Molecular Mechanics Force Fields for Cyclopentadienyl Complexes

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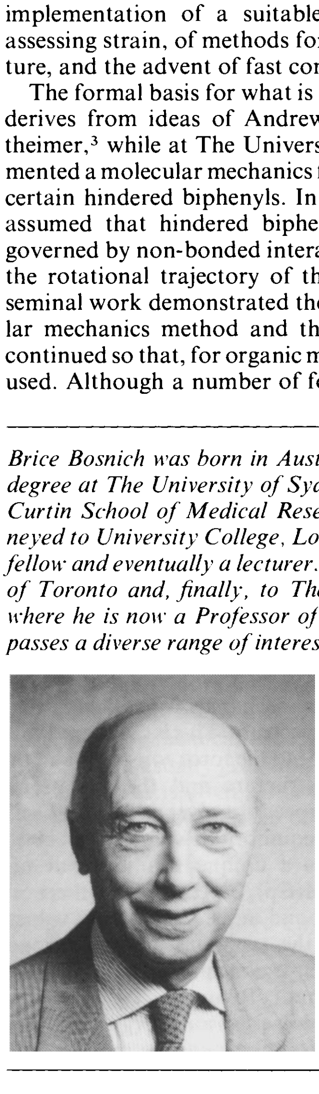
1 Introduction

The notion that molecules might be treated as ball and spring objects has pervaded chemical thinking from the time that molecular geometry was recognized. Although primitive at first, the idea that stretching bonds and bending angles from their 'natural' lengths and angles resembled deformations of a spring was widely accepted. Moreover, it was noted that atoms of a molecule occupied a volume and may carry partial charges. Consequently, these atoms were not expected to penetrate each others volume and their positions could be governed to some extent by charge–charge interaction. It was therefore logical to conclude that bond length and angle deformations, steric and charge interactions would raise the energy of a molecule compared to an analogous molecule possessing fewer deformations and interactions. It could then be said that one molecule was more 'strained' than the other. If one were able to calculate the energy of each of the components contributing to the strain one would have a quantitative measure of the total strain energy. Implied in this quantitative model is the expectation that variations in structure could be determined by finding the least strained structure of the molecule. This promise of calculating the strain energy and structure of molecules had to await the implementation of a suitable mathematical framework for assessing strain, of methods for finding the least strained structure, and the advent of fast computational machines.

The formal basis for what is now called molecular mechanics derives from ideas of Andrews[1] and Hill;[2] but it was Westheimer,[3] while at The University of Chicago, who first implemented a molecular mechanics force field for the racemization of certain hindered biphenyls. In his considerations, Westheimer assumed that hindered biphenyl racemization was basically governed by non-bonded interactions and by bond strain along the rotational trajectory of the rotating phenyl groups. This seminal work demonstrated the utility of the empirical molecular mechanics method and the development of the field has continued so that, for organic molecules, the method is routinely used. Although a number of force fields have been developed, the early work of Allinger[4] is notable for it is now one of the most comprehensive programs for organic molecules.

Brice Bosnich was born in Australia, received his undergraduate degree at The University of Sydney and his Ph.D. from the John Curtin School of Medical Research in Canberra. He then journeyed to University College, London where he was a postdoctoral fellow and eventually a lecturer. He then moved to The University of Toronto and, finally, to The University of Chicago in 1987 where he is now a Professor of Chemistry. His research encompasses a diverse range of interests which include, the development of asymmetric catalysts and studies of their mechanisms, synthesis, and reactivity of organometallic and coordination compounds and occasional forays into quasi-theoretical studies such as those described here. A constant thread which has characterized his work is an interest in stereochemistry, particularly the chirality of molecules. He is the 1995/96 Nyholm Lecturer. This article is dedicated in memory of Ron Nyholm.



In contrast to organic force fields, those involving inorganic complexes are less well developed – particularly those that attempt to model organometallic π-complexes. Starting with the work of Hawkins[5] and Snow[6] there now exists a reliable body of empirical information which can be used to reproduce structures of first row transition metal coordination compounds containing nitrogen and oxygen donor atoms. These coordination compound force fields[7] were derived on a less formal basis than their organic counterparts. Force constants were derived by trial and error and certain arbitrary assumptions about non-bonded interactions were incorporated. Even so, for practical purposes, the methods work well if only the reproduction of structure is required. Until very recently, very little attention has been given to transition metal organometallic complexes, particularly those incorporating π-ligands. These systems are conceptually more difficult to handle because of the peculiarity of the topologies of binding. These require special treatments.

This review describes our attempts to develop self-consistent force fields for organometallic π-complexes. We deal with linear metallocenes of the type $[M(Cp')_2]$ and bent metallocenes of the type, $[M(Cp')_2X_2]$ where Cp′ is a generic cyclopentadienyl ligand which may or may not be substituted. In addition we illustrate by molecular mechanics why certain $[M(Cp^*)_2]$, Cp* is the pentamethylcyclopentadienyl ligand, complexes of alkaline earth and lanthanide elements are bent instead of being linear as intuition might suggest.

2 The Force Field

The total molecular mechanics energy, E_T, is given by the sum of the energies associated with bond stretching, E_b, angle bending, E_a, torsional deformations, E_t, and van der Waals interactions, E_{VDW}.

$$E_T = \sum\nolimits_{\text{bonds}} k_b(r - r_o)^2 + \sum\nolimits_{\text{angles}} k_a(\theta - \theta_o)^2 + \sum\nolimits_{\text{torsions}} k_t[1 - \cos(n(\theta - \theta_0))] + \sum_{i<j} \epsilon_{ij}[(r_o/r_{ij})^{12} - 2(r_o/r_{ij})^6]$$

In these equations k_b, k_a, k_t are the respective force constants, r_o and θ_o are the 'equilibrium' bond lengths and angles, respectively, n is the periodicity and θ is the angle. In the Lennard–Jones VDW equation, ϵ_{ij} is the well-depth of the i^th^ and j^th^ interactions, $r_o = \frac{1}{2}(r_{ii} + r_{jj})$ and r_{ij} is the internuclear distance. It will be noted that the harmonic Hooke's law is used for the bond and angle terms and the truncated Fourier expression is used for dihedral terms. More realistic and fancier equations can be substituted but experience suggests that these simple representations suffice. Most organic atoms have been assigned van der Waals parameters which adequately generate the energies of these non-bonded interactions. Parameters for metals are not known but we have found that assigning values of − 0.001 kcal/mole for ϵ and r_o = 1.0 Å for all metals leads to satisfactory results. Changing r_o to 2.0 Å and ϵ to − 0.01 kcal/mole did not affect the structures calculated. In many force fields electrostatic interactions are added but this requires the ability to calculate partial charges on each of the atoms and a knowledge of the microscopic dielectric constant. For organometallic complexes there is no reliable method of calculating partial charges with any accuracy. The electrostatic contribution is therefore omitted.

