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Molecular Mechanics Force Fields for Bent Metallocenes of the Type [M(Cp)$_2$Cl$_2$]

Thompson N. Doman, T. Keith Hollis, and B. Bosnich*

Contribution from the Department of Chemistry, The University of Chicago,
5735 South Ellis Avenue, Chicago, Illinois 60637

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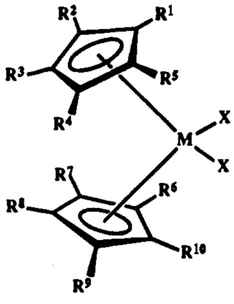
Abstract: A self-consistent molecular mechanics force field for complexes of the type [M(Cp′)$_2$Cl$_2$] (M = Ti, Zr, Hf; Cp′ = a substituted cyclopentadienyl ligand) has been developed. Force constants were derived from vibrational data of the [M(Cp)$_2$Cl$_2$] complexes. The force field reproduces known structures with high precision, and it was demonstrated that crystal packing forces can affect the orientations of the Cp′ rings and the conformations of substituents. Crystal packing calculations reproduce structures in the crystal well. Systems where the Cp′ rings are joined by aliphatic carbon straps and where the Cp′ rings are fused to six-membered rings containing aliphatic carbon atoms generate diastereomers due to the chiral puckering of the strap, the six-membered rings, and the chiral binding of the Cp′ rings. It is calculated that these various conformations are close in energy and are likely to interchange rapidly in solution. When the strap is chiral the energetic interplay between these conformations can lead to preferred binding of prochiral Cp′ ligands. Interplay of these energetically closely spaced conformations is likely to guide consideration of the steric origins of stereoselective reactions promoted by derivatives of these complexes. It is shown that the conformation observed in the crystal is generally not the most stable.

Derivatives of the bent metallocene complexes formed by titanium(IV), zirconium(IV), and of hafnium(IV) are finding increasing applications in a variety of asymmetric catalytic and stoichiometric reactions.[1−5] Perhaps the most notable application of these complexes is in the isotatic polymerization of propylene.[6] The origin of the stereoselection in these reactions is at least in part related to the steric interactions between the substrate and the complex. If this is so, then a fuller understanding of these discriminatory interactions could be provided by a rigorous molecular mechanics force field from which structures and diastereomeric energy differences could be derived. This paper presents such a force field from which the sometimes subtle stereochemical features of these complexes is elicited.

For the present purposes, the derivatives of the [M(Cp)$_2$X$_2$] complexes, where Cp is the cyclopentadienyl ligand, can be classified as those where the Cp ligands are substituted (**1**) and those where the substituted ligands are linked by a variety of straps (**2**). These strapped metallocenes, also called *ansa*-metallocenes, were developed principally by Brintzinger[7] who also first made the racemic ethylene-1,1′-bis(tetrahydroindenyl)-zirconium dichloro complex **3** which provides the precursor for isotactic polymerization of propylene. The main questions which we address here are the following. First, how do the R groups affect the relative orientations of the Cp rings with respect to each other and with respect to the X ligands? Second, how are the metal centered angles and bond distances affected by Cp substitution and what ligand distortions occur upon Cp substitution? Third, what are the preferred conformations of the straps and the Cp substituents? Fourth, how do crystal packing forces affect the conformations? Fifth, when racemic and meso forms exist which is the more stable? Sixth, when the strap is chiral and the Cp ring appropriately substituted for



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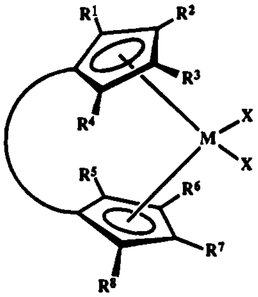

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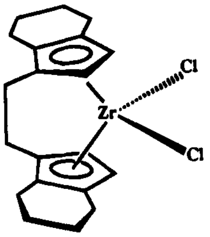

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the formation of racemic complexes, which of the internal diastereomers is preferred? Seventh, how does the strap span affect the structure? Answers to these questions should provide a deeper understanding of the stereochemistry of the complexes, a rational basis for design of new ligands, and ultimately an explanation of stereoselective reactions.

A number of reports of varying degrees of sophistication attempting to model these types of complexes have appeared.[8] Most of these were concerned with stereoselective polymerization. More recently a more sophisticated approach has been reported for generating the structures of zirconium metallocenes.[9] We reported the development of a rigorous molecular mechanics force field for linear metallocences such as ferrocene[10] and for bent metallocenes of the type, [M(Cp*)$_2$], where Cp* is the pentamethylcyclopentadienyl ligand.[11] In this model the force constants are derived from vibrational data using a general π-ligand topology which accounts for all of the forces on the system. This approach is adopted here.

1. General Force Field

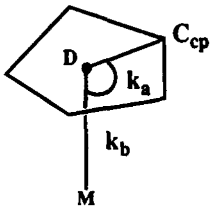
We define the total molecular mechanics energy, E, in kilocalories/mole, as the sum of the energy terms due to bond stretches, angle bends, torsonal deformations, and van der Waals (VDW) interactions, where the symbols have the usual meanings.[10] As was done previously,[10] $\epsilon = 0.001$ kcal/mol for the

$$E = \sum\nolimits_{\text{bonds}} k_b(r - r_0)^2 + \sum\nolimits_{\text{angles}} k_a(\theta - \theta_0)^2 + \sum\nolimits_{\text{torsions}} k_t[1 + \cos(n\phi - \delta)] + \sum_{i<j} \epsilon_{ij}[(r_0/r_{ij})^{12} - 2(r_0/r_{ij})^6]$$

metal ion and its radius is taken as being 1.0 Å. Electrostatic charge interactions are excluded because application of the "charge equilibration method" [12] to these Cp systems gave unrealistic values of the charge on the metal. This method indicated that Cp was more electron donating than Cp* which runs counter to expectation and experiment.

