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Molecular Mechanics Explanation of the Metallocene Bent Sandwich Structure

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Abstract: A new approach is proposed which allows us to calculate molecular conformations of organometallic molecules within the framework of the MM3 force field. The ligand positions in the coordination sphere of the metal atom are mainly determined by minimization of the interligand nonbonded energy. For a description of the metal−ligand interactions (π-bonding), a very strong but otherwise ordinary (Hill type) van der Waals potential is used. Using this approach, the conformations of the bent sandwich metallocenes MCp$_2$ (where M are metals of main groups II or IVA or lanthanides II) were reproduced. It was shown that, when the interplanar distance between the planes of the Cp ligands are short, the ligands have a parallel orientation. When the distance is large (when the metal atom has a large radius), the interplanar distances become longer and the ligand planes do not stay parallel, but the molecule "bends" so that these planes intersect. The influence of bulky substituents on the bending angle was shown. Calculations were also carried out on crystals of these molecules, to determine the effect of crystal packing. The possibilities for the accurate prediction of the conformations of molecules of this type of structures (not yet investigated experimentally) on the basis of quantum mechanics and molecular mechanics are discussed.

Introduction

During the last two decades, molecular mechanics (MM) has become a practical tool for the rapid calculation of structures and properties for a wide variety of organic molecules.[1,2] One of the attractive characteristics of this method is that it allows one to understand phenomena in terms of a simple model.

In recent years molecular mechanics has begun to penetrate the wide field of organometallic chemistry.[3,4] The first applications were reported about 25 years ago,[5] but in the last few years, a substantial number of papers have been published. Applications have included catalytic chemistry[6−9] and the synthesis of chiral organic molecules.[10,11]

It is well-known that the most characteristic ligands of organometallic chemistry, such as carbonyl (CO) and cyclopentadienyl (Cp = C$_5$H$_5$), are π-ligands. These ligands usually have no consistent bond angles to describe their positions in the coordination sphere of the metal atom. One way to deal with the CO ligands on a metal cluster surface was proposed by Lauher,[12] who showed that it is possible to describe their positions with the help of minimization of only the energies of the nonbonded ligand−ligand interactions.

In our previous work we proposed the same type of description for a Cp ligand position in the coordination sphere of a metal atom.[13,14] We assumed the uniform occupation of the metal atom sphere by the ligand atoms. The criterion of the uniformity is a minimum of the total nonbonded interligand interaction energy. To use this approach within the framework of molecular mechanics, we need to fix in some way the M−Cp distances, but not use any restrictions on the values of the L−M−L bond angles. In our previous work,[13−17] we used a dummy atom situated at the Cp ring centroid (CR), fixed the M−CR distance with high values of the K_1 constant, and fixed the orientation of the M−CR vector normal to the plane of Cp

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Table 1. Main Geometrical Parameters of MCp_2 Molecules of Group IV

L[a]	M	M−CR (Å)	M−C, mean (Å)	M−C, interval (Å)	Cr−M−CR, β (deg)	∠Cp−Cp, α (deg)	conf[d]	method	ref
Cp*	Si	2,11	2.42	2.41−2.44	180,0	0,0	st	X−ray[b]	22
		2.12	2.43	2.32−2.54	167.4	25.3			
Cp*	Si	2.13	2.45	*c*	169.6	22.3	st	GED	22
Cp	Ge	2.20	2,50	2.35−2,73	*c*	50.4	ec	X-ray	23
Cp′	Ge	2.22	2.53	*c*	146	34	st	GED	24
CpBz	Ge	2.26	2.56	2.43−2.72	163.1	31.0	st	X-ray	25
CpSi	Ge	2.26	2.56	2.46−2.66	169.5	*c*	ec	X-ray[b]	26
		2.25	2.56	2.49−2.53	171.8				
Cp	Sn	2.42	2.71	*c*	125	55	*c*	GED	27
Cp	Sn	2.40	2.67	2.58−2,75	148.0[28]	48.4[24]	ec	X-ray[b]	28
		2.42	2.68	2.56−2.85	143,7[28]	45.9[24]			
Cp′	Sn	2,40	2.69	*c*	130	50	st	GED	24
Cp*	Sn	2.39	2.68	2.57−2.78	143.6	36	st	X-ray[b]	29
		2.38	2.68	2.59−2.77	144.6	36	st		
CpBz	Sn	2.42	2.71	2.62−2.82	155.9	32.8		X-ray	25
CpPh	Sn	2.40	2.69	2.69−2.70	180.0	0	st	X-ray	30
Cp	Pb	2.50	2,78	*c*	135	45	*c*	GED	27, 31
Cp*	Pb	2.48	2.79	2.60−2.90	151	37.1	st	X-ray	28
CpBz	Pb	2.50	2.79	2.68−2.87	153.4	33.3	st	X-ray	25

[a] Cp, C_5H_5; Cp*, C_5Me_5; Cp′, C_5H_4Me; CpBz, $[C_5(CH_2Ph_5)]$; CpSi, $C_5H_2(SiMe_3)_3$. [b] Two symmetrically independent molecules. [c] Not present in the original paper. [d] st, staggered; ec, eclipsed conformation.