At this stage it is important to note that the energy associated with the first three terms assumes that an equilibrium value can be determined In other words, there exist bond lengths and angles which are 'natural' for the system in question, so that when $r = r_0$ and $\theta = \theta_0$ there are no contributions to the strain energy To illustrate the problem consider the angle bending term in 5-coordinate complexes For distorted 5-coordinate structures, do we assume that the final structure is derived from a trigonal bipyramid or square pyramid structure? Similarly, in the present context, we might debate the 'natural' angles in $[M(Cp)_2X_2]$ complexes This dilemma is neither commonly recognized nor is it a trivial problem in molecular mechanics calculations We require some formal method of determining 'equilibrium' parameters Clearly, the final minimized structure will depend critically on the equilibrium parameters as well as on the associated force constants So will the energy In this respect one should be circumspect in using some of the commercial programs which attempt to derive structures of organometallic compounds Their 'success' is based on selecting equilibrium bond lengths and angles which are essentially the same as the final structure The structure is driven to the desired result by application of impossibly large force constants In a sense these programs are almost self-fulfilling One might say that they are ball and stick rather than ball and spring representations

3 A Molecular Mechanics Topology for Organometallic π-complexes

Organometallic complexes bearing π-bonding ligands present special challenges in defining the topology For example, in the case of an olefin complex, do we define the topology as consisting of two bonds to the metal, one for each of the carbon atoms, or do we make one bond to the centroid of the double bond? In the case of ferrocene, do we make ten bonds or just two, one each to the two ring centroids? Although not insurmountable, the topology defined by ten bonds in ferrocene presents difficulties in defining the molecular mechanics force field because of the presence of contiguous three-membered rings One can simplify the topology by defining a dummy atom (D) at the ring centroids and applying appropriate force constants to the bonds and angles associated with it Such a topology, although a fiction, can be used to reproduce structures but it has difficulties The first is that unrealistically large force constants are needed to maintain the dummy atom at the centroid during minimization The second is that spurious vibrational modes are generated when the force field is used to reproduce the vibrational spectrum Since we use vibrational spectra to derive self-consistent force constants, this scheme will not generate the proper force field

The use of the dummy atom topology is simple and appealing, however, and we have devised a way of retaining its simplicity but at the same time constructing a physically realistic model of the forces on the molecule [8] This can be illustrated by the simple example of ethylene π-bonded to a metal (Figure 1) where C_1 and C_2 are the ethylene carbon atoms and D is the dummy atom placed at the centroid in this case, but, in what follows, it is not required that it be at the centroid, M is the metal The x-coordinate of the dummy atom X_D is defined by the x-coordinates of the carbon atoms, X_{C1} and X_{C2} as follows

$$X_D = (X_{C1} + X_{C2})/2$$

and $$r = X_D - X_M$$

where X_M is the x-coordinate of the metal For the M–D stretch the energy, E, is

$$E = k_b(r - r_o)^2$$

and $$\partial E/\partial r = 2k_b(r - r_o)$$

also $$\partial E/\partial X_D = (\partial E/\partial r)(\partial r/\partial X_D) = [2k_b(r - r_o)][1] = 2k_b(r - r_o)$$

The force on the dummy atom can be transferred to C_1 by application of the chain rule

$$\partial E/\partial X_{C1} = (\partial E/\partial X_D)(\partial X_D/\partial X_{C1}) = \tfrac{1}{2}[2k_b(r - r_o)]$$

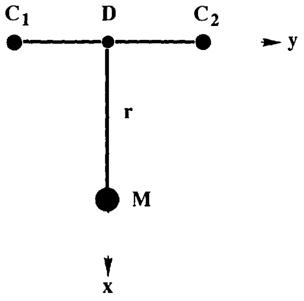


Figure 1

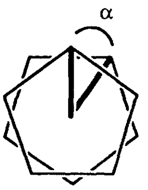
Thus half of the force on the dummy atom has been passed on to C_1 Similarly, the other half can be passed on to C_2, leaving no forces on the dummy atom The second derivative needed for the vibrational analysis can be transferred to the carbon atoms in a similar way It is clear that this method can be applied to more complex systems Thus the simple dummy atom topology can be used to provide a rigorous description of the forces We note that during minimization the position of the dummy atom is recalculated after each step

4 Derivation of Force Constants

In order to derive a force field one requires to know force constants and their corresponding equilibrium parameters and parameters for the VDW non-bonded interactions The VDW parameters have been developed for most of the atoms of concern here, except for the metals The procedure for finding the force constants and equilibrium values is an iterative process and relies on no assumptions about bonding, although bonding schemes can be used as a guide The first step is to select a parent molecule of known structure This molecule must contain all the elements we wish to define for the force field and which is considered to be the least strained Thus we would select a $[M(Cp)_2]$ complex for the linear metallocenes and $[M(Cp)_2Cl_2]$ for those said to be bent The assumption is that substitution of the Cp rings will lead to more strain than is present in the parent Cp-containing molecule Unless we are to make assumptions based on bonding schemes we usually know only two things about the parent molecule, its structure and its vibrational spectrum We require that the (approximate) molecular mechanics force field reproduce both the structure and the vibrational spectrum using a set of force constants, equilibrium bond lengths and angles, and VDW parameters Although there are a number of approaches to this problem, we have adopted the following Having chosen a parent molecule, each of the bonds and angles is assigned a force constant and an equilibrium value The choice of the force constant is basically an educated guess initially and the choice of the initial set of equilibrium parameters can be based on the crystal structure values or based on some supposed bonding scheme A computer-driven routine can be implemented which, with the given set of force constants, searches for equilibrium values which will minimize to the known structure The molecular mechanics force field is then used to generate the vibrational spectrum This is compared with experiment, adjustments are made to the force constants and the process is repeated until the structure and the vibrational spectrum is reproduced This procedure gives us a set of self-consistent force constants and equilibrium values For many molecules this process provides a unique solution, but not always For example, with the $[M(Cp)_2Cl_2]$ complexes there are many solutions to the skeletal bond angle equilibrium values These solutions all reproduce the structure and vibrational spectrum with the same set of force constants The minimized energies, of course, are all different Requiring, by definition, that the parent molecule have the lowest strain energy, a decision on the preferred equilibrium parameters can be made by the requirement that they provide the lowest minimized energy

5 Force Constants

For the force constants of $[M(Cp)_2]$ and $[M(Cp)_2Cl_2]$ complexes, it is convenient to divide them into those associated with the Cp rings and those related to the skeletal deformations involving metal–ligand bonds. This separation is an approximation, but a good one, because the internal ligand modes are well separated in energy from the skeletal modes. We found that to a very good approximation the internal Cp force constants can be transferred from metal to metal but the skeletal force constants are strongly metal-dependent. For linear metallocenes four skeletal force constants are required in the dummy atom formulation, (1) and (2). They involve Cp tilting, γ, metal angle bending, β, metal–dummy stretching, a, and dihedral rotation of the Cp rings, α. There is a similar but more extensive set of skeletal force constants for the $[M(Cp)_2Cl_2]$ systems. The dihedral rotation force constant was found to have a small force constant for linear metallocenes of the transition metals but, for $[M(Cp)_2Cl_2]$M = Ti, Zr, Hf systems, we have demonstrated that no dihedral force constant for the Cp ring rotations need be used. Although the process of arriving at the force constants can be tedious they are self-consistent because they are based on the vibrational spectra.