2. Force Constants and [M(Cp)$_2$Cl$_2$] Force Field

All of the calculations reported here were carried out using the CHARMM[13] suite of programs which we previously modified for organometallic π-complexes.[10] The most notable modification was in the implementation of the "dummy atom topology" for the bound Cp ligand. In this formulation a dummy atom is placed at the centroid of the Cp ring and is joined to the metal (**4**). The dummy atom (D)−metal (M) bond is given a bond stretching force constant, and the angle (C_{Cp}−D−M) is given a bond angle bending force constant. This simple scheme, although a bonding fiction, can be used to transfer the forces on the dummy atom to the Cp carbon atoms by methods described previously.[10]



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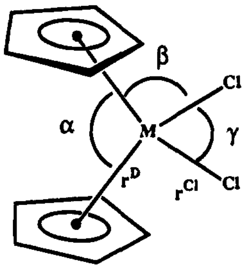
In order to arrive at the molecular mechanics force field, one needs to find force constants, equilibrium bond lengths (r_0), and equilibrium bond angles (θ_0) for a parent molecule. We chose [M(Cp)$_2$Cl$_2$] as the parent molecule. Vibrational data are available for the [Ti(Cp)$_2$Cl$_2$], [Zr(Cp)$_2$Cl$_2$], and [Hf(Cp)$_2$Cl$_2$] molecules,[14] and the crystal structures of [Ti(Cp)$_2$Cl$_2$][15] and [Zr(Cp)$_2$Cl$_2$][16] have been determined. A crystal structure of [Hf(Cp)$_2$Cl$_2$] is not available, and we have used the structural parameters found for the crystal structure of [Hf(EtCp)$_2$Cl$_2$],[17] where EtCp is ethylcyclopentadienyl. In none of these structures were the hydrogen atoms located, but the carbon−hydrogen bond lengths of [Ti(Cp)$_2$Cl$_2$] and [Zr(Cp)$_2$Cl$_2$] were determined by gas-phase electron diffraction.[18] A compilation of bond length data for these types of complexes indicates[19] that the average Cp carbon−Cp carbon and Cp carbon−hydrogen bond lengths are 1.40 Å and 0.94 Å, respectively. We have used these values throughout.

The generic molecule **5** is of low symmetry so that there is extensive mixing of the normal modes of vibration. The vibrational energies of the skeletal and the Cp modes, however, are well separated in energy so that, to a reasonable approximation, these two sets of modes can be treated separately. Further, as we have demonstrated previously,[10] the vibrational frequencies of the Cp rings do not vary greatly when the metal is changed[14] so that it is possible to transfer the Cp force constants from one metal to another. The skeletal force constants are strongly dependent on the nature of the metal and need to be determined for each metal.



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For the skeletal part of the force field, we must find the appropriate force constants (k_a and k_b), the equilibrium bond lengths (r_0^D and r_0^{Cl}), and the equilibrium bond angles (α_0, β_0, γ_0); see **5**. The equilibrium bond angles of a class of molecules are usually chosen on the basis of some bonding scheme. For

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Table 1. Molecular Mechanics Vibrational Analysis of the Skeletal Modes of $[M(Cp)_2Cl_2]$ Complexes

label[a]	M = Ti frequencies (cm^{-1})			M = Zr frequencies (cm^{-1})			M = Hf frequencies (cm^{-1})			
(C_{2v})	obs	calc	dev	obs	calc	dev	obs	calc	dev	vib mode[b]
A_2	98	37	−61	80	26	−54	75	30	−45	ring torsion(s)
B_1	128	65	−63	128	43	−85	128	43	−85	ring torsion(as)
A_1	123	170	47	123	137	14	128	128	0	$D_{Cp}-M-D_{Cp}$(s)
A_2	144	186	42	144	139	−5	144	139	−5	$D_{Cp}-M-Cl$(as)
A_1	160	162	2	158	141	−17	150	142	−8	Cl−M−Cl(s)
B_2	184	190	6	175	166	−9	170	161	−9	$D_{Cp}-M-D_{Cp}$(as)
B_1	204	211	7	185	185	0	183	184	1	Cl−M−Cl(as)
A_1,B_1	272	262, 229	−10, −43	262	247, 233	−15, −29	252	231, 225	−21, −27	tilt(s)
A_2,B_2	312	295, 274	−17, −38	298	281, 254	−17, −44	285	259, 253	−26, −32	tilt(as)
A_1	350	303	−47	330	324	−6	305	318	13	M−Cl(s)
A_1	374	361	−13	338	336	−2	322	324	2	$M-D_{Cp}$(s)
B_1	384	380	−4	359	366	7	351	350	−1	M−Cl(as)
B_2	396	393	−3	373	367	−6	372	353	−19	$M-D_{Cp}$(as)
		RMS dev[c] = 34 cm^{-1}			RMS dev = 31 cm^{-1}			RMS dev = 29 cm^{-1}		

[a] Symmetry labels are from ref 14. [b] s = symmetric; as = antisymmetric description as in ref 14. [c] Root-mean-square deviation.

example, one would assert that tetrahedral angles obtain for unstrained tetravalent carbon compounds. For the present $[M(Cp)_2Cl_2]$ complexes, it is not obvious which bonding scheme to adopt in order to find α_0, β_0, and γ_0 since molecular orbital methods indicate that for these complexes the metal−ligand orbital overlap is almost constant over large angle displacements.[20] This question is inherent in all molecular mechanics calculations although it is not always recognized. It is possible, however, to arrive at a set of self-consistent force constants and equilibrium parameters for a known basis molecule (or molecules) without reference to a bonding scheme. This is based on three criteria, namely, that the calculated structure match the known basis structure accurately, that the calculated vibrational spectrum match the observed vibrational spectrum, and that the energy of the derived force field be at a minimum.

The procedure adopted for finding the force constants and equilibrium values was the following iterative process. We assigned a reasonable set of force constants to the skeletal modes and used the known parameters for the Cp ligands.[10] A set of initial equilibrium skeletal bond lengths and skeletal bond angles was chosen. The OPTI routine in CHARMM searched for a set of equilibrium parameters (r_0^D, r_0^{Cl}, α_0, β_0, γ_0) which, with the given set of force constants, minimized the $[M(Cp)_2Cl_2]$ (M = Ti, Zr) and $[Hf(EtCp)_2Cl_2]$ molecules to their crystallographically determined structure. A vibrational analysis was then performed and the results were compared to experiment. Adjustments were made to the force constants, and the procedure was repeated until there was found a set of force constants and equilibrium parameters which reproduced accurately both the structure and its vibrational spectrum.