Table 2. Main Geometrical Parameters of MCp_2 Molecules of Group II

L[a]	M	M−CR, (Å)	M−C, mean (Å)	M−C, interval (Å)	Cr−M−Cr, β (deg)	∠Cp−Cp, α (deg)	conf[e]	method	ref
Cp	Mg	*c*	2.30	2.28−2.32	180	0	st	X-ray	32
Cp*	Mg	*c*	2.35		180[d]	0	st	GED	33
Cp*	Ca	2.36	2.64	*c*	147.7	33.5	st, 19.1	X-ray[b]	34
		2.36	2.64		146.3	36.0	st, 24.7		
Cp*	Ca	*c*	2.61	2.55−2.67	154	20	st	GED	33, 35
Cp4i	Ca	2.35	2.64	*c*	162.3	*c*	st, 29.4	X-ray	36
Cp*	Sr	*c*	2.75	2.70−2.80	149	25	*c*	GED	37, 38
Cp*	Ba	2.73	2.98	*c*	130.9	46.9	st, 32.1	X-ray[b]	34
		2,74	2.99	*c*	131.0	48.5	st, 28,1		
Cp*	Ba	*c*	2.90	2.84−2.96	148	26	*c*	GED	37, 38
Cp4i	Ba	2.678	2.94	*c*	154.3	*c*	st, 31.4	X-ray[b]	36
		2.682	2.94		154.1		st, 32.0		
Cp*	Sm	*c*	2.79	2.78−2.82	140,1	40,0	st, 19	X-ray	39
Cp*	Eu	*c*	2.79	2.76−2.82	140.3	40,2	st	X-ray	37
Cp*	Yb	*c*	2.62	2.61−2.63	158	21	st	GED	33
Cp*	Yb	1.376	2.662	2.64−2.69	145.7	34,9	st	X-ray[b]	40
		2.384	2.667		145.0	37.0			

[a] Definitions of ligands the same as in previous table: Cp4i, $[C_5H(i\text{-}Pr)_4]$, [b] Two symmetrically independent molecules, [c] Not present in the original paper. [d] Fixed parameter. [e] st, staggered; ec, elipsed conformations. Values are in deg.

ring with high values of the bending constants of the M−CR−C angles. This is a convenient description when one wants to vary the orientation of the Cp rings and substituents.[18,19] A modified version of the dummy atom technique was developed for ferrocene-like molecules and used for calculations of vibrational spectra.[20] Another possibility for the fixation of a Cp ligand near a metal atom is with the help of electrostatic metal−ligand interactions. This method has been used for ferrocene and its derivatives.[6,7] The evident deficiencies of this model are the necessity of fitting of the charge values for different types of ferrocene-like molecules and the difficulties in reproducing nonparallel ring orientations (usually called "bent" orientations), which are quite common. A third possibility is the fixation of the Cp ligand with the help of M−C bonds. In the present work, this model not only was found to reproduce geometries and relative energies of conformers but also gives us an opportunity to utilize this unusual type of interatomic bonding with the MM3 program without any alteration of the program itself.

The present paper includes the results of calculations on the so-called bent sandwich molecules in the free state based on this model and also some results of crystal structure calculations on the same compounds. The first bent metallocene sandwich geometries were described in 1967 on the basis of experimental gas electron diffraction data for dicyclopentadienyllead and dicyclopentadienyltin.[21] During the last decade, more than 20 compounds with bent sandwich structures of the MCp_2 and MCp^*_2 ($Cp^* = C_5Me_5$) types were synthesized and characterized by X-ray analysis in crystals and by electron diffraction in the gas phase (Tables 1 and 2). The definitions of the geometrical parameters used to describe these molecules are

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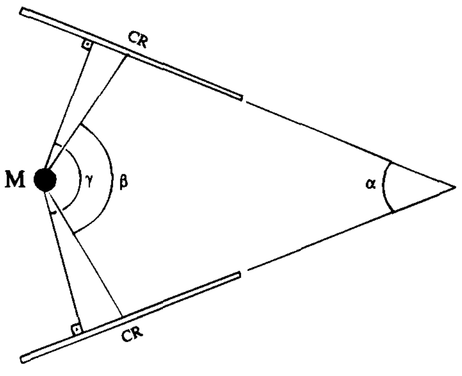

Figure 1. Main geometrical parameters of bent sandwich molecules. For definitions see ref 25.

shown in Figure 1. These molecules have bent sandwich structures, dissimilar to the parallel sandwich structures of ferrocene-like molecules.[41]

When a large number of Cp-containing molecules of the elements of the IVA group were investigated, in both the gas phase and crystals, it appeared that most of them had bent conformations (Table 1), except for overcrowded molecules which have parallel or nearly parallel ring orientations for steric reasons. Bent structures for molecules of this type were also supported by spectroscopic investigations. The vibrational spectra of $SnCp_2$ and $Sn(C_5H_4Me)_2$ can be adequately described in terms of local C_{2v} symmetries, which are characteristic of angular molecular conformations.[42]

In order to explain the bent conformations of the group IVA π-complexes, some MO calculations were carried out earlier.[22,24,29,43] Summing up the results of these calculations, the presence of the lone pair on the metal atom was considered to be the main reason for bending.