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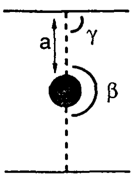


(2)

For the calculations described here and for the derivation of the force constants the CHARMM[9] suite of programs was used. It was interfaced with CHEM-X[10] which was used as a graphics and input front end. The CHARMM program was modified to accommodate our force field formulation of organometallic π-complexes. Parameters for organic groups attached to the Cp rings were those included in the standard CHARMM parameter list.

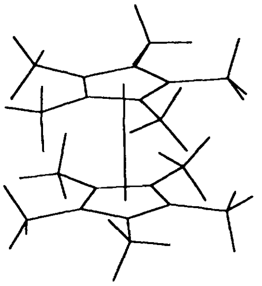
6 Linear Metallocenes of the Transition Metals

The structure of $[Fe(Cp)_2]$ has a history of controversy[11] related to relative rotation of the Cp rings. Both *X*-ray and neutron diffraction analyses of the crystals indicate disorder even at low temperatures. Gas phase electron diffraction indicates that the ferrocene molecule prefers to adopt an eclipsed conformation with a small internal rotational barrier of about 0.9 kcal/mole. From vibrational data we calculated the barrier to be 0.7 kcal/mole.[8] A prevalent supposition favouring the staggered conformation is that the non-bonded interactions are greater in the eclipsed form. Molecular mechanics can resolve this issue. Table 1 contains the energies associated with the various terms in the two forms. The total energy difference between the two forms found by molecular mechanics (~ 0.8 kcal/mole) is consistent with experiment. Whereas it is true that VDW interactions are slightly less for the staggered form, the major difference resides in the torsion term which is equal to that derived from vibrational data for ring rotation. Thus molecular mechanics provides a clear demonstration that the impediment to Cp rotation in ferrocene is electronic, rather than steric, in origin. Both ruthenocene and osmocene are found to exist in the eclipsed form in the solid.[12,13] From the vibrational data of ruthenocene we calculated a rotational barrier of 6.8 kcal/mole. A thermal motion study of crystalline ruthenocene estimates a barrier of 8.1 kcal/mole. No data are available to estimate the barrier for osmocene but we suspect it is higher. As for ferrocene, molecular mechanics indicates that the rotational barrier of ruthenocene is electronic in origin. The barrier for $[Co(Cp)_2]^+$ was calculated[11] to be the same as ferrocene suggesting that the rotational barrier increases for the higher mass elements of the same electronic configuration.

Table 1 Energy terms (kcal/mole) of the eclipsed and staggered forms of ferrocene

	Bond	Angle	Torsion	VDW	Total
Eclipsed	0.079	0.000	0.004	−5.225	−5.142
Staggered	0.073	0.000	0.724	−5.251	−4.454

The small barrier in ferrocene suggests that substitution could lead to a preference for the staggered conformation. This is the case for the decamethyl derivative, $[Fe((CH_3)_5Cp)_2]$ which in the crystal is perfectly staggered ($\alpha = 36°$).[14] Using the crystallographic coordinates, gas phase electron diffraction indicates that the molecule is staggered with a rotation barrier of about 1 kcal/mole.[11] Upon minimization, we find that $[Fe((CH_3)_5Cp)_2]$ has a structure which is partially staggered ($\alpha = 18°$). Two perspectives of the minimized structure are shown in (3) and (4). It will be noted that the orientations of the methyl group hydrogen atoms are such that, in both rings, one hydrogen atom of each methyl group lies approximately in the Cp plane, the other two hydrogen atoms lie above and below the Cp plane. Further, if we refer to the in-plane hydrogen atoms as the 'head', one ring has a head-to-tail clockwise sequence whereas the other is oriented head-to-tail anticlockwise. In the crystal the hydrogen atoms orientations are more complex with a number of the hydrogen atoms disposed perpendicular to the Cp plane away from the metal. On the assumptions that, first, the hydrogen atom conformations can affect the stagger angle and, second, that crystal packing forces can affect the hydrogen atom orientations, molecular mechanics calculations were performed on $[Fe((CH_3)_5Cp)_2]$ in its crystal environment. The resultant structure was perfectly staggered ($\alpha = 36°$) but the individual methyl group hydrogen atom orientations were the same as shown in (3) and (4) except that the hydrogen atoms were head-to-tail in the same direction for both rings. Although there is a cluster of these conformations of similar energy, the energy of the crystallographically found conformations is about 5 kcal/mole less stable than that of the minimized structure. We noted earlier that the rotational barrier of ruthenocene was much higher than that of ferrocene and it might be that, for example, $[Ru((Cl)_5Cp)_2]$, exists in an eclipsed conformation. This is found to be the case both by experiment and by the present calculations. Unfortunately, the $[Ru((CH_3)_5Cp)_2]$ molecule is disordered in the solid state and the conformation is uncertain.



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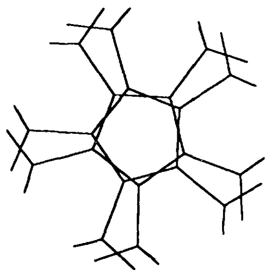
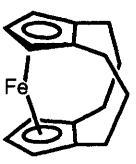


(4)

So far the problem of the rotamers of the linear metallocenes has been compared with experiment. These questions do not test the validity of the derived skeletal force constants because little skeletal strain is contained in these molecules. The two strapped ferrocenes, (5)[15] and (6)[16], do have skeletal strain, particularly the latter. For (6) we developed a number of spectroscopically based silicon parameters. We show the superimposed structures of the calculated and observed structures in (7) and (8). It will be seen that the fit is almost identical in both cases giving assurance



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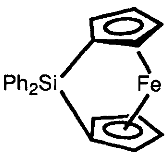

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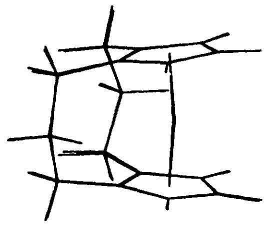

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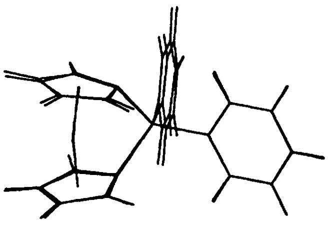

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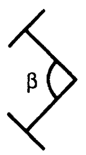

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that the force field is a good one and that the methods described can be extended to other systems.