In this procedure we used initial bond lengths (M−D, M−Cl) which were close to those found in the crystal structure, and OPTI always converged on the same values for the equilibrium bond lengths irrespective of the initial values. This, however, was not the case for the three skeletal bond angles. For example, using tetrahedral angles for the pre-OPTI set gave different equilibrium angles than if the crystallographically determined angles were used for the pre-OPTI set. In both cases, the same angle bend force constants with either set of final equilibrium values gave a minimized structure which matched that found in the crystal, and the vibrational spectrum was matched equally well. Thus the structure−vibrational spectra criteria alone were not sufficient to provide a unique solution to arriving at equilibrium skeletal angles. In order to make a choice, we assumed that the parent molecules, $[M(Cp)_2Cl_2]$, were the least strained compared to analogous molecules incorporating Cp substituents. On this basis we chose equilibrium angles which resulted in the lowest minimized energy for the parent $[M(Cp)_2Cl_2]$ systems.

The final skeletal mode is the rotation of the Cp rings with respect to each other and with respect to the chloro groups. These modes are important in determining the conformations of substituted Cp systems. The question arises as to whether force constants should be applied to these motions. In order to test this, we have performed a number of minimizations with and without force constants and have concluded that the Cp orientations are determined solely by nonbonded interactions. This is perhaps best illustrated by fixing the coordinates of the atoms of Cp* to their crystallographically determined values in $[Ti(Cp^*)_2Cl_2]$[21] and then minimizing the structure without restraining the Cp* rotations. The final minimized structure is almost identical with that found in the crystal.

The observed and calculated vibrational frequencies of the skeletal modes of $[M(Cp)_2Cl_2]$ (M = Ti, Zr, Hf) are listed in Table 1. Given the extensive mixing of the vibrational modes and the approximate nature of the force field, the correlation between calculated and observed frequencies is good. Table 2 lists the observed and calculated frequencies of the internal Cp modes for the three complexes.

The calculated vibrational data were derived using the skeletal parameters listed in Table 3 and the Cp parameters listed in Table 4. All other parameters were those included in the CHARMM parameter set. It should be noted that the torsion parameters were derived empirically by adjusting the force constants to fit a series of known structures which displayed large torsional deformations.

3. Calculated Structures of $[M(Cp')_2Cl_2]$ Complexes

Table 5 lists the important calculated and observed geometric parameters of a number of $[M(Cp')_2Cl_2]$ complexes, where M = Ti, Zr, Hf, and Cp′ refers to a general substituted cyclopentadienyl ligand. The structures shown are rigid fits (superimpositions) of the calculated and the observed crystal structures. The rigid fits were calculated by applying equal weights to the positions of the two chloro ligands and the two dummy atoms and by applying a 10:1 weighting favoring the metal atom coordinates. Hydrogen atoms are included only when their positions were reported in the X-ray diffraction study.

Most of the calculated and observed bond lengths and bond angles of the $[Ti(Cp)_2Cl_2]$, $[Zr(Cp)_2Cl_2]$, and $[Hf(EtCp)_2Cl_2]$ complexes correspond because the force field parameters were

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Table 2. Molecular Mechanics Vibrational Analysis of the Ligand Modes of [M(Cp)$_2$Cl$_2$] Complexes[a]

M = Ti frequencies (cm^{-1})		M = Zr frequencies (cm^{-1})		M = Hf frequencies (cm^{-1})	
obs	calc	obs	calc	obs	calc
562	569, 573, 580, 583	560	589, 592, 595, 597	560	589, 593, 596, 598
820	815, 816, 818, 818	818	816, 817, 817, 817	816	816, 817, 817, 817
876	893, 908, 1004, 1004	860	871, 878, 1003, 1004	853	872, 880, 1003, 1004
1016	1044, 1051	1015	1041, 1044	1012	1042, 1046
1024	1069, 1072	1022	1058, 1058	1020	1059, 1059
1070	1074, 1077, 1082, 1086	1070	1072, 1073, 1076, 1076	1070	1072, 1073, 1076, 1077
1122	1158, 1160	1122	1141, 1144	1122	1142, 1145
1135	1168, 1173	1134	1149, 1151	1130	1150, 1153
1252	1226, 1227	1260	1224, 1224	1260	1224, 1224
1356	1231, 1232	1354	1226, 1226	1352	1226, 1226
1364	1425, 1427	1362	1423, 1424	1362	1423, 1424
1368	1575, 1575, 1578, 1580	1368	1575, 1575, 1576, 1577	1360	1575, 1575, 1576, 1577
1432	1637, 1637	1433	1636, 1636	1435	1636, 1636
1444	1638, 1638	1446	1637, 1637	1449	1637, 1637
3096	3103, 3103, 3104, 3104	3096	3104, 3104, 3104, 3104	3098	3104, 3104, 3104, 3104
3113	3110, 3110, 3111, 3111	3112	3111, 3111, 3111, 3111	3107	3111, 3111, 3111, 3111
3118	3115, 3116	3121	3116, 3116	3130	3116, 3116

[a] Cyclopentadienyl observed frequencies were assigned according to C_{5v} local symmetry in ref 14.

