbitals energies with the bending angle α can be given as shown in Fig. 2. The two values were chosen for the ratio *k* so as to encompass the lowest and highest *k* values found for a family of *d^N* (*N* = 3–8) [M(Cp)₂] metallocenes¹⁴. Surprisingly, a comparison of the d-orbital patterns following from the two theoretically different approaches demonstrates their very close correspondence (Fig. 2 in ref.¹³ compared with Fig. 2 in this paper). The only remarkable difference proves to be a somewhat larger LFT value of the angle α, *viz.* ≈135°, where the 2*a₁* and *b₁* intersect. Thus, the basic MO as well as LFT trends of all the five d levels

TABLE VI
Characteristics and assignments of the d-d bands in the electronic spectra of *d¹* [M(Cp)₂Cl₂] (M = V, Nb) complexes

Complex	Band	$\tilde{\nu}_{\max}$, cm ⁻¹	ε_{\max} , m ² mol ⁻¹	Assignment
[V(Cp) ₂ Cl ₂]	1	10 920	5.0	² A ₁ → ² B ₁ (1 <i>a₁</i> → <i>b₁</i>)
	2	12 860	5.5	² A ₁ → ² B ₂ (1 <i>a₁</i> → <i>b₂</i>)
	3	15 790	4.3	² A ₁ → ² A ₁ (1 <i>a₁</i> →2 <i>a₁</i>)
	4	19 790	2.5	² A ₁ → ² A ₂ (1 <i>a₁</i> → <i>a₂</i>)
[Nb(Cp) ₂ Cl ₂]	1	14 115	2.0	² A ₁ → ² B ₁ (1 <i>a₁</i> → <i>b₁</i>)
	2	17 715	2.7	² A ₁ → ² B ₂ (1 <i>a₁</i> → <i>b₂</i>)
	3	22 105	4.7	² A ₁ → ² A ₁ (1 <i>a₁</i> →2 <i>a₁</i>)
	4	23 280	0.9	² A ₁ → ² A ₂ (1 <i>a₁</i> → <i>a₂</i>)

with fragment bending are similar. So, the parent e''_1 (D_{5h} ; $\alpha = 180^\circ$) set splits under C_{2v} symmetry yielding the $a_2(xy)$ and $b_1(xz)$ orbitals which are stabilized with increasing bending (decreasing α) and, consequently, occur at lower energies than did the e''_1 set, whereas the orbitals $2a_1$ (descended from $a'_1(z^2)$ (D_{5h} ; $\alpha = 180^\circ$)), $1a_1$ and b_2 (both descended from e''_2 (D_{5h} ; $\alpha = 180^\circ$) set, the former being its $x^2 - y^2$ component and the latter yz component at $\alpha = 180^\circ$) are destabilized. While the trends of the three fragment orbitals a_2 , b_1 , and b_2 are well conceivable even on the basis of naive electrostatic arguments (the relevant MO arguments have been given by Lauher and Hoffmann¹³), those of the $1a_1$ and $2a_1$ deserve some comments. In fact, they mix and repel each other under C_{2v} symmetry. Their interaction gives rise to an increase in the upward slope of the $2a_1$ on the one hand and keeps the $1a_1$ nearly constant in energy on the other.

It is of interest to get a deeper insight into the $1a_1/2a_1$ interaction and to analyze the variation in the composition of the $|1a_1\rangle$ and $|2a_1\rangle$ functions with fragment bending. Their component orbitals $|z^2\rangle$ and $|x^2 - y^2\rangle$ having

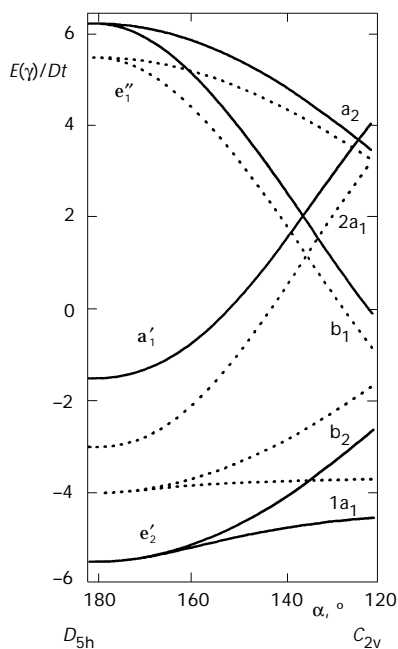


FIG. 2

d-Orbital energies as a function of the bending angle α ($k = Ds/Dt$) in the d^1 $M(Cp)_2$ (C_{2v}) fragment; $k = 1.5$ (dotted lines), $k = 2.25$ (solid lines)