For the bent structures of group II, such an obvious reason for the bending as a lone electron pair is not present. Nevertheless, semiempirical and *ab initio* calculations show bent structures for the hypothetical cations Cp_2Sm^+ [44] and Cp_2Sc^+ and Cp_2La^+.[45] The calculations on $LnCp_2$ molecules (Ln = Sm, Eu, Yb) in a quasi-relativistic CSF-X-α approximation do not explain the bending of the $LnCp^*_2$ molecules as observed in the gas phase.[46] Hartree–Fock calculations on $MgCp_2$ and $CaCp_2$[38] show that for the former, in agreement with experiment, there is a pronounced minimum corresponding to a parallel ring orientation. For $CaCp_2$, the results were dependent of the basis set and the M–CR distance used. It was possible to reproduce the observed bending with certain values for these quantities, but for most of the basis sets, the potential curve for the bending is flat, with a minimum at 180° and nearly equal energies over the range 160–180°. The failure of high-quality *ab initio* Hartree–Fock calculations does not, in our opinion, cast doubt on the existence of bent conformations for MCp_2 molecules,[38] as has been proposed.[47] As will be shown, the bending is mainly due to electron correlation, so Hartree–Fock calculations are inadequate.

The pseudopotential *ab initio* calculations (including electron correlation) of group II and lanthanide (II) metallocenes MCp_2 (M = Ca, Sr, Ba, Sm, Eu, Yb)[47,48] show distinctly bent structures only for the $BaCp_2$ molecule.[47] Some deviations from a parallel sandwich structure were also found for the $SmCp_2$ and $EuCp_2$ molecules. The bending potentials for all of these molecules were found to be very shallow. The latter fact led to the conclusion that all of these molecules in the gas phase are, in the author's terminology, actually linear (with a parallel sandwich structure) or quasilinear. So the results of the gas electron diffraction work are considered to be artifacts "due to different temperatures of measurement and the large uncertainties in the bending angles".[47] The bent structures in crystals, at least for MCp_2^* (M = Ca, Yb, Sr) molecules, have been explained as resulting from the influence of the crystal field. The same objection could be raised against the results of the experimental investigations of the molecules of group IVA, but usually these results have been considered to be reasonable. Note that no MCp_2 molecules of group II have been investigated experimentally, either in the gas phase or in the crystal (see Table 2). The computed geometries of the molecules were compared for the corresponding MCp^*_2 compounds.

Computational Details

All molecular mechanics calculations were carried out with the MM3 program[49–51] on MicroVAX and IBM RISC 6000 computers, using standard optimization procedures. Since the program was not parameterized for Cp-ligand-containing molecules, we added several parameters to allow us to deal with them (Table 3). This preliminary parameterization allows us to reproduce conformational peculiarities of these molecules, but not the vibrational spectra, and we do not wish to finalize the parameterization until we can reproduce vibrational frequencies as well.

The l_0 bond lengths for the Cp residues were taken from the results of a statistical analysis of the Cambridge Crystallographic Data Base for Cp- and Cp*-containing moelcules.[52] The force constants were taken to be the same as for C(sp^2) atoms. The parameters for other types were considered to be equal for Cp and Cp* rings. The θ_0 values for the bond angles in the Cp ligands were taken as for an ideal pentagonal ring. We used for these angles the same force parameters as were used for the ferrocene molecule in ref 6.

The most important problem was to deal with in a proper way the interactions between the metal atom and the Cp ligand (π-bonding). In our previous work,[13,14] this was done with the aid of a dummy atom. The main disadvantage of this description is the difficulty in reproducing the fine details of the Cp orientation in the coordination sphere of the metal atom, such as the inclination of the Cp ring relative to the M–CR

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Table 3. Force Field Parameters for Metallocenes[a],[b]

Bond Lengths and Stretching Parameters

bond	l_0	K_s
113-113	1.397	7.50
114-114	1.417	7.50
113-5	1.101	5.15
114-1	1.512	6.30

Angle Bending

atoms	θ_0	K_θ
113-113-113	108.0	0.60
113-113-5	126.0	0.40
114-114-1	126.0	0.47

Torsion Parameters

atom types	V_1	V_2	V_3
113-113-113-113	0.0	10.0	0.0
113-113-113-5	0.0	10.0	0.0
5-113-113-5	0.0	10.0	0.0
114-114-114-114	0.0	10.0	0.0
114-114-114-1	0.0	10.0	0.0
1-114-114-1	0.0	10.0	0.0

van der Waals Parameters

element	atom type	ϵ	R_{vdw}
C	113	0.056	1.96
C	114	0.056	1.96

Metal−Carbon Bond Parameters in π-Complexes (π-Bonding)

elements	atom type	ϵ	R(M−C)
Si	113-19	15.0	2.45
Ge	113-31	15.0	2.50
Sn	113-32	15.0	2.71
Pb	113-33	15.0	2.78
Ca	113-125	15.0	2.61
Sr	113-126	15.0	2.75
Ba	113-127	15.0	2.90
Sm	113-133	15.0	2.79
Eu	113-134	15.0	2.79
Yb	113-141	15.0	2.62

[a] Bond lengths in Å; angles in deg; stretching, bending, and torsion parameters are in mdyn/Å, mdyn Å/rad^2, and kcal/mol, respectively. [b] Atom types: 113, carbon atom in unsubstituted Cp ring; 114, carbon atom in substituted Cp* ring. These atoms are considered to be uncharged, as is the bonded metal, and the bonding is taken to be covalent.

bond. A more convenient way to describe such pecularities is a "soft" fixation of M−C(Cp) bond lengths. This has been done in the present work with the help of a Hill equation, as previously utilized in the MM3 program[53] to describe hydrogen bonding.