Table 3. Spectroscopically Derived Skeletal Parmeters[a]

deformation	force const[b]	equil value
	Stretch	
Ti−Cl	60.0	2.242 Å
Zr−Cl	60.0	2.389 Å
Hf−Cl	60.0	2.372 Å
$Ti-D_{Cp}$	110.0	1.911 Å
$Zr-D_{Cp}$	110.0	2.138 Å
$Hf-D_{Cp}$	110.0	2.112 Å
	Bend	
Cl−Ti−Cl	95.0	99.0°
Cl−Zr−Cl	130.0	99.0°
Cl−Hf−Cl	130.0	97.0°
$D_{Cp}-Ti-D_{Cp}$	25.0	133.0°
$D_{Cp}-Zr-D_{Cp}$	25.0	135.0°
$D_{Cp}-Hf-D_{Cp}$	25.0	141.0°
$D_{Cp}-Ti-Cl$	20.0	100.0°
$D_{Cp}-Zr-Cl$	20.0	106.0°
$D_{Cp}-Hf-Cl$	20.0	112.0°
$Ti-D_{Cp}-C_{Cp}$	35.0	90.0°
$Zr-D_{Cp}-C_{Cp}$	70.0	90.0°
$Hf-D_{Cp}-C_{Cp}$	70.0	90.0°
	Torsion	
$X-Ti-D_{Cp}-X$	0.0	$n = 0, \delta = 0.0$
$X-Zr-D_{Cp}-X$	0.0	$n = 0, \delta = 0.0$
$X-Hf-D_{Cp}-X$	0.0	$n = 0, \delta = 0.0$
	van der Waals	
Ti	$\epsilon = -0.001$	$r_i = 1.0$
Zr	$\epsilon = -0.001$	$r_i = 1.0$
Hf	$\epsilon = -0.001$	$r_i = 1.0$

[a] Definition of symbols: D_{Cp} = dummy centroid of the cyclopentadienyl ring; C_{Cp} = cyclopentadienyl carbon; X = any atom. [b] Units for the force constants: stretch, kcal/·Å^2; bend, kcal/mol·rad^2; torsion, kcal/mol.

Table 4. Cyclopentadienyl Parameters[a]

deformation	force const[b]	equil value
	Stretch[c]	
$C_{Cp}-C_{Cp}$	400.0	1.40 Å
$C_{Cp}-C_t$	345.0	1.49 Å
$C_{Cp}-H$	375.0	0.94 Å
C_t-H	345.0	0.96 Å
$C_{Cp}-Si$[f]	250.0	1.87 Å
C_t-Si[f]	220.0	1.888 Å
	Bend[d]	
$C_{Cp}-C_{Cp}-C_{Cp}$[f]	100.0	108.0°
$C_{Cp}-C_{Cp}-C_t$[f]	70.0	126.0°
$C_{Cp}-C_{Cp}-H$[f]	30.0	126.0°
$C_{Cp}-C_t-C_t$[f]	70.0	109.47°
$C_{Cp}-C_t-C_{Cp}$[f]	70.0	109.47°
$C_{Cp}-C_t-H$[f]	40.0	109.47°
$C_{Cp}-Si-C_t$	35.0	109.5°
$C_{Cp}-Si-C_{Cp}$[f]	60.0	109.5°
$C_{Cp}-Si-C_t$[f]	35.0	109.5°
C_t-Si-C_t[f]	40.0	109.5°
$Si-C_{Cp}-C_{Cp}$[f]	40.0	126.0°
$Si-C_t-H$[f]	34.0	109.5°
$Si-C_t-C_t$[f]	40.0	109.5°
	Torsion[e]	
$C_{Cp}-C_{Cp}-C_{Cp}-C_{Cp}$[f]	6.0	$n = 2, \delta = 180.0$
$C_{Cp}-C_{Cp}-C_{Cp}-C_t$	4.0	$n = 2, \delta = 180.0$
$C_{Cp}-C_{Cp}-C_t-H$[f]	0.333	$n = 2, \delta = 180.0$
$X-C_{Cp}-C_t-X$[f]	0.5	$n = 3, \delta = 0.0$
$X-C_t-C_t-X$[f]	0.178	$n = 3, \delta = 0.0$
$C_t-C_{Cp}-C_{Cp}-C_t$	1.5	$n = 2, \delta = 180.0$
$C_{Cp}-C_{Cp}-C_{Cp}-H$[f]	4.0	$n = 2, \delta = 180.0$
$C_t-C_{Cp}-C_{Cp}-H$[f]	5.0	$n = 2, \delta = 180.0$
$H-C_{Cp}-C_{Cp}-H$[f]	1.5	$n = 2, \delta = 180.0$
$Si-C_{Cp}-C_{Cp}-C_t$	3.0	$n = 2, \delta = 180.0$
$Si-C_{Cp}-C_{Cp}-H$[f]	3.0	$n = 2, \delta = 180.0$
$Si-C_{Cp}-C_{Cp}-C_{Cp}$[f]	3.0	$n = 2, \delta = 180.0$

[a] Definition of symbols: C_t, tetrahedral carbon; C_{Cp}, cyclopentadienyl carbon. [b] Units for the force constants: stretch, kcal/mol·Å^2; bend, kcal/mol·rad; torsion, kcal/mol. [c] $D_{Cp}-C_{Cp}$ stretches are removed by the dummy atom facility. [d] Nonmetal centered bends involving D_{Cp} were set to zero. [e] All remaining torsions were set to zero. [f] These parameters are the same as those found in ref 10.

derived from their known structures. The dihedral angles involving ring rotations and the ethyl group orientation in [Hf(EtCp)$_2$Cl$_2$] do not match perfectly, possibly because of crystal packing forces which were not included and for other reasons which we now discuss.

The definition of the dihedral angles involving Cp′ rotations relative to each other and relative to the chloro ligands has been simplified for clarity of presentation by adopting the following procedure. The relative rotations of the Cp′ rings with respect to each other are defined by the dihedral angle $C_{Cp'}-D_{Cp'}-D_{Cp'}-C_{Cp'}$ and the smallest angle is quoted. The relative rotations of the Cp′ rings with respect to the two chloro groups are defined by the dihedral angle $B_{Cl}-M-D_{Cp'}-C_{Cp'}$ where B_{Cl} is a point on the line which bisects the Cl−M−Cl angle and lies in the Cl−M−Cl plane. This dihedral angle has two values, one for each Cp′ ring, and can be positive (clockwise) or negative (anticlockwise). The smallest values of these two dihedral angles are quoted. For monosubstituted Cp rings the three dihedral angles refer to the sequence which includes the Cp′ ring carbon atoms ($C_{Cp'}$) bearing the substituent. With

Table 5. Calculated and Observed Structures of [M(Cp′)$_2$Cl$_2$] Complexes[a]