different symmetries in D_{5h} , viz. a'_1 and e'_2 , respectively, do not interact under D_{5h} symmetry, but they do undergo a strong interaction with the bending $D_{5h} \rightarrow C_{2v}$ motion of the $M(Cp)_2$ fragment, both assuming the same a_1 (C_{2v}) symmetry. Thus, they are not eigenfunctions of the ligand field operator and only their linear combinations will diagonalize the corresponding secular determinant

$$\begin{vmatrix} H_{11} - E(a_1) & H_{12} \\ H_{21} & H_{11} - E(a_1) \end{vmatrix} = 0 \quad (22)$$

Furthermore, a continuous variation in the composition of the $|1a_1\rangle$ and $|2a_1\rangle$ as a function of angle α can be expected because the increasing bending continuously increases the absolute value of the H_{12} integral characteristic of the extent of interaction between $|z^2\rangle$ and $|x^2 - y^2\rangle$. To analyze these questions in more detail, we presume the orthonormal ligand field operator a_1 eigenfunctions to be defined as follows

$$\begin{aligned} |1a_1\rangle &= (1 + x^2)^{-1/2} (|z^2\rangle - x|x^2 - y^2\rangle) \\ |2a_1\rangle &= (1 + x^2)^{-1/2} (-x|z^2\rangle + |x^2 - y^2\rangle). \end{aligned} \quad (23)$$

The mixing coefficient x can be expressed from

$$\begin{aligned} E(1a_1) &= \langle 1a_1 | \hat{V}_{LF} | 1a_1 \rangle = (1 + x^2)^{-1} (H_{11} + 2xH_{12} + x^2 H_{22}) \\ E(2a_1) &= \langle 2a_1 | \hat{V}_{LF} | 2a_1 \rangle = (1 + x^2)^{-1} (x^2 H_{11} - 2xH_{12} + H_{22}) \end{aligned} \quad (24)$$

by solving the corresponding quadratic equations ensuing from (24) and applying the requirement of the unambiguous definition of the functions (23) to their roots, i.e., the square roots in solutions of both quadratic equations have to vanish for the x coefficient to be single-valued. Thus, one gets

$$H_{12}^2 = (H_{11} - E(1a_1))(H_{22} - E(1a_1)) = (H_{11} - E(2a_1))(H_{22} - E(2a_1)) \quad (25)$$

and

$$x = (-H_{12})(H_{22} - E(1a_1))^{-1} = H_{12}(H_{11} - E(2a_1))^{-1}. \quad (26)$$

Since $E(2a_1) > H_{11}$, $H_{22} > E(1a_1)$, and $H_{12} < 0$, $x > 0$ holds. By combining Eqs (25) and (26), the relation $xH_{12} = H_{22} - E(2a_1)$ results and from Eq. (26), the

relation $(-H_{12}) = \mathbf{x}(H_{22} - E(1a_1))$ follows. When these two relations are put into

$$\langle 1a_1 | \hat{V}_{LF} | 2a_1 \rangle = (1 + \mathbf{x}^2)^{-1} (\mathbf{x}H_{11} + \mathbf{x}^2 H_{12} - H_{12} - \mathbf{x}H_{22}),$$

it is possible to write

$$\langle 1a_1 | \hat{V}_{LF} | 2a_1 \rangle = (1 + \mathbf{x}^2)^{-1} [\mathbf{x}(H_{11} + H_{22}) - \mathbf{x}(E(1a_1) + E(2a_1))]. \quad (27)$$

As $H_{11} + H_{22} = E(1a_1) + E(2a_1)$, the secular determinant induced by the basis set (23) will assume the diagonal form

$$\begin{vmatrix} \langle 1a_1 | \hat{V}_{LF} | 1a_1 \rangle - E(a_1) & 0 \\ 0 & \langle 2a_1 | \hat{V}_{LF} | 2a_1 \rangle - E(2a_1) \end{vmatrix} = 0.$$

The conclusion ensuing from the outlined treatment is self-evident: the $|1a_1\rangle$ and $|2a_1\rangle$ orbitals defined conformably to Eqs (23) and (26) are true eigenfunctions of the perturbation operator \hat{V}_{LF} . Now, the participation of the $|z^2\rangle$ and $|x^2 - y^2\rangle$ functions in the $|1a_1\rangle$ and $|2a_1\rangle$ as a function of the bending angle α may be assessed. The analysis of the $|1a_1\rangle$ and $|2a_1\rangle$ compositions, performed on the basis of Eq. (23) and Fig. 3, demonstrates that an