The Hill function is at least semiquantitatively correct for the potential of interest. It has an adjustable energy minimum at an adjustable distance. It shows a strong repulsion when the distance becomes too short but goes to zero at long distances, allowing dissociation. Since at this point it is only necessary that it give us a reasonable energy vs distance relationship near the energy minimum and the correct dissociation energy, which it does, it is adequate for present purposes. The function is already available in MM3 and so may be used. In order to fit spectroscopic data, it may be desirable to modify this function, but this is beyond the scope of the present work.

The value of the depth of the potential curve (characterized by ϵ) was taken from the experimental value of the M−Cp bond energy. Unfortunately data on the values of M−Cp bond energies are available for only a limited number of Cp-containing molecules. For 3d-metallocenes (M = Fe, Co, Cr, Ni, V, Mn), the enthalpies of dissociation of M−Cp bonds are in the range 51−88 kcal/mol,[41] or according to the more recent investigations[54] (M = V, Mn, Fe, Ni) 59−95 kcal/mol. The first bond dissociation energy of $YbCp_3$ is equal to 58 ± 5 kcal/mol according to ref 55. The same value for the $MgCp_2$ molecule is 54.5 ± 12 kcal/mol.[56] We chose the lower limits of these data for our calculations. The l_0 values for the M−C(Cp) distances were taken for every molecule as the mean of the experimental gas phase values (Tables 1 and 2). The values of the π-bonding parameters are given in Table 3.

In our previous work,[13,14] it was shown that we need not include an angle bending potential for the metal-containing angles for a description of the relative positions of the Cp ligands in the coordination sphere of the metal atom. This approximation was based on the experimental structural data of mononuclear π-complexes with complete and partial occupations of the coordination sphere of a metal atom and an assumption that the occupation of this sphere is optimum.[57,58] As a calculational criterion of optimum occupancy, we chose the energy minimum of the interligand nonbonded interactions. In our MM3 model, the positions of the ligands are mainly determined by the sum of the interligand van der Waals interactions. To keep our model simple, we do not include atomic charges on the metal atoms or on the atoms of the Cp rings or terms describing the conjugation. A more general model might want to consider these, but they are not required at present.

For crystal structure calculations, programs CRYST[51] and CRYSTGEN[59,60] were used. The same force field parameters (Table 3) were used for all calculations.

Results and Discussion

Dependence of the Bending Angle on the Metal−Ligand Distance. Before the computation of the conformations of the distinctly bent sandwich molecules, we calculated the dependence of the bending angle (angle between planes of Cp rings, see Figure 1) on the M−C(Cp) distance, as reported earlier.[13,14] We first optimized the geometries of the bent sandwich molecules with a series of fixed M−C(Cp) distances from 1.8 to 2.8 Å, with a step size of 0.1 Å for MCp_2 molecules, and from 2.0 to 3.1 Å with the same step size for MCp^*_2. The results of the calculations show that the molecules prefer staggered ring conformations for Cp- and Cp*-substituted complexes, and the curves showing the dependence of bending on the M−C distance for such conformations are shown in Figures 2 and 3. Both curves adequately reproduce the experimental trends in the dependence of the interplane angle on the distances between the metal atoms and the cyclopentadienyl rings. In the case of the unsubstituted Cp complexes, all of which belong to the IVB group (Figure 2), some results from gas electron diffraction better correlate with the computational results. The X-ray data and the computational results for group IVA MCp_2 molecules are not strictly comparable because the Sn and Ge derivatives have an eclipsed ring orientation in the crystal.

In our MM3 model we have no terms corresponding to electron lone pairs on the metal atom. Figure 2 shows that the consideration of only nonbonded interligand interactions is sufficient to well describe the observed bending in these molecules. This does not exclude the physical existence of stereochemically active lone pairs on metal atoms, but only says that they are not required by our model. Only investigations of the electron density distribution[61,62] can show exactly the

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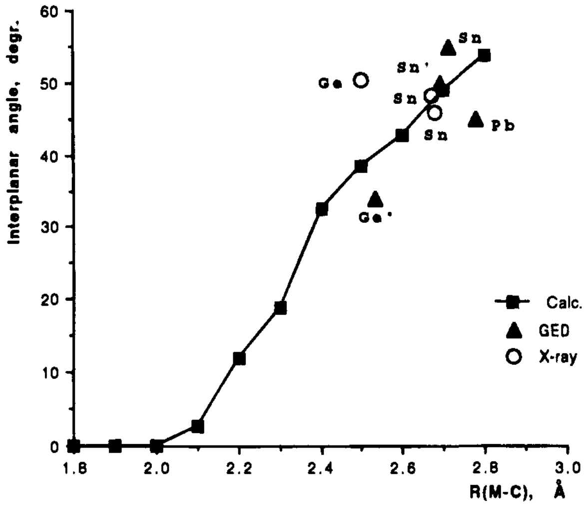

Figure 2. Calculated dependence of the gas phase interplanar angle (α) in MCp_2 molecules on the M−C(Cp) distance for IVA group molecules. Sn′ and Ge′ are monomethyl-substituted Cp rings; for the X-ray structures, the values of α for each crystallographically independent molecule are shown.