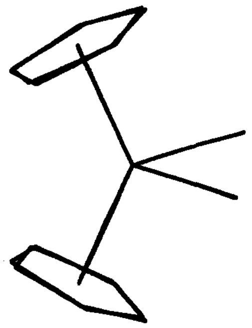
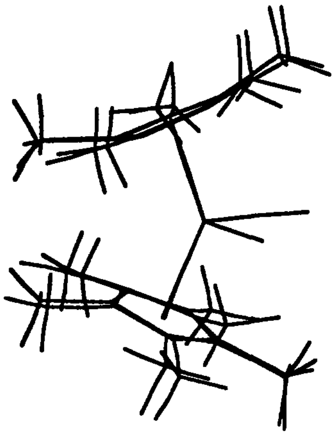
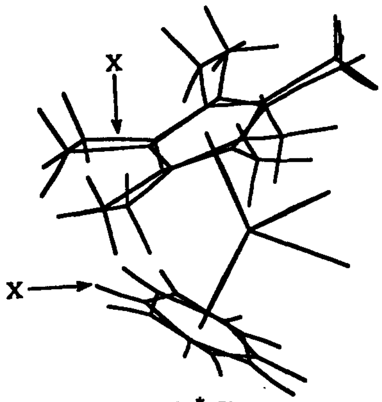
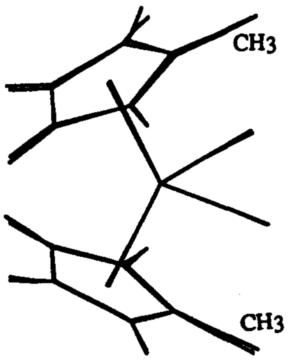
Rigid Fit	Geometry	Calc.	Obs.
 [Ti(Cp)$_2$Cl$_2$]	Ti - D_{Cp}	2.06Å	2.06Å
	Ti - Cl	2.37Å	2.36Å
	D_{Cp}-Ti-D_{Cp}	131°	131°
	D_{Cp}-Ti-Cl	106°	106°
	Cl-Ti-Cl	95°	95°
	C_{Cp}-D_{Cp}-D_{Cp}-C_{Cp}	28°	28°
	B_{Cl}-Ti-D_{Cp}-C_{Cp}	14°, 14°	19°, 8°
 [Ti(Cp*)$_2$Cl$_2$]	Ti - D_{Cp*}	2.12Å	2.13Å
	Ti - Cl	2.37Å	2.35Å
	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°
 [Ti(CpCp*)Cl$_2$]	Ti - D_{Cp}	2.07Å	2.07Å
	Ti - D_{Cp*}	2.09Å	2.10Å
	Ti - Cl	2.37Å	2.35Å
	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(MeCp)$_2$Cl$_2$]	Ti - $D_{Cp'}$	2.07Å	2.07Å
	Ti - Cl	2.37Å	2.36Å
	$D_{Cp'}$-Ti-$D_{Cp'}$	132°	130°
	$D_{Cp'}$-Ti-Cl	106°	107°
	Cl-Ti-Cl	94°	93°
	$D_{Cp'}$-$C_{Cp'}$-C_{Me}	3°	7°
	$C_{Cp'}$-$D_{Cp'}$-$D_{Cp'}$-$C_{Cp'}$	0°	0°
	B_{Cl}-Ti-$D_{Cp'}$-$C_{Cp'}$	4°, -4°	3°, -3°

Table 5 (Continued)

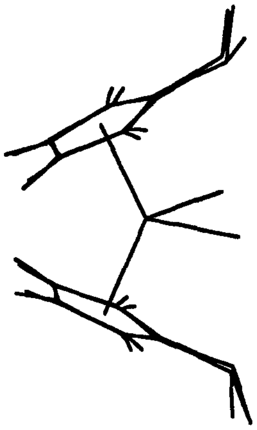
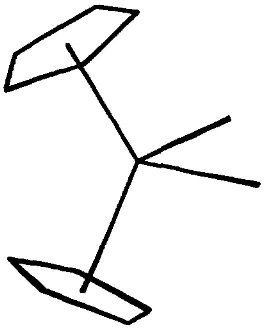
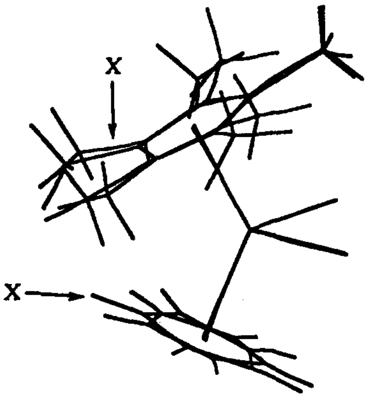
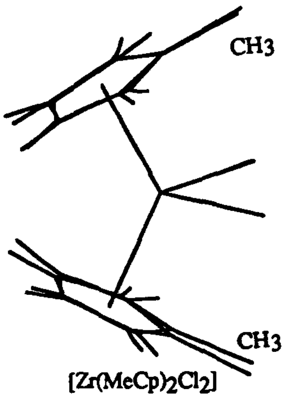
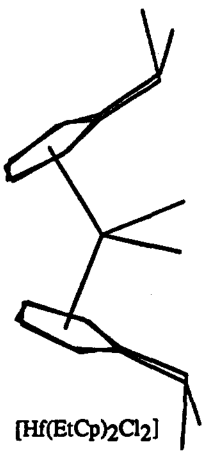
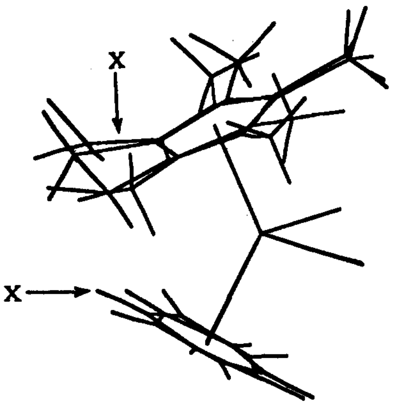
Rigid Fit	Geometry	Calc.	Obs.
 [Ti(i-PrCp)$_2$Cl$_2$]	Ti - $D_{Cp'}$	2.07Å	2.07Å
	Ti - Cl	2.36Å	2.37Å
	$D_{Cp'}$-Ti-$D_{Cp'}$	132°	133°
	$D_{Cp'}$-Ti-Cl	106°	106°
	Cl-Ti-Cl	94°	93°
	$D_{Cp'}$-$C_{Cp'}$-$C_{i\text{-}Pr}$	2°	0°
	$C_{Cp'}$-$D_{Cp'}$-$D_{Cp'}$-$C_{Cp'}$	13°	0°
	B_{Cl}-Ti-$D_{Cp'}$-$C_{Cp'}$	6°,6°	0°, 0°
 [Zr(Cp)$_2$Cl$_2$]	Zr - D_{Cp}	2.20Å	2.20Å, 2.19Å
	Zr - Cl	2.44Å	2.45Å, 2.44Å
	D_{Cp}-Zr-D_{Cp}	129°	129°
	D_{Cp}-Zr-Cl	106°, 107°	107°
	Cl-Zr-Cl	97°	97°
	C_{Cp}-D_{Cp}-D_{Cp}-C_{Cp}	30°	33°
	B_{Cl}-Zr-D_{Cp}-C_{Cp}	13°, 13°	16°, 14°
 [Zr(CpCp*)Cl$_2$]	Zr - D_{Cp}	2.21Å	2.21Å
	Zr - D_{Cp^*}	2.22Å	2.22Å
	Zr - Cl	2.44Å	2.44Å
	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°
 [Zr(MeCp)$_2$Cl$_2$]	Zr - $D_{Cp'}$	2.20Å	2.21Å
	Zr - Cl	2.44Å	2.44Å
	$D_{Cp'}$-Zr-$D_{Cp'}$	130°	129°
	$D_{Cp'}$-Zr-Cl	106°	107°
	Cl-Zr-Cl	97°	95°
	$D_{Cp'}$-$C_{Cp'}$-C_{Me}	2°	3°
	$C_{Cp'}$-$D_{Cp'}$-$D_{Cp'}$-$C_{Cp'}$	0°	0°
	B_{Cl}-Zr-$D_{Cp'}$-$C_{Cp'}$	4°, -4°	5°, -5°