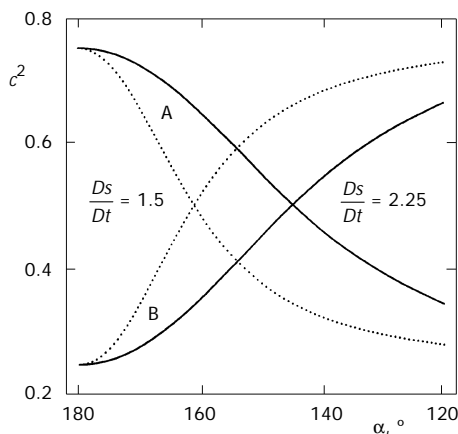


FIG. 3

The $d^1 M(Cp)_2 (C_{2v})$ fragment: dependence of the squared mixing coefficients $c^2 = (1 + \mathbf{x}^2)^{-1}$ (A) and $c^2 = \mathbf{x}^2(1 + \mathbf{x}^2)^{-1}$ (B) for $|z^2\rangle$ and $|x^2 - y^2\rangle$ (see Eqs (23) and (26)) on the bending angle α

increase in bending increases the contribution of $|z^2\rangle$ to $|2a_1\rangle$ which, consequently, localizes more and more along the z axis, and contribution of $|x^2 - y^2\rangle$ to $|1a_1\rangle$ which envelops more and more the y axis (note that $|z^2\rangle$ and $|x^2 - y^2\rangle$ add along the y axis, but subtract along the x axis).

To sum up, the bent d^N metallocenes we are interested in carry one to four d electrons (dihalides only one or two) and so it is the three low-energy orbitals $1a_1$, b_2 , and $2a_1$ of the bent $M(\text{Cp})_2$ fragment which will play role in coordinating further L_n ligands. All three orbitals are significantly situated in the yz plane. The $1a_1$ orbital is directed strongly along the y axis, looking like a d_{y^2} orbital. The b_2 orbital is purely d_{yz} in character. The $2a_1$ orbital is highest in energy of the three fragment d orbitals and is directed along the z axis. This orbital trio constitutes the true frontier orbitals of the bent d^N ($N = 1-4$) $M(\text{Cp})_2$ fragment.

d-d Spectra of d^1 Vanadocene and Niobocene Dichlorides

The application of C_{2v} ligand field model to the interpretation of bent d^N metallocene complexes differs in an important respect from the axial or pseudo-axial ($D_{\infty h}$ or $C_{\infty v}$) ligand field of d^N metallocenes $[M(\text{Cp})_2]$. Thus, whereas in $D_{\infty h}$ or $C_{\infty v}$ symmetry, only two one-electron ligand field splitting parameters, D_s and D_t , are needed to express the one-electron energies of the M^{2+} d -level split by the perturbing field of the two $C_5H_5^-$ ligands, in bent C_{2v} metallocene systems $[M(\text{Cp})_2L_n]$, four splitting parameters, D_s , D_t , D_q , and D_r , are required. However, the bent d^1 metallocene complexes lead to the exceptionally simple situation in which four one-electron $d-d$ transition (one of which is symmetry-forbidden) are possible. Thus, the assignment and fitting of the four $d-d$ bands should enable the four one-electron ligand field splitting parameters, which arise for bent metallocene species of C_{2v} symmetry, to be determined. If no *a priori* presumptions are made regarding both the lowest, singly occupied ground state d orbital and relative energy order of other four unfilled d orbitals, then there are 120 possible assignments of the four experimental $d-d$ transitions, provided that all the four $d-d$ transition energies have been extracted from the respective spectral absorption curve. Unfortunately, the available spectral data for d^1 systems are rather scarce being not so complete as desirable. So, for example, the hitherto reported experimental $d-d$ spectra of several bent d^1 metallocene complexes, such as $[M(\text{Cp})_2\text{Cl}_2]$ ($M = \text{V}, \text{Nb}$) (ref.^{7b}), $[\text{V}(\text{Cp})_2\text{Et}_2]$ (ref.²²) or $[\text{Ti}(\text{C}_5\text{Me}_5)_2\text{L}]$ (ref.^{5e}), show only two or three $d-d$ bands at most.