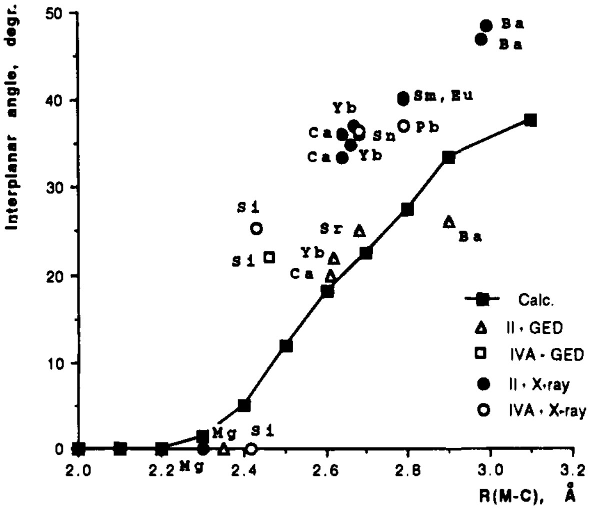

Figure 3. Calculated dependence of the gas phase interplanar angle (α) in MCp^*_2 molecules on the M−C(Cp) distance. For X-ray structures, the values of α for each crystallographically independent molecule are shown.

presence or absence of a stereochemically active lone electron pair on a metal atom. On the basis of the present work, we can only propose a predominantly s character for the lone pair orbital on the metal atom.

The dependence of the interplanar angle on the M−C(Cp) distance for methyl-substituted molecules of the groups II and IVA is shown in Figure 3. It is apparent that the calculated curve reasonably well reproduces the observed dependence of the bending angle on the M−C(Cp) distance for the gas phase structures of the molecules of the group II. We can also see that the values of these angles are systematically higher in the crystal than in the gas phase. This phenomenon was pointed out earlier,[34] where the dependence of bending angles on the ionic metal radii was described. This leads us to the necessity of the calculation of the influence of the crystal field on the molecular conformations for MCp^*_2 molecules for comparisons with crystallographic data.

The situation is not so obvious and predictable in the case of the group IVA π-complexes (especially $SiCp^*_2$). It is possible that in the $SiCp^*_2$ molecule (the only available gas phase structure for a group IVA molecule) the influence of the lone pair makes the molecule more bent than the corresponding molecules of group II. The same regularity of the molecular conformations of group IVA compounds in crystals was found as for group II molecules, with one exception for the $SiCp^*_2$ structure. In this case, two additional factors need to be considered—the crystal field and the lone pair on the metal atom. This is the most obvious case of the influence of the crystal field, where parallel and bent sandwich molecules are present. The explanation of this fact is the small energy difference between the two conformations of the free molecules (in our calculation it is less than 0.1 kcal/mol for $SiCp^*_2$ molecules and only ca. 0.2 kcal/mol for $SiCp_2$). The increase in the M−C(Cp) distance increases the energy difference between the two conformations, but in any case, this difference is small enough (less than 2.0 kcal/mol[13]) so that the coexistence of two different molecules in the crystal is possible. We can see from Tables 1 and 2 that in the majority of the available crystal structures two symmetry independent molecules are present, but in most cases, the conformations and bending angles are nearly the same for the two molecules.

Comparison of the calculated bending/distance curves for unsubstituted and Me-substituted molecules (Figures 2 and 3) shows that these two types of π-complexes are characterized by different values of the interplanar angles when the M−C(Cp) distances are the same. This is understandable because the equilibrium van der Waals distances between the hydrogen atoms are shorter, and so the amount of bending is larger, than for methyl-substituted molecules. Bending begins to be possible for unsubstituted molecules starting with a M−C(Cp) distance of ca. 2.0 Å, and for the methyl-substituted rings, from about 2.2 Å. The corresponding distances for π-complexes with parallel ring orientations are usually on the border of this range or shorter.[41] Bending becomes quite obvious when the M−C(Cp) distance is approximately 0.2 Å greater than this borderline distance. The energy differences between the bent and parallel sandwich molecules in this range are very low, and bending usually is observed if there are additional ligands in the coordination sphere of the metal atom or if there are bridging groups between the Cp ligands.

Influence of the Crystal Field on Molecular Conformation. Because there are some restrictions and limitations in MM3 and in the CRYST programs, we carried out complete crystal structure calculations only for the $SmCp^*_2$ crystal, which consists of a single system of symmetry independent molecules (Table 2). To find the influence of molecular packing on conformation, we performed a standard crystal packing analysis of rigid molecules inside a soft environment (see for instance ref 63) for four different models. We treated a discrete set of conformations as starting points during the optimization process. Model I: bending angle $\alpha = 40.0°$, space group $P2_1/n$, $Z = 4$ as in the experimental crystal structure. Model II: $\alpha = 40.0°$, space group $P1$, $Z = 4$. Model III: $\alpha = 32.4°$, as the staggered gas phase conformation, space group $P2_1/n$, $Z = 4$. Model IV: $\alpha = 32.4°$, space group $P1$, $Z = 4$. During the energy minimization, all molecules which are inside a block of 27 unit cells (with the referenced unit cell in the center of this block) were taken into account. The initial unit cell parameters were taken to be 20% larger than experimental. In the case of model I, after the lattice was optimized, the central molecule in the new lattice was optimized, then a new block was constructed from the optimized molecules, and iterations were carried out