Table 5 (Continued)

Rigid Fit	Geometry	Calc.	Obs.
 [Hf(EtCp)$_2$Cl$_2$]	$Hf-D_{Cp'}$	2.18Å	2.18Å
	$Hf-Cl$	2.43Å	2.43Å
	$D_{Cp'}-Hf-D_{Cp'}$	130°	130°
	$D_{Cp'}-Hf-Cl$	107°	107°
	$Cl-Hf-Cl$	95°	95°
	$D_{Cp*}-C_{Cp*}-C_{Et}$	4°	5°
	$C_{Cp'}-C_{Cp'}-C_{Et}-C_{Et}$	87°	8°
	$C_{Cp'}-D_{Cp'}-D_{Cp'}-C_{Cp'}$	0°	23°
	$B_{Cl}-Hf-D_{Cp'}-C_{Cp'}$	0°, 0°	10°, 10°
 [Hf(CpCp*)Cl$_2$]	$Hf-D_{Cp}$	2.19Å	2.18Å
	$Hf-D_{Cp}^*$	2.20Å	2.19Å
	$Hf-Cl$	2.43Å	2.41Å
	$D_{Cp}-Hf-D_{Cp*}$	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°

[a] X indicates the structure determined by X-ray diffraction.

respect to the calculated dihedral angles, two features should be noted. First, our calculations cannot reproduce $C_{Cp'}-C_{Cp'}$ bond length variations that are observed in the crystal structures of these molecules. These bond lengths can vary in some cases by as much as 1.38 to 1.43 Å within the same Cp′ ring. Because all $C_{Cp'}-C_{Cp'}$ bond stretch constants are the same, all of the $C_{Cp'}-C_{Cp'}$ bond lengths are calculated to be about the same, 1.40 Å. These differences sometimes create apparent discrepancies between the calculated and the observed dihedral angles, and these discrepancies can lead to different nonbonded interactions which can cause rotation of the Cp′ rings. The second feature to note is that the coordinates of the hydrogen atoms in some of the reported crystal structures probably have large errors so that comparisons of the hydrogen positions should be viewed with caution.

The hydrogen atom positions also affect the relative Cp′ rotations. The X-ray structure of [Ti(Cp*)$_2$Cl$_2$] has been reported for all atoms, and the calculated and observed structures are shown in Table 5. It will be noted that our calculations reproduce the skeletal parameters exceptionally well. The deviations of the methyl groups out of the Cp* plane, defined by $D_{Cp*}-C_{Cp*}-C_{Me}$, are also reproduced well. Those methyl groups furthest from the chloro ligands have the largest out-of-plane deviations. The orientations of the hydrogen atoms of the methyl groups are in rough correspondence, but variations are observed. These differences could arise from the relative displacement of the methyl groups caused by $C_{Cp*}-C_{Cp*}$ bond variations in the crystal. The H−C−H angles are observed to vary greatly in the crystal structure.[21]

It can be seen from Table 5 that the skeletal parameters of [Ti(CpCp*)Cl$_2$],[22] [Ti(MeCp)$_2$Cl$_2$],[23] [Ti(i-PrCp)$_2$Cl$_2$],[24] [Zr(CpCp*)Cl$_2$],[22] [Zr(MeCp)$_2$Cl$_2$],[25] [Hf(EtCp)$_2$Cl$_2$],[17] and [Hf(CpCp*)Cl$_2$],[22] representing a broad range of ligand structures, are reproduced extremely well. Where located, it will be noted that the orientations of the methyl group hydrogen atoms are matched reasonably well. As discussed previously, the calculated orientations of the Cp′ ligands are at variance with the crystal structures in some cases.