7 Structures of Bent Metallocenes [M(Cp*)$_2$]

We now turn to a structural feature associated with certain [M(Cp*)$_2$] complexes which has been the subject of extensive debate. It was discovered that [M(Cp*)$_2$] (M = Ca, Sr, Ba, Sm, Eu, Yb) complexes did not possess parallel Cp* ring dispositions as is found in, for example, [Fe(Cp*)$_2$]. Rather, the rings were tilted, (9).[17] This is not a consequence of crystal packing, although packing effects can alter the tilt angle. A number of these molecules were found to be bent in the gas phase.[18] The [Mg(Cp*)$_2$] complex, however, contains parallel rings as does its parent, [Mg(Cp)$_2$]. The other alkaline earth and lanthanide metals give polymeric structures in the solid state when Cp is incorporated. Before these so called bent metallocenes were discovered it was known that [M(Cp)$_2$] complexes of Ge, Sn and Pb were bent and the facile assumption was made that a 'stereochemically active' lone pair of electrons was responsible for the tilt of the Cp rings. The [Sn(Ph$_5$C$_5$)$_2$] complex was found to be linear, however, and it was assumed that steric repulsion emanating from the phenyl groups led to the linear structure. Similarly, the complex, [Si(Cp*)$_2$] exists as both a linear and bent structure in the solid. These two forms presumably reflect the exigencies of crystal packing. Given the inter- or intra-molecular steric effects can result in a linear structure one is left questioning whether the putative lone pair of electrons is really responsible for the bent structures observed with the Si, Ge, Sn and Pb complexes. It is possible that these complexes belong to the same category as the alkaline earth and lanthanide complexes.

The existence of the bent metallocenes provoked numerous theoretical studies[19,20] seeking an electronic explanation for the bent structures. None was forthcoming, except that there appears to be an electronic component which may induce the Mg complexes to be linear.[20] Given the flexible predictive power of theoretical calculations on molecules of such complexity it seemed prudent to search elsewhere for an explanation.

It was noted[21] that in the bent [M(Cp*)$_2$] metallocenes the shortest interligand methyl group VDW contact distances were constant ($\sim$ 4.1 Å). Consequently, the tilt angle β, (9), decreases with increases in metal radius. The possible implication was that the tilt in these complexes was governed by VDW attractive forces of the ligands. It will be recalled that the VDW expression has both an attractive and repulsive part and that in the absence of other restraints an assembly of atoms will rest in an energy well. What is counterintuitive about this explanation is the expectation that a tilted unsymmetrical structure rather than a symmetrical topology will be produced. This hypothesis can be tested by the molecular mechanics force field derived here.

In order to derive a generic force field for these complexes we used the vibrational data of the [Mg(Cp)$_2$] complex which gave force constants for the M–D stretch and for the γ-bending term, (1). The D–M–D (β) bend force constant was set to zero in order to determine how the VDW interactions would affect the tilt of the Cp* rings. No force constant was applied to Cp* rotation.

The results are collected in Table 2.[22] The symbols r_x, β_x, α_x refer to bond lengths and angles found in the crystal, r_g, β_g refer to those in the gas phase. Where two entries appear, they refer to different molecules in the unit cell of the crystal. The energy difference, in kcal/mole, ΔE_T and ΔE_{VDW} refer to the total and VDW energies, respectively, and ΔE refers to the difference; E for the bent, minus E for the linear forms. Thus the bent form is more stable than the linear form in all cases. (For the Mg complex the difference is trivial compared to the thermal energy at 25 °C.) Inspection of Table 2 reveals a remarkable agreement with experiment when potential deviations due to crystal packing are considered and when the assumptions used in the gas phase electron diffraction analysis are recognized. Further, the difference in energy between the bent and linear forms is almost totally accounted for by the differences in VDW energy (ΔE_{VDW}), confirming the original hypothesis. These small energy differences indicate that these are floppy molecules which have ready access to both linear and bent forms at 25 °C. Two other features should be noted. First, the larger the metal radius the greater the tilt, that is the β-angle decreases with increase in radius. This is expected if VDW attractive forces are the important contributor to the structure. Second, the VDW energy differences, ΔE_{VDW}, increase in magnitude with increase in metal radius. This is because the VDW energy decreases in the linear form with increase in metal radius.

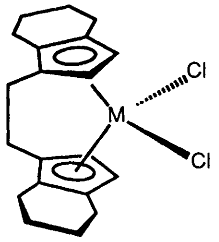
Table 2 Calculated and observed bond lengths and angles and the energy differences between the bent and linear forms of [M(Cp)$^*_2$] complexes

	Bond Length (Å)			Tilt Angle (°)			Stagger Angle (°)		Energy Difference (kcal/mole)	
M	r_{calc}	r_x	r_g	β_{calc}	β_x	β_g	α_{calc}	α_x	ΔE_T	ΔE_{VDW}
Mg	2.00		2.02	172		180	20		−0.08	0.10
Yb	2.33		2.33	153		158	22		−1.21	−1.07
Ca	2.35	2.33,2.36	2.31	152	146, 148	154	19	19, 25	−1.29	−1.15
Sr	2.48		2.47	147		149	18		−1.65	−1.58
Sm	2.52	2.53		145	140		18	19	−1.74	−1.68
Eu	2.52	2.53		145	140		18	19	−1.74	−1.68
Ba	2.73	2.70,2.78	2.63	138	131	148	26	32, 28	−2.03	−2.10

If, as it appears, VDW attractive forces control the topology of these metallocenes it is probable that with appropriate Cp substitution there will exist linear forms of these metals. We calculated that the bis-penta-iso-propylcyclopentadienyl complexes of all of the metals listed in Table 2 should be linear. If these can be made, it will be interesting to see if this prediction is correct. It should be noted, however, that full iso-propyl substitution is required to obtain the linear forms by our calculations. The $[Ba((Pr^i)_4C_5H_2)_2]$ complex is found to be bent both by experiment and by our calculations.

Returning to the bent metallocenes of Si, Ge, Sn, and Pb, for which stereochemically active lone pair electrons are invoked in order to explain the topology, our calculations predict that these molecules will be bent because of VDW attractive forces in both the Cp* and Cp complexes. Although these calculations do not preclude the stereochemical effect of lone pair electrons, they do indicate that the structures can be explained without invoking them.