Since of the bent metallocene complexes, the d^1 vanadocene and niobocene dichlorides seemed to constitute especially favorable species for deriv-

ing values of D_s , D_t , D_q , and D_r , the C_{2v} ligand field model has been applied to the d-d spectra of these two dichlorides, the former comprising the 3d central metal ion, whereas the latter 4d one. One may expect that the latter fact will reflect both in the D_s , D_t , D_q , and D_r values and overall d-level splitting value. The measured near-infrared and visible spectra of vanadocene and niobocene dichlorides are both very much alike. They could be resolved each in four weak separate Gaussian bands (the ν_{\max} and ε_{\max} values obtained by Gaussian analysis are listed in Table VI) in the 10 000–24 000 cm^{-1} region, which may be reasonably assigned as d-d or ligand field bands involving transitions between the V^{4+} or Nb^{4+} d orbitals split by the perturbing field of two $C_5H_5^-$ and two Cl^- ligands. In both d-d spectra, the highest-energy d-d band is of lowest intensity of all the respective four bands. Since there are four experimental d-d transition energies and four splitting parameters, we can determine their values from the experimental data. First, the LFT treatment without spin-orbit coupling will be carried out, and last, the effect of spin-orbit coupling inclusion will be investigated.

Spin-orbit coupling neglected. The d-d excitation energies from the optional ground state d level to the four excited d states can be expressed, spin-orbit coupling being neglected, in terms of the one-electron d-orbital energies (15), where, for the α and β angles, the mean values from the X-ray studies of vanadocene dichloride^{5f} and niobocene dichloride^{5a} were used. A combination of excitation energies with four experimental d-d transition energies (ν_{\max}) lead to the 120 possible assignments which all have been carried out. The only acceptable assignment both for vanadium and niobium bent metallocene species has appeared to be that yielding the electronic ground state ${}^2A_1(1a_1)$ and the relative d-orbital energy order $1a_1 < b_1 < b_2 < 2a_1 < a_2$. In this connection, it should be pointed out, that 96 of the assignments based on the ground state other than ${}^2A_1(1a_1)$ yielded imaginary or negative values of splitting parameters and 23 of 24 assignments assuming the ${}^2A_1(1a_1)$ ground state gave either negative or absurd values for some of the four splitting parameters. The values of the four splitting parameters deduced from the d-d spectra of both dichloride complexes and ensued from the only acceptable assignment are presented, together with the values of parameter ratios D_s/D_t and D_r/D_q and with the corresponding assignments of the d-d transitions (Table VII).

It is very satisfactory and in line with the deduced assignment that the highest energy band of lowest intensity in the d-d spectra of vanadium and niobium complexes does correspond to the formally symmetry-forbidden

d-d transition ${}^2A_1(1a_1) \rightarrow {}^2A_2(a_2)$ and that the same ${}^2A_1(1a_1)$ ground states deduced from the d-d spectra of both dichlorides have been found by analysis of their EPR spectra^{5b,6,7}. The values of the D_s and D_t parameters as well as of their ratio D_s/D_t for the V(IV) bent metallocene dichloride (see Table VII) correlate well with the corresponding quantities for the V(II) metallocene, vanadocene $[V(Cp)_2]$, where $D_s = 3\,756\text{ cm}^{-1}$, $D_t = 3\,756\text{ cm}^{-1}$, $D_s/D_t = 1.88$ (ref.^{14b}), if one takes into consideration the well-known fact that the value(s) of the ligand field splitting parameter(s) of any transition metal complex increase(s) with increasing oxidation state of the central metal ion. The D_q value found for the vanadocene dichloride compares reasonably with the value $D_q(C_{2v}) \approx 850\text{ cm}^{-1}$ deduced from the $D_q(T_d) \approx 660\text{ cm}^{-1}$ for vanadium tetrachloride^{23a} as well as with $D_q(C_{2v}) \approx 880\text{ cm}^{-1}$ deduced from the $D_q(O_h) \approx 1\,540\text{ cm}^{-1}$ for the hexachlorovanadate (2-) anion^{23b} (the $D_q(C_{2v})$ values were calculated from the $D_q(T_d)$ or $D_q(O_h)$ values using relation (14)). As to the niobocene dichloride, all its splitting parameter values are higher than those for the vanadium complex in line with the well-known fact that the splitting parameter values of analogous transition metal complexes comprising the central metals of the same Group in the Periodic Table increase when going from the first to the second transition row. It is worthwhile to mention similar trends observed for the 3d metallocene, ferrocene ($D_s = 5\,171\text{ cm}^{-1}$, $D_t = 2\,717\text{ cm}^{-1}$, $D_s/D_t = 1.90$), and the 4d metallocene, ruthenocene ($D_s = 6\,143\text{ cm}^{-1}$, $D_t = 3\,594\text{ cm}^{-1}$, $D_s/D_t = 1.71$)^{14f,24}. The D_q value found for the niobium complex compares very well with the value $D_q(C_{2v}) \approx 1\,165\text{ cm}^{-1}$ deduced from the $D_q(O_h) \approx 2\,040\text{ cm}^{-1}$ for the hexachloroniobate (2-) anion^{23c}. Using the fitted values of the four splitting parameters and the α and β values mentioned above, the five one-electron d-orbital energies have been calculated from Eqs (15) as illustrated in Fig. 4. It is evident that the overall ligand field splitting $E(a_2) - E(1a_1)$ is significantly greater in the case of niobocene dichloride