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Table 4. Unit Cell Parameters for $SmCp^*_2$

parameters	model I	model II	model III	model IV	exptl cryst
a	9.813	9.741	9.525	9.611	9.815
b	13.426	13.147	13.431	13.575	13.436
c	14.153	14.205	14.671	14.651	14.163
α	90.0	90.0	90.0	90.0	90.0
β	94.98	95.25	93.20	93.82	94.98
γ	90.0	90.0	90.0	90.0	90.0
vol	1844	1825	1874	1907	1861
lattice energy	−27.42	−24.68	−19.32	−20.42	

Table 5. Interplane (Bending) Angles (deg) in the Gas Phase and Crystal in Some CCp^*_2 Complexes

		Ca	Ba	Sm	Yb
gas	exptl	20	26		21
	calcd	21.2	32.8	25.4	24.4
crystal	exptl	33.5; 36.0	46.9; 48.5	40.0	34.9; 37.0
	calcd	30.4; 33.6	49.1; 46.0	41.9	35.3; 39.1

to establish that convergence had occurred. Further changes were negligible. If the initial lattice is too different from the experimental one, convergence may occur to a different (polymorphic) structure. Such structures so far found are higher in energy than the experimental structure, and they will be discussed in a later paper.

The crystal energy and the unit cell parameters which correspond to the energy minimum are listed in Table 4. The packing of the molecules with the larger bending angle (I and II, $\alpha = 40°$) leads to a crystal of lower energy than does that with the smaller angle (III and IV, $\alpha = 32.4°$), i.e. the structure which corresponds to the experimental one is preferable. The difference between the experimental and calculated unit cell parameters (Table 4) shows the reliability of approximations used, according to Williams' criterion.[64]

The other part of crystal packing analysis was calculation of conformationally flexible molecules inside a rigid crystal environment which corresponded to the experimental data. These calculations were carried out for $SmCp^*_2$ and for its Ca, Ba, and Yb analogs as well. After the molecular structure optimization in the crystal environment, the latter was removed, and the molecule was allowed to relax without the influence of the crystal field. The results of these calculations are shown in Table 5. It can be seen that, when we optimized the X-ray molecular conformations in the crystal environment, they did not change significantly. On the contrary, when we removed the crystal environment, the changes in the bending angle were quite pronounced. As usual, the bending angle in the crystal is larger than in the gas phase, as a result of intermolecular interactions.[34]

So both types of crystal structure calculations (flexible molecules inside a rigid environment and rigid molecules with different conformations inside a soft molecular environment) lead us to the same conclusion, that crystal packing has a significant influence on the molecular conformation and that this influence increases the interplanar angle between the Cp rings. The presence of the crystal forces is not, however, the fundamental cause of the bending. So we cannot completely agree with the conclusions of ref 47, where the existence of a bent sandwich metallocene structure was considered to be due to the intramolecular interactions only for Ba, Sm, and Yb MCp_2 molecules. All molecules of these series (including Mg with a parallel ring orientation) have their degree of bending determined by the balance between the interligand repulsion (short M−C distances) and attraction (long M−C distances).

Calculations on Overcrowded Bent Sandwich Molecules. To confirm the generality of our model, we carried out calculations on several molecules with bulky substituents. Usually the metal atom in such molecules is completely screened by ligands. The ligands of neighboring molecules cannot access the metal coordination sphere, so such molecules should be less influenced by the crystal field than molecules with "light" ligands (i.e., Cp). The results of X-ray investigations of such crystals are summarized in Tables 1 and 2, and they show quite clearly that bulky substituents can significantly change the bending angle. If we compare these angles with the unsubstituted complexes, the substituents force the complexes to be parallel or nearly so. This trend is clear, for example, in the series of tin complexes (Table 1), where the interplanar angle changes from 55° for the unsubstituted complex to 0° for the phenyl-substituted molecule.

We carried out calculations on four complexes of group IVA and two of group II. Initial molecular geometries were generated by the MEDIT program[65] and/or on the basis of X-ray data. Experimentally, the complexes $M[C_5(CH_2Ph)_5]_2$ (M = Ge, Sn, Pb) are bent in the crystal (conformation I, Figure 4). Note that two phenyl rings from one Cp ligand of the molecule and one phenyl ring from the other ligand screen the cavity near the metal atom on the "open" side. For optimization of the molecular structures, we began with both this conformation (I) and also the conformation in which all the phenyl substituents were turned out away from the metal atom (II). These (isolated molecule) conformations were optimized to yield two different structures, of which I was the more stable. The computational results on the decabenzylmetallocene molecules are shown in Table 6. Our model correctly reproduced the trend of the changes in the bending angles, but all experimental values are slightly larger than calculated. This may be from the influence of the lone pair, which is not taken into account in the calculations. The conformation which exists in the crystal is significantly preferred for the isolated molecule as well. This is understandable because in this conformation more nonbonded interatomic distances are near the sum of the van der Waals radii.