4. Structures of Strapped Metallocenes

Two types of strapped metallocenes were investigated, those that can form only a single isomer and those that can form diastereomers by virtue of different Cp′ face coordination. Table 6 contains a comparison of the structures and selected geometric parameters for a number of single isomer strapped metallocenes. The bond angles and distances for the ligands are reproduced well in all cases as are the skeletal geometries. The main

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(22) Rogers, R. D.; Benning, M. M.; Kurihara, L. K.; Moriarty, K. J.; Rausch, M. D. *J. Organomet. Chem.* **1985**, *293*, 51.

(23) Petersen, J. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6422.

(24) Howie, R. A.; McQuillan, G. P.; Thompson, D. W. *Acta Crystallogr., Sect. C* **1985**, *41*, 1045.

(25) Petersen, J. L.; Egan, J. W., Jr. *Inorg. Chem.* **1983**, *22*, 3571.

Table 6. Calculated and Observed Structures of Achiral Strapped Metallocenes[a]

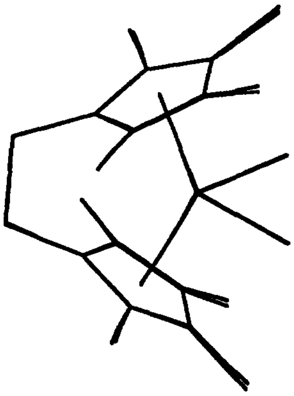
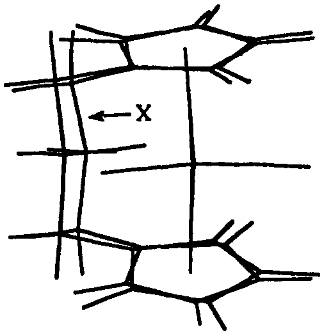
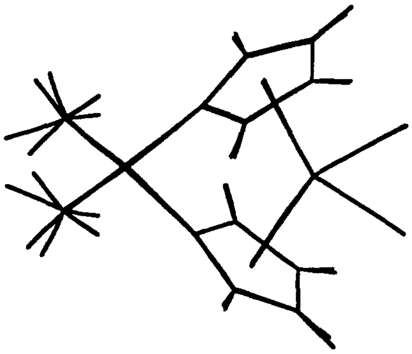
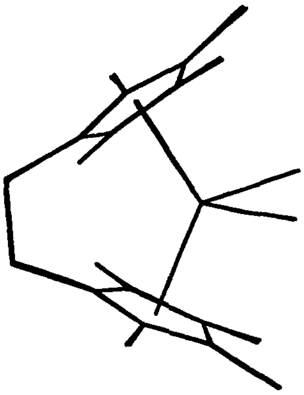
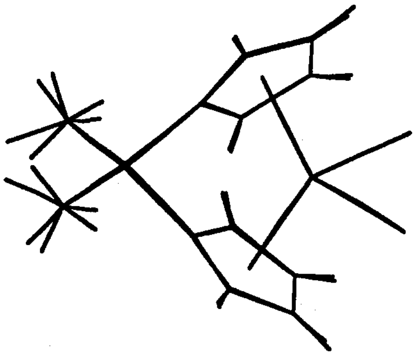
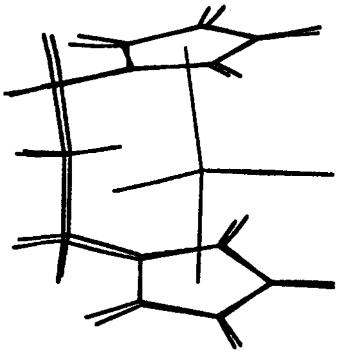
Rigid Fit	Geometry	Calc.	Obs.
 $[\mathrm{Ti(C_2H_4\,(C_5Me_4)_2)Cl_2}]$	Ti - $D_{Cp'}$	2.09Å	2.09Å
	Ti - Cl	2.34Å	2.33Å
	$D_{Cp'}$-Ti- $D_{Cp'}$	132°	131°
	$D_{Cp'}$-Ti-Cl	106°	106°
	Cl-Ti-Cl	95°	96°
	$D_{Cp'}$-$C_{Cp'}$-C_s	3°	2°
	$D_{Cp'}$-$C_{Cp'}$-C_{Me}	6-9°	5-7°
	$C_{Cp'}$- $D_{Cp'}$- $D_{Cp'}$-$C_{Cp'}$	14°	16°
	$C_{Cp'}$-C_s-C_s- $C_{Cp'}$	29°	33°
	B_{Cl}-Ti- $D_{Cp'}$-$C_{Cp'}$	-174°, -174°	-173°, -173°
 $[\mathrm{Ti(C_3H_6\,(C_5H_4)_2)Cl_2}]$	Ti - $D_{Cp'}$	2.06Å	2.06Å
	Ti - Cl	2.38Å	2.37Å
	$D_{Cp'}$-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°
	B_{Cl}-Ti- $D_{Cp'}$-$C_{Cp'}$	135°,-135°	-143°,145°
 $[\mathrm{Ti(Me_2Si(C_5H_4)_2)Cl_2}]$	Ti - $D_{Cp'}$	2.08Å	2.08Å
	Ti - Cl	2.34Å	2.36Å
	$D_{Cp'}$-Ti- $D_{Cp'}$	131°	129°
	$D_{Cp'}$-Ti-Cl	106°	107°
	Cl-Ti-Cl	96°	96°
	$D_{Cp'}$-$C_{Cp'}$-Si	17°	18°
	$C_{Cp'}$-Si-$C_{Cp'}$	91°	89°
	$C_{Cp'}$-Si-C_{Me}	113°	112°
	C_{Me}-Si-C_{Me}	113°	117°
	$C_{Cp'}$- $D_{Cp'}$- $D_{Cp'}$-$C_{Cp'}$	0°	0°
	B_{Cl}-Ti- $D_{Cp'}$-$C_{Cp'}$	180°, 180°	180°, 180°
 $[\mathrm{Zr(C_2H_4\,(C_5Me_4)_2)Cl_2}$	Zr - $D_{Cp'}$	2.22Å	2.21Å
	Zr - Cl	2.43Å	2.44Å
	$D_{Cp'}$-Zr- $D_{Cp'}$	127°	128°
	$D_{Cp'}$-Zr-Cl	107°	107°
	Cl-Zr-Cl	97°	98°
	$D_{Cp'}$-$C_{Cp'}$-C_s	2°	1°
	$D_{Cp'}$-$C_{Cp'}$-C_{Me}	5-7°	4-6°
	$C_{Cp'}$- $D_{Cp'}$- $D_{Cp'}$-$C_{Cp'}$	15°	15°
	$C_{Cp'}$-C_s- C_s-$C_{Cp'}$	33°	34°
	B_{Cl}-Zr- $D_{Cp'}$-$C_{Cp'}$	174°, 174°	173°, 173°