TABLE VII

The ligand field splitting parameters found for $d^1 [M(Cp)_2Cl_2]$ ($M = V, Nb$) complexes

Complex	$D_s, \text{ cm}^{-1}$	$D_t, \text{ cm}^{-1}$	$D_q, \text{ cm}^{-1}$	$D_r, \text{ cm}^{-1}$	D_s/D_t	D_r/D_q
$[V(Cp)_2Cl_2]$	5 230	3 042	780	5 587	1.72	7.16
$[Nb(Cp)_2Cl_2]$	7 848	3 557	1 132	8 873	2.21	7.84

compared with its vanadium analogue, as expected on the basis of 3d/4d effects.

The order of d orbitals deduced from the d-d spectrum of vanadocene dichloride is in qualitative agreement with extended Hückel MO calculation^{7b}, but does not agree with the order calculated by the Fenske–Hall MO method^{12c} (note that the coordinate systems used by others^{7b,12c} have to be transformed to the system in Fig. 1 together with d-orbital symmetry labels).

Spin-orbit coupling included. In order to generate the energies of the five d orbitals in the C_{2v} ligand field, inclusive of the spin-orbit coupling, the secular determinant associated with the matrix (18) can be solved. Three various values were chosen for the spin-orbit coupling parameter $\zeta_{nd,M}$: the zero value, *i.e.*, no spin-orbit coupling, the reduced value (due to a covalency delocalizing d electron from the metal nucleus onto the ligands or to the so-called relativistic nephelauxetic effect²⁵), and the free M^{4+} ion value. The reduced $\zeta_{nd,M}$ values have been deduced by analysis of the EPR spectral data^{7b}. The results of the energy level calculation are reported in Table VIII.

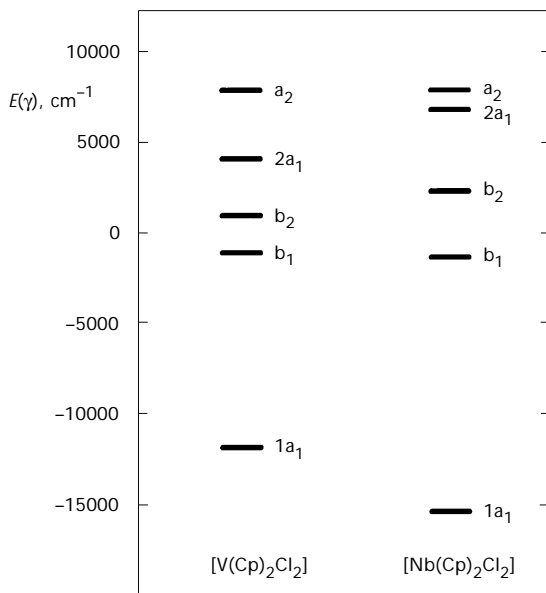


FIG. 4

One-electron energies of the split d orbitals for vanadocene and niobocene dichlorides

The calculated d-orbital energies of vanadocene dichloride show, not surprisingly, that the influence of spin-orbit coupling is imperceptible, the shifts of individual d levels amounting to a few cm^{-1} for the reduced $\zeta_{3d,V}$ value. Nor in the case of the 4d bent metallocene analogue is the effect of the spin-orbit coupling significant: the d-level shifts range from -5 to 184 cm^{-1} for the reduced $\zeta_{4d,Nb}$ value and are likely to be absorbed in the bandwidths of respective d-d bands of niobocene dichloride, whose halfwidths vary from $1\ 305 \text{ cm}^{-1}$ (symmetry-forbidden 2A_2 band) to $4\ 485 \text{ cm}^{-1}$ (2B_2 band). In short, the spin-orbit coupling does not seriously influence the observed d-d electronic spectra of the two d^1 metallocene dichlorides studied. However, spin-orbit coupling must be considered in EPR and magnetic susceptibility studies of these or related bent d^1 metallocene derivatives.