The initial geometry for the calculation of the conformation of $Sn(C_5Ph_5)_2$ was obtained from the MEDIT program.[65] Since we have no torsional potential for the description of the rotation around the C(Cp)−C(Ph) bond, initially we considered these torsion potentials to be zero. The results definitely show the parallel ring orientation in the free decaphenylstannocene moelcule, but they did not reproduce the dihedral angles between the planes of the Cp and Ph rings. These showed too much twist, in the range 60−70° (Figure 5). We adjusted the torsional parameters in order to reproduce the ring orientations and obtained the following values: $V_1 = 0.0$, $V_2 = 1.5$, $V_3 = 0.0$. These parameters are similar to those for the central bond in biphenyl.[66] The calculated torsion angles for the isolated stannocene molecules are then in the range 46−52°, and the torsion angles for the same molecule in the crystal are 48−59°. The X-ray values for molecules with the same pentaphenylcyclopentadienyl residue are 42.0−61.5° for $[PPN][(C_5Ph_5)Cr(CO)_3]$ and 46.6−54.3° and 43.3−66.0 for two conformers of $(C_5Ph_5)Cr(CO)_3$.[67]

Bis(tetraisopropylcyclopentadienyl)calcium and -barium ($Ca(Cp4i)_2$ and $Ba(Cp4i)_2$, Table 2) are the most stable Cp

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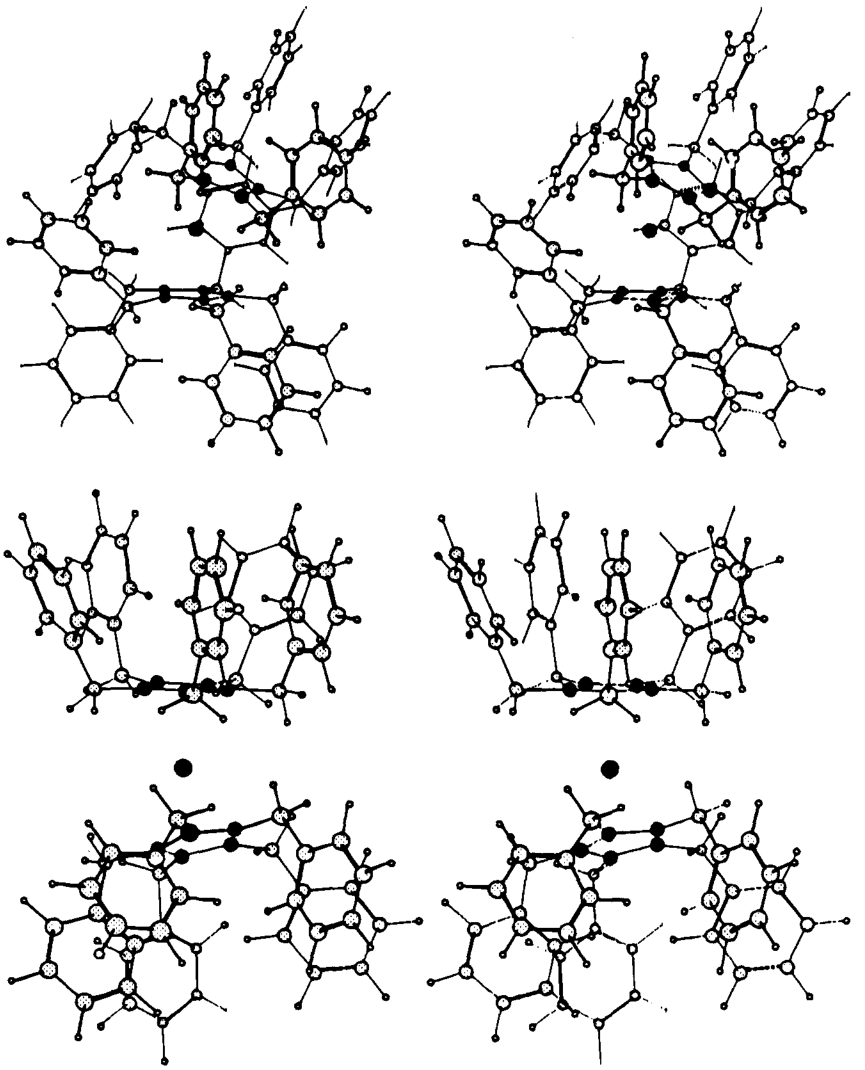

Figure 4. Optimized conformations of decabenzylstannocene molecule: (a) from X-ray geometry and (b) from the model with "opened" cavity.

Table 6. Main Geometrical Parameters and Conformational Energies of Bent Sandwich Decabenzylmetallocenes

metal	M−C(Cp) (Å)	α, deg I	α, deg II	α, deg exptl	ΔE, I-II (kcal/mol)
Ge	2.56	26.9	25.2	31.0	−4.59
Sn	2.71	28.6	25.5	32.8	−4.93
Pb	2.79	29.7	29.6	33.3	−7.66

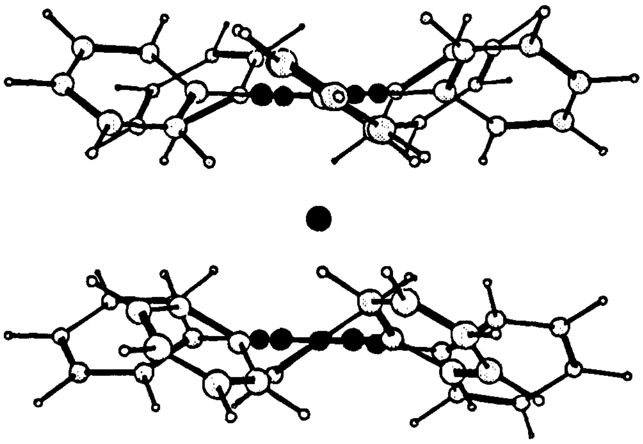

Figure 5. Optimized conformation of the $Sn(C_5Ph_5)_2$ molecule.

complexes of group II, which is understandable because here, as in the molecules described above, the cavity around the metal center is surrounded by substituents. The initial geometries for these molecules were obtained with the MEDIT program in accordance with the description of the orientations of the isopropyl groups given in ref 36. The comparison of the calculated/experimental bending angles (17.7/14.6, Ca; 25.9/22.8, Ba) shows reasonable agreement.