The results of the molecular mechanics calculations on these bent metallocenes demonstrate the usefulness of the method. Without this technique it would not be possible to define the 'mechanical' forces which lead to the bent structures. Moreover, it gives pause to explanations of these structural features on the basis of molecular orbital calculations.



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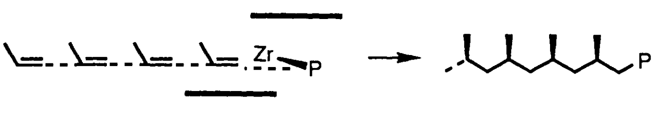
8 Structures of $[M(Cp)_2X_2]$ Complexes

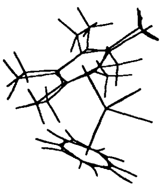
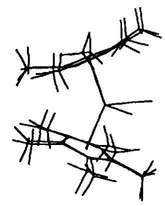
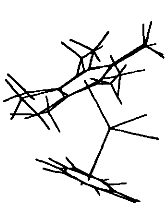
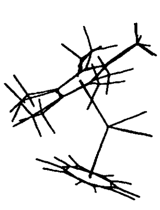
Derivatives of complexes of the types, $[M(Cp)_2Cl_2]$(M = Ti, Zr, Hf) are finding increasing application in stereoselective transformations.[23] Currently the chiral complexes of the ligand[24] ethylene-1,1'-bis(tetrahydroindenyl), (10), have proven to be the most effective precursors for these stereoselective transformations. Perhaps the most impressive discovery was that, after suitable activation, the Zr complex of (10) was an excellent catalyst for the isotactic polymerization of propylene.[25] The mechanism of this stereoselectivity is believed to occur by successive head-to-tail insertions of the propylene molecules as shown in Scheme 1 where the mean molecular planes of the two tetrahydroindenyl groups are shown as bars and P is the polymer chain. The scheme, as drawn, shows that each successive insertion involves the same (prochiral) face of propylene so that the pseudo-chiral centres of the product polymer are all of the same configuration. It is supposed that the face selection is to some extent governed by the chiral disposition of the tetrahydroindenyl groups. In the scheme this is implied by the assumption that the methyl group of propylene experiences less steric interaction in the shown orientation than when the olefin face is reversed leading to methyl group interaction with the lower drawn tetrahydroindenyl group. The selectivity almost certainly encompasses more steric and orienting effects than is implied in the simple scheme but ultimately the isotacticity of the product can be traced back to the chiral structure of the catalyst. Thus the first prerequisite to delineating the origins of the stereoselectivity provided by these catalysts and to designing new catalysts is a precise understanding of the steric interactions that can occur. This is provided by molecular mechanics. In this section we do not attempt to give an explanation for any stereoselective reaction. Rather we develop an accurate force field for these complexes which is necessary before such explanations can be attempted.



Scheme 1

Table 3 contains structural data for a number of complexes for which the crystal structures have been reported, superimpositions of calculated and crystal structures are shown. In the jargon of the trade such presentations are called 'rigid fits' where the superimposition is made by selecting the coordinates of a number of key atoms of each of the molecules and then superimposing them by assigning different weights to the atom coordinates. For the present purposes the two dummy atoms (Cp centroids), the two chloro ligands, and the metal were rigidly fitted with the metal being assigned ten times the weight over the other atoms. Cyclopentadienyl ligands are designated as Cp for an unsubstituted Cp, Cp* for pentamethyl Cp, and Cp' means a generic substituted Cp ligand. The angle designation $D_{Cp^*}–C_{Cp^*}–C_{Me}$ refers to the out-of-plane angle formed by the carbon atom of the methyl group substituent attached to the Cp* ring. Positive values indicate that the methyl group is tilted away from the metal. The Cp' ligands can rotate with respect to

Table 3 Calculated and observed structures of $[M(Cp')_2Cl_2]$

Rigid Fit	Geometry	Calculated	Observed
 [Ti(CpCp*)Cl_2]	Ti–D_{Cp}	2.07 Å	2.07 Å
	Ti–D_{Cp^*}	2.09 Å	2.10 Å
	Ti–Cl	2.37 Å	2.35 Å
	D_{Cp}–Ti–D_{Cp^*}	133°	132°
	D_{Cp}–Ti–Cl	105°	105°
	D_{Cp^*}–Ti–Cl	107°	107°
	Cl–Ti–Cl	94°	94°
	D_{Cp^*}–C_{Cp^*}–C_{Me}	5°—10°	4°—8°
	C_{Cp}–D_{Cp}–D_{Cp^*}–C_{Cp^*}	29°	39°
	B_{Cl}–Ti–D_{Cp}–C_{Cp}	14°	36°
	B_{Cl}–Ti–D_{Cp^*}–C_{Cp^*}	13°	0°
 [Ti(Cp*)$_2$$Cl_2$]	Ti–D_{Cp^*}	2.12 Å	2.13 Å
	Ti–Cl	2.37 Å	2.35 Å
	D_{Cp^*}–Ti–D_{Cp^*}	137°	138°
	D_{Cp^*}–Ti–Cl	105°	104°
	Cl–Ti–Cl	93°	93°
	D_{Cp^*}–C_{Cp^*}–C_{Me}	6°—17°	3°—16°
	C_{Cp^*}–D_{Cp^*}–D_{Cp^*}–C_{Cp^*}	35°	34°
	B_{Cl}–Ti–D_{Cp^*}–C_{Cp^*}	−1°, 34°	0°, 32°
 [Hf(CpCp*)Cl_2]	Hf–D_{Cp}	2.19 Å	2.18 Å
	Hf–D_{Cp^*}	2.20 Å	2.19 Å
	Hf–Cl	2.43 Å	2.41 Å
	D_{Cp}–Hf–D_{Cp^*}	132°	131°
	D_{Cp}–Hf–Cl	105°	105°
	D_{Cp^*}–Hf–Cl	107°	107°
	Cl–Hf–Cl	94°	96°
	D_{Cp^*}–C_{Cp^*}–C_{Me}	4°—7°	3°—7°
	C_{Cp}–D_{Cp}–D_{Cp^*}–C_{Cp^*}	27°	38°
	B_{Cl}–Hf–D_{Cp}–C_{Cp}	14°	35°
	B_{Cl}–Hf–D_{Cp^*}–C_{Cp^*}	11°	0°
 [Zr(CpCp*)Cl_2]	Zr–D_{Cp}	2.21 Å	2.21 Å
	Zr–D_{Cp^*}	2.22 Å	2.22 Å
	Zr–Cl	2.44 Å	2.44 Å
	D_{Cp}–Zr–D_{Cp^*}	131°	130°
	D_{Cp}–Zr–Cl	105°	105°
	D_{Cp^*}–Zr–Cl	107°	107°
	Cl–Zr–Cl	97°	98°
	D_{Cp^*}–C_{Cp^*}–C_{Me}	3°—7°	4°—6°
	C_{Cp}–D_{Cp}–D_{Cp^*}–C_{Cp^*}	28°	39°
	B_{Cl}–Zr–D_{Cp}–C_{Cp}	14°	36°
	B_{Cl}–Zr–D_{Cp^*}–C_{Cp^*}	12°	0°