Table 6 (Continued)

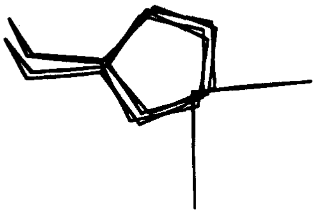
Rigid Fit	Geometry	Calc.	Obs.
	$Zr-D_{Cp'}$	2.21Å	2.20Å
	$Zr-Cl$	2.43Å	2.44Å
	$D_{Cp'}-Zr-D_{Cp'}$	126°	125°
	$D_{Cp'}-Zr-Cl$	107°	108°
	$Cl-Zr-Cl$	98°	98°
	$D_{Cp'}-C_{Cp'}-Si$	18°	17°
	$C_{Cp'}-Si-C_{Cp'}$	96°	93°
	$C_{Me}-Si-C_{Me}$	112°	116°
	$C_{Me}-Si-C_{Cp'}$	112°	112°
	$C_{Cp'}-D_{Cp'}-D_{Cp'}-C_{Cp'}$	0°	0°
	$B_{Cl}-Zr-D_{Cp'}-C_{Cp'}$	180°, 180°	180°, 180°
$[Zr(Me_2Si(C_5H_4)_2)Cl_2]$			
	$Hf-D_{Cp'}$	2.17Å, 2.17Å	2.18Å, 2.17Å
	$Hf-Cl$	2.43Å, 2.44Å	2.41Å, 2.43Å
	$D_{Cp'}-Hf-D_{Cp'}$	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°
	$B_{Cl}-Hf-D_{Cp'}-C_{Cp'}$	-136°,136°	-143°, 141°
$[Hf(C_3H_6(C_5H_4)_2)Cl_2]$			

[a] X indicates the structure determined by X-ray diffraction.

discrepancies were found in the conformations of the ligands which we define in terms of the four-atom torsion angles. The four-atom sequences are defined as including the Cp′ carbon atom ($C_{Cp'}$) which is attached to the strap; again B_{Cl} refers to a point on the bisector of the Cl−M−Cl angle. The designation C_s refers to the strap carbon atom attached to the Cp′.

The structure of the dimethylene strapped complex, $[Ti(C_2H_4(C_5Me_4)_2)Cl_2]$, has been determined,[26] but the hydrogen atoms were not located. As can be seen by the superimposed calculated and observed structures and the geometric parameters (Table 6), the two structures are nearly identical. The same is true for the calculated and observed[26] structures of the zirconium analogue, $[Zr(C_2H_4(C_5Me_4)_2)Cl_2]$, for which the hydrogen locations were not found in the crystal structure. Both structures are C_2 symmetric.

Crystal structures of the trimethylene linked complexes $[Ti(C_3H_6(C_5H_4)_2)Cl_2]$[27] and $[Hf(C_3H_6(C_5H_4)_2)Cl_2]$[28] have been reported and the hydrogen atoms were located in both cases. The structure of the zirconium analogue has, as yet, not been reported. The calculated and observed structures are given in Table 6 where it will be noted that significant differences occur in the dihedral twisting of the Cp′ rings and the strap. The twist away from the Cl−M−Cl bisector is less in the calculated structure. This is shown in **6** where the hydrogen atoms are removed for clarity and the calculated and observed structures are superimposed. This rotation can be traced to the C−C distances in the strap which are 1.51 Å in the Ti crystal and 1.49 Å and 1.52 Å in the Hf crystal compared to 1.56−1.57 Å for the calculated values. These longer distances create a larger bridge span requirement resulting in rotation of the ligand to accommodate the larger strap span. Structure **6**, however, is not the global minimum structure, and we find that structure **7** is more stable than **6** by 1.0 kcal/mol for the titanium complex, by 1.4 kcal/mol for the zirconium complex, and by 1.3 kcal/mol for the hafnium complex. These energy differences correlate with the differences in radii of the metals, and the presence of structure **6** in the crystal presumably arises from the exigencies of crystal packing. It is convenient to represent structures **7** and **8** by connecting the strap carbon atoms with the joining Cp′ carbon, the dummy atom, and the metal as



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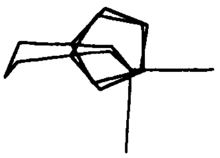
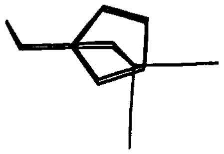
(26) Wochner, F.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1985**, *288*, 69.

(27) Davis, B. R.; Bernal, I. *J. Organomet. Chem.* **1971**, *30*, 75.

(28) Saldarriaga-Molina, C. H.; Clearfield, A.; Bernal, I. *Inorg. Chem.* **1974**, *13*, 2880.



7



8

shown. Such representation allows us to refer to **7** as the boat conformation and **8** as the chair conformation. The two structures **7** and **8** do not possess a C_2 axis bisecting the Cl−M−Cl angle, and hence such static structures should make all of Cp′ hydrogen atoms distinct. In solution, ^{1}H NMR spectroscopy indicates[29] that such molecules are C_2 symmetric on an NMR time scale at 30 °C. This suggests that the molecules are fluxional and interconvert between forms where the strap is first nearer to one Cl and then nearer to the other Cl by concerted Cp′ rotation. During the Cp′ rotation the strap will undergo conformation change, either a chair to chair or a boat to boat flip. Such conformational flipping may involve the boat and chair conformations or distorted structures resembling them. It is therefore gratifying to find that such interconversion is likely to be constrained by only a few kilocalories/mole in energy which is consistent with experiment.