d-d Spectra of Many-Electron Bent Metallocene Complexes ($N = 2-4$)

In the preceding paragraph, we were using the C_{2v} ligand field procedure to assign and interpret the d-d spectra of the two bent d^1 metallocene complexes. In view of good performance of this ligand field model, it was tempting to consider and predict the d-d transitions of many-electron, *viz.*

TABLE VIII
Energy levels of d orbitals of d^1 metallocene dichloride in the C_{2v} ligand field including spin-orbit coupling (all entries are in cm^{-1})

Coupling parameter	Energy of d orbitals				
	$1a_1$	b_1	b_2	$2a_1$	a_2
$\zeta_{3d,V}$	Vanadocene dichloride				
0	-11 872	-952	988	3 918	7 918
133^a	-11 874	-954	989	3 916	7 923
250^b	-11 880	-960	990	3 912	7 937
$\zeta_{4d,Nb}$	Niobocene dichloride				
0	-15 442	-1 329	2 273	6 663	7 835
490^a	-15 465	-1 344	2 268	6 522	8 019
750^b	-15 497	-1 361	2 252	6 397	8 210

^a Reduced value from ref.^{7b}; ^b Free-ion value from ref.²⁶

d^2 , d^3 , and d^4 bent metallocene entities, whose experimental d-d spectra are, to our knowledge, still lacking.

The d-d excitation energies of these many-electron systems may be expressed in terms of the four one-electron ligand field splitting parameters, D_s , D_t , D_q , and D_r , and two Racah interelectronic repulsion parameters, B and C . The approach, which could be, in principle, taken is to obtain numerical values of these six parameters from fits to d-d spectra consisting of at least six resolved and correctly assigned d-d bands.

For the low-spin (diamagnetic) d^2 systems (e.g. $[\text{Mo}(\text{Cp})_2\text{Cl}_2]$ or $[\text{Ti}(\text{Cp})_2(\text{CO})_2]$), only four spin-allowed (singlet-singlet) one-electron d-d transitions (one of which is symmetry-forbidden) are expected. To obtain, therefore, numerical values of six parameters by fitting the experimental d-d spectrum, the additional two one-electron transitions are needed, namely, the spin-forbidden (singlet-triplet) ones (if only one could be observed, than an appropriate value of the ratio C/B has to be assumed). On the contrary, for the high-spin (paramagnetic) d^2 systems (e.g. $[\text{V}(\text{Cp})_2\text{Cl}]$), six spin-allowed (triplet-triplet) one-electron d-d transitions (two symmetry-forbidden) are predicted so that the values of all the parameters can be, in principle, determined from the experimental data if these are complete. For the low-spin (paramagnetic, one unpaired electron) d^3 system like $[\text{V}(\text{Cp})_2(\text{CO})]$, seven spin-allowed (doublet-doublet) one-electron d-d transitions (two symmetry-forbidden) are predicted. Since there are only six parameters whose numerical values are to be evaluated, but seven experimental d-d transition energies, this system may be solvable. Finally, for the low-spin (diamagnetic) d^4 system (e.g. $[\text{Mo}(\text{Cp})_2(\text{CO})]$), six spin-allowed (singlet-singlet) one-electron d-d transitions (two symmetry-forbidden) can be predicted and so the values of the six parameters may be derived from experiment.

It should be born in mind that there is a considerable difference between such a spectral prediction including all its consequential potentialities and the actual treatment including the necessary spectral measurement on the one hand and the correct spectral assignments leading to the calculation of the parameter values on the other, especially if one takes into account not only the experimental requirements, but also the algebraic difficulties arising from the number and dimensions of the relevant strong-field energy matrices. Nevertheless, the d-d spectra of many-electron bent metallocenes provide a challenge for the future experimental as well as theoretical work.

The authors (I. P., J. V.) thank the Grant Agency of the Czech Republic for support by grants No. 203/97/502, No. 203/00/0920, and No. 203/98/P235. The project LN00A028 (New Inorganic Com-

pounds and Advanced Materials) was supported by the Ministry of Education, Youth and Sports of the Czech Republic.

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