The barriers to internal rotation were found by means of DNMR experiments[36] for $M(Cp4i)_2$ molecules. It was not definitely established what kind of internal rotation was observed, the rotation of the *i*-Pr groups or rotation of the five-membered rings. We calculated the dependence of the energy on the angles of rotation for the *i*-Pr groups at different ring positions, which were characterized by different places relative to the hydrogen position in the Cp ring and by different orientations of the neighboring substituents in the molecule. This is a rough approximation for the experimental barrier which properly would require that we take all internal rotations into account simultaneously. Nevertheless, such a calculation can show us the order of magnitude of this barrier. We calculated the energy dependence on torsion angle for the *i*-Pr groups at the various positions of the Cp ring. The global energy minimum calculated has the same orientations of these groups as are found in the crystal. We obtained the following values for barriers to rotation at positions 2−5, respectively: 12.0, 10.3, 15.3, and 8.0 kcal/mol. These values are similar to the experimental activation energies for both the Ba and Ca complexes: $\Delta G^{\ddagger} \geq 11.1$ kcal/mol. So the experimental values

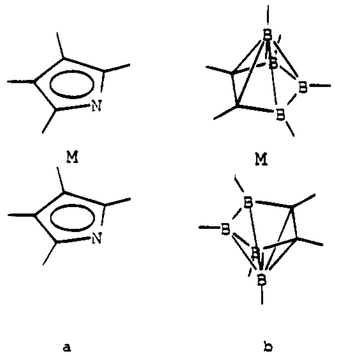

Figure 6. New representatives of bent π-complexes: (a) diazametallocene and (b) metallocarborane.

are consistent with the internal rotations of the *i*-Pr groups, although the possibility of ring rotation cannot be excluded.

Using this information, we not only can reproduce molecular structures but also can predict the structures of unknown compounds. So, for SrCp$_2$, we can suppose in accordance with the M−C(Cp) distance that the bending angle will be between 40 and 50°, and for BaCp$_2$, this angle should be about 60°. It is very probable that, in crystals, these compounds will form polymeric structures. This is observed, for instance, with PbCp$_2$,[68] where the metal atom is not screened very much by the substituents of the Cp ring. In fact, it was found that CaCp$_2$ is polymeric in the crystal, with additional metal coordination.[69] We therefore do not support the conclusion[47] that these molecules should be planar or nearly so.

To illustrate the predictional possibilities of the present model, we can cite other examples of molecules with other types of Cp-like π-ligands which form parallel sandwich structures when the interplanar distances between ligands are short and bent structures when these distances are sufficiently long. There are substituted diazametallocenes (Figure 6a), which have parallel structures for M = Fe[70] and Co[71] (interplanar distances of 3.33 Å for Fe and 3.56 Å for Co, and metal−ring distances of 1.66 and 1.78 Å, respectively) and bent structures for M = Pb[72] (metal−ring distance, 2.68 Å; CR−M−CR, 142.7°).

The other groups of molecules are π-complexes 1,1′-*commo*-M[2-R-3-R′-2,3-C$_2$B$_4$H$_4$]$_2$, where M = Si, R = Me, R′ = SiMe$_3$;[73] M = Ge, R = R′ = SiMe$_3$;[74] and M = Sn, R = Me, R′ = SiMe$_3$[75] (Figure 6b). These metallocarboranes contain two carborane anions with formal charges of 2−, together with 4+ metals of group IVA. These anions are π-coordinated with metal atoms, and they represent 2− analogs of the Cp ligand with 1− charge. In this series, molecules with short interplanar distances are not bent (interplanar distances of 3.32 Å for Si and 3.4 Å for Ge), whereas stannacarborane (with a M−plane distance of 2.05 Å) is.[76]

Conclusions

The aim of our calculations was to reproduce, and enable us to understand within the framework of molecular mechanics, the unusual experimentally known molecular conformations of sandwich molecules, where some are planar and some are bent to varying degrees. The experimental results are clearly understood in terms of our model in a simple way. We conclude that this bending is mainly a result of the nonbonded interactions, especially attraction (or in other words dispersion, or electron correlation) between the Cp ligands. Crystal packing forces influence bending to some extent, but they are neither the cause of the bending nor the major force in determining the degree of bending. It should be pointed out that only by taking into account electron correlation in quantum mechanical calculations was it possible to reproduce quantitatively the ring−ring distance in the ferrocene molecule itself.[77]

After this paper was submitted, an independent paper on molecular mechanics calculations of the bent metallocene molecules was published.[78] In that work, the same model was used as was proposed in our earlier papers.[13,14] The results and conclusions described in that paper are similar to those presented here insofar as they overlap.

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