each other and with respect to the two chloro groups The rotations are defined in terms of (four-atom) dihedral angles The relative orientation of the Cp′ rings with respect to each other is defined by the dihedral angle $C_{Cp}-D_{Cp}-D_{Cp}-C_{Cp}$ and the smallest angle is quoted The Cp′ orientation with respect to the two chloro groups is defined by the sequence $B_{Cl}-M-D_{Cp}-C_{Cp}$ where B_{Cl} is a point which is in the Cl–M–Cl plane and bisects this angle It has two values, one for each Cp′ ring, and can be positive (clockwise) or negative (anticlockwise) The smallest angle is quoted

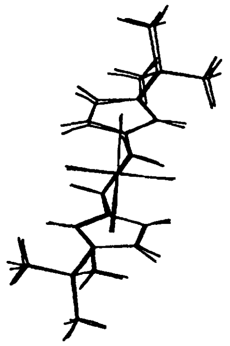
Inspection of Table 3 reveals that our force field reproduces the skeletal bond lengths and angles with a high degree of precision The tilting of the methyl groups out of the Cp* plane is also well reproduced Although some of the Cp′ dihedral angles show a good correspondence between the observed and calculated values, a number of these angles do not match well Aside from crystal packing forces which could affect the Cp′ dihedral orientations there are two other possible sources for the disparity between the calculated and observed structures That crystal packing effects are real, and not an all-purpose incantation, will be demonstrated presently The first possible reason for the dihedral differences could be because we did not include dihedral force constants in our calculations That these force constants are zero or nearly zero can be demonstrated in a number of ways Perhaps the most persuasive was the minimization of [$Ti(Cp^*)_2Cl_2$] where the coordinates of all of the atoms of the Cp* rings were fixed to their crystallographic positions but the rings were allowed to rotate without dihedral restraint and the derived force constants were applied to the skeletal modes The resultant minimized structure was identical to that observed in the crystal This observation indicates that the orientations of the Cp* ligands is essentially governed by intramolecular non-bonded interactions and, parenthetically, that crystal packing forces do not control the Cp* orientations in this case If this be so, why is it that the Cp′ orientations are not always well reproduced?

The major reason for the lack of correspondence for the torsion angles is related to variations in the C–C bond lengths of the Cp′ ligands that are observed These bond lengths can vary from as much as 1 38 to 1 43 Å in some cases Our force field has the same force constant for all C–C bonds of the Cp′ ligand and the minimized structures almost always give a C–C bond distance of 1 40 Å for these metallocenes Because of the C–C bond length variations, small differences in non-bonded interactions lead to torsion angles different from those calculated for Cp′ rings with identical C–C distances The C–C variations can be caused by steric strain which the force field can calculate, but if, as is probable, the variations have an electronic origin, molecular mechanics is mute on this issue Although the consequences of these C–C bond variations are minor and are probably inconsequential in assessing steric interactions, the variations do point to the difficulty of developing general force fields for π-complexes where transferability of the ligand force field is desired A clear example of the potential problem is the case of olefin complexes which can be described as metallocyclopropenes at one extreme and metallocyclopropanes at the other canonical bonding extreme Clearly, force constants and equilibrium bond distances derived for one extreme are not transferable to the other, and it may be necessary to narrowly specify the group of olefin compounds to which a particular force field applies For the present Cp′ systems the ligand force field can be transferred without seriously affecting either the structures or the energy differences between isomers

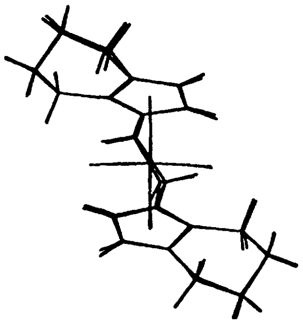
Table 4 lists superimposed structures and selected parameter comparisons for a number of strapped metallocenes The strap joining the two Cp′ rings can consist of one or more atoms Inspection of Table 4 reveals that excellent fits for the calculated and observed structures are generally found The two structures with silicon straps, [$Zr(Me_2Si(C_5H_4)_2)Cl_2$] and the racemic isomer of [$Zr(Me_2Si(3\text{-}Bu^t\text{-}5\text{-}Me(C_5H_2)_2))Cl_2$], are C_2 symmetric The chirality of the latter arises from the particular binding of the Cp′ groups The three-carbon strapped metallocenes, [$Ti(C_3H_6(C_5H_4)_2)Cl_2$] and [$Hf(C_3H_6(C_5H_4)_2)Cl_2$] are also well reproduced except that the strap in the former is rotated further from the Cl–Ti–Cl bisector in the calculated structure than in the crystal structure A similar greater rotation is observed in the calculated structure of the meso isomer of [$Ti(Me_4C_2(3\text{-}Bu_tC_5H_3)_2)Cl_2$] Aside from this the fit is excellent

It is possible that this greater rotation of the straps in the calculated structures could be caused by crystal packing effects An opportunity to test this supposition is provided by the racemic [$Ti(C_2H_4(3\text{-}Bu^tC_5H_3)_2)Cl_2$] complex which crystallizes in monoclinic and tetragonal modifications, in which the rotation of the strap is different for the two forms [26] The calculated and observed structures are shown in Table 4 without hydrogen atoms It will be noted that the calculated strap is spanned by those of the two crystal structures The hydrogen atoms were located for the tetragonal form but not for the monoclinic Since the hydrogen atoms were located for the tetragonal form it is possible to test the assertion that torsional rotation of the strap is controlled to some extent by crystal packing forces

Crystal packing minimization calculation on the tetragonal form was carried out in the following way The selected molecule was minimized in the presence of 16 of its rigidly positioned crystal nearest neighbours Included were all surrounding molecules, the Ti atoms of which were within 12 5 Å of the Ti atom of the molecule to be minimized In this way the crystal forces exerted on the molecule to be minimized were replicated Although this method is approximate it allows for ready calculation The two superimposed structures are shown in (11) It can be seen that the fit is almost perfect lending credence to the supposition that crystal packing forces can affect the rotational structures of these systems



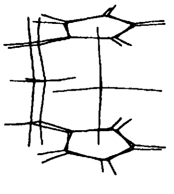
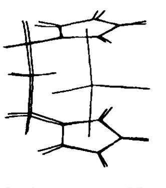
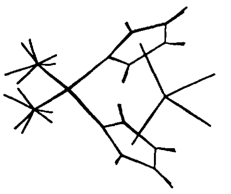
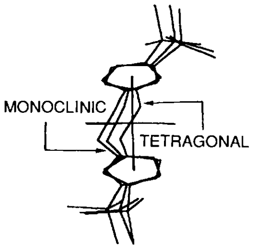
(11)



(12)

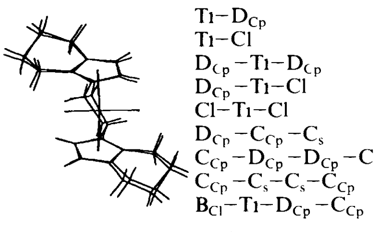
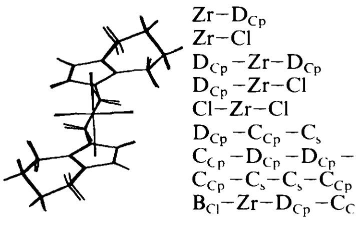
Table 5 shows the superimposed structures of the Ti and Zr complexes of the ethylene-1,1′-bis(tetrahydroindenyl), ($C_2H_4(THIND)_2$), ligand The fit for the Zr complex is excellent but the minimized structure of the Ti complex has its strap rotated from the Cl–Ti–Cl bisector A crystal packing calculation was performed on the racemic crystal[27] of [$Ti(C_2H_4(THIND)_2Cl_2$] The superimposed structures are shown in (12) where the fit is almost perfect

Table 4 Calculated and observed structures of strapped metallocenes

Rigid Fit	Geometry	Calculated	Observed	
	$Ti-D_{Cp}$	2 06 Å	2 06 Å	
	$Ti-Cl$	2 38 Å	2 37 Å	
	$D_{Cp}-Ti-D_{Cp}$	132°	133°	
	$D_{Cp}-Ti-Cl$	106°	106°	
	$Cl-Ti-Cl$	94°	94°	
	$D_{Cp}-C_{Cp}-C_s$	7°	8°	
	$C_{Cp}-D_{Cp}-D_{Cp}-C_{Cp}$	0°	3°	
$[Ti(C_3H_6(C_5H_4)_2)Cl_2]$	$B_{Cl}-Ti-D_{Cp}-C_{Cp}$	135°, −135°	−143°, 145°	
	$Hf-D_{Cp}$	2 17 Å, 2 17 Å	2 18 Å 2 17 Å	
	$Hf-Cl$	2 43 Å, 2 44 Å	2 41 Å, 2 43 Å	
	$D_{Cp}-Hf-D_{Cp}$	131°	130°	
	$D_{Cp}-Hf-Cl$	107°	107°	
	$Cl-Hf-Cl$	95°	96°	
	$D_{Cp}-C_{Cp}-C_s$	6°	8°	
	$C_{Cp}-D_{Cp}-D_{Cp}-C_{Cp}$	0°	2°	
$[Hf(C_3H_6(C_5H_4)_2)Cl_2]$	$B_{Cl}-Hf-D_{Cp}-C_{Cp}$	−136°, 136°	−143°, 141°	
	$Zr-D_{Cp}$	2 21 Å	2 20 Å	
	$Zr-Cl$	2 43 Å	2 44 Å	
	$D_{Cp}-Zr-D_{Cp}$	126°	125°	
	$D_{Cp}-Zr-Cl$	107°	108°	
	$Cl-Zr-Cl$	98°	98°	
	$D_{Cp}-C_{Cp}-Si$	18°	17°	
	$C_{Cp}-Si-C_{Cp}$	96°	93°	
	$C_{Me}-Si-C_{Me}$	112°	116°	
	$C_{Me}-Si-C_{Cp}$	112°	112°	
	$C_{Cp}-D_{Cp}-D_{Cp}-C_{Cp}$	0°	0°	
$[Zr(Me_2Si(C_5H_4)_2)Cl_2]$	$B_{Cl}-Zr-D_{Cp}-C_{Cp}$	180°, 180°	180°, 180°	
			monoclinic	tetragonal
 	$Ti-D_{Cp}$	2 09 Å, 2 08 Å	2 10 Å, 2 09 Å	2 11 Å, 2 10 Å
	$Ti-Cl$	2 35 Å, 2 32 Å	2 35 Å, 2 32 °A	2 38 Å, 2 33 Å
	$D_{Cp}-Ti-D_{Cp}$	131°	127°	129°
	$D_{Cp}-Ti-Cl$	105°—108°	106°—110°	105°—108°
	$Cl-Ti-Cl$	95°	96°	97°
	$D_{Cp}-Ti-C_{Bu^t}$	16°, 11°	13°, 10°	10° 8°
	$D_{Cp}-Ti-C_s$	2°, 1°	2°	1°
	$C_{Cp}-D_{Cp}-D_{Cp}-C_{Cp}$	18°	20°	22°
	$C_{Cp}-C_s-C_s-C_{Cp}$	41°	45°	46°
rac-$[Ti(C_2H_4(3Bu^tC_5H_3)_2)Cl_2]$	$B_{Cl}-Ti-D_{Cp}-C_{Cp}$	−171°, 155°	−164°. 147°	175°, 166°

C refers to the Cp carbon atom bonded to the strap

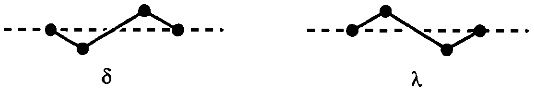
Table 5 Calculated and observed structures of strapped tetrahydroindenyl complexes

Rigid Fit	Geometry	Calculated	Observed
	$Ti-D_{Cp}$	2 09 Å	2 10 Å
	$Ti-Cl$	2 34 Å	2 35 Å
	$D_{Cp}-Ti-D_{Cp}$	131°	128°
	$D_{Cp}-Ti-Cl$	106°	107°
	$Cl-Ti-Cl$	95°	96°
	$D_{Cp}-C_{Cp}-C_s$	2°	0°
	$C_{Cp}-D_{Cp}-D_{Cp}-C_{Cp}$	19°	20°
	$C_{Cp}-C_s-C_s-C_{Cp}$	42°	46°
rac-$[Ti(C_2H_4(THIND)_2)Cl_2]$	$B_{Cl}-Ti-D_{Cp}-C_{Cp}$	−165°, −177°	−171°, −171°
	$Zr-D_{Cp}$	2 22 Å	2 21 Å
	$Zr-Cl$	2 43 Å	2 44 Å
	$D_{Cp}-Zr-D_{Cp}$	125°	125°
	$D_{Cp}-Zr-Cl$	105°, 111°	108°, 107°
	$Cl-Zr-Cl$	97°	99°
	$D_{Cp}-C_{Cp}-C_s$	1°	1°
	$C_{Cp}-D_{Cp}-D_{Cp}-C_{Cp}$	20°	20°
	$C_{Cp}-C_s-C_s-C_{Cp}$	45°	49°
rac-$[Zr(C_2H_4(THIND)_2)Cl_2]$	$B_{Cl}-Zr-D_{Cp}-C_{Cp}$	171°, 171°	171°, 171°

C refers to the Cp carbon atom bonded to the strap

An inspection of the structure (12) reveals that the molecule is a diastereomer with three sources of chirality, one due to the conformation of the strap, one due to the conformation of the cyclohexenyl groups, and one due to the binding of the tetrahydroindenyl groups to the metal The chirality of the conformations can be defined by the four-atom puckering shown below If the dotted line, drawn behind the four-atom sequence, is regarded as the major axis of a helix then the 2nd and 3rd atoms either form a right-handed helix, δ, or a left-handed helix, λ The chirality of the tetrahydroindenyl binding to the Ti is specified by defining the chirality of the Cp′ carbon atom bonded to the strap carbon atom The strap carbon has the lowest priority and hence a clockwise sequence, Ti → cyclohexenyl Cp carbon → Cp carbon, obtains for the Cp′ binding in (12) and hence the Cp′ binding is *R*,*R* The diastereomer (12) can be written as *R*,*R*-$[Ti(\delta\text{-}C_2H_4(\lambda\text{-}THIND)_2Cl_2]$ or simply as δ-*R*,*R*-λ,λ It should be noted for future discussion that, for example, the mirror image isomers δ-*R*,*R*-λ,λ and λ-*S*,*S*-δ,δ are of the same energy

We have investigated the minimized energies of all of the conformational diastereomers of *R*,*R*-$[M(C_2H_4(THIND)_2)Cl_2]$ (M = Ti, Zr, Hf) complexes We find that the δ-*R*,*R*-λ,λ (or λ-*S*,*S*-δ,δ) diastereomer found in the crystal is not the most stable



conformer The λ-*R R*-δ,δ diastereomer is 2 2 to 3 kcal/mole more stable than the δ-*R R*-λ,λ conformer found in the crystal Presumably the δ-*R R*-λ,λ form produces the less soluble crystal and under different solvent conditions other conformers might be isolated if conformer interconversion is facile

Table 6 lists the relative strain energies found for the different conformers

Table 6 Relative energies of the various conformers of *R*,*R*-[$M(C_2H_4(THIND)_2)Cl_2$] complexes

Conformer	M = Ti	Zr	Hf
		ΔE (kcal/mole)	
λ-*R R*-δ,δ	0	0	0
λ-*R R*-λ,δ	1 6	1 5	1 5
δ-*R R*-δ,λ	1 8	1 5	1 6
δ-*R R*-δ,δ	2 0	1 8	1 8
δ-*R R*-λ,λ*	3 0	2 2	2 4
λ *R R*-λ,λ	3 4	2 9	3 0

* Conformer found by *X* ray diffraction for all metals

Given the small energy differences calculated for the various conformers, it is probable that these molecules undergo rapid interconversion between conformers in solution The activation energy for conformer interconversion is likely to be small because in some crystal structures the cyclohexenyl carbon atoms are found to be disordered because of rapid conformational interconversion in the crystal The flexible nature of parts of these molecules suggests that during enantioselective catalysis there is a considerable amount of low energy ligand steric accommodation available to meet the steric demands of substrate reaction Thus any attempts at defining the steric origins of enantioselective reactions promoted by these systems requires recognition of the conformational flexibility as well as the steric strain that may accompany the reaction intermediates and transition states It is clear that just simply accepting the crystal structure coordinates as a steric framework for assessing steric interactions is likely to be a poor approximation, although it is commonly used

9 Perspective

It is hoped that this overview of our work in the development of molecular mechanics force fields of metallocene complexes has provided the reader with a comprehension of the potential power of the technique The method, if properly used, can predict structures accurately, it can define differences in strain energy accurately, and it is capable of defining the origins of structural features As we have seen, the old controversy concerning the relative orientations of the Cp rings in ferrocene has been defined in terms of the force field contribution to the orientation Similarly, the bent metallocenes of the alkaline earths, the lanthanides and, perhaps of the divalent silicon group of metals now have a cogent explanation for their structures The reproduction of the structures and conformational energy differences associated with the strapped and unstrapped metallocenes of Ti, Zr, and Hf both provide the basis for assessing steric interactions of stereoselective reactions promoted by derivatives of these complexes The effects of crystal packing on structures can also be determined One of the important aspects demonstrated by this work is that certain structural features can be explained by molecular mechanics without resorting to molecular orbital calculations

Organic chemists have routinely used molecular mechanics in order to understand strain and steric hinderance for some time Organometallic chemists, however, are presented by a considerably more formidable challenge because, unlike organic chemists, they are faced with innumerable bonding schemes and structures When confronted with the prospect of developing force fields for organometallic complexes one has three choices The first is to do nothing and hope that the issue will either go away or will be resolved some other way The second is to develop generic force fields for a wide variety of structures and ligand types This second response is the one adopted by a number of commercial software houses If the objective is to be able to reproduce a wide variety of structures to a tolerable degree of accuracy and to obtain an approximate estimate of non-bonded interactions, the generic force fields suffice at least until more sophisticated force fields are developed Provided these generic force fields are not pushed beyond what they are capable of doing they can be very useful because they amount to a sophisticated method of model building superior to the mechanical balls-and-sticks found in most laboratories The third approach is to begin by carefully selecting certain general classes of organometallic systems and then constructing a self-consistent force field for these types of complexes This is the approach we have adopted in the expectation that certain narrowly defined structural issues could be unambiguously resolved We expect that in future all three approaches will be adopted but for those concerned with structure and reactivity the generic and rigorous force fields will be applied according to inclinations If work continues in developing self-consistent force fields one might expect that organometallic molecular mechanics will be applied as routinely as is now the case for purely organic systems Our expectation is that work is likely to expand rapidly in this area because the notion of treating molecules as spring and ball entities remains as attractive now as it did over a century ago

Acknowledgements I am grateful to my coworkers Dr T N Doman and Mr T K Hollis and to Professor C R Landis who provided us with access to the CHARMM program The work was supported by the National Institutes of Health My indebtedness to my co-workers goes beyond normal civilities This is because of my singular ignorance and apprehension of computers I am yet to be persuaded that they are not an obstacle to thought and do not amount to little more than another file in the register of human folly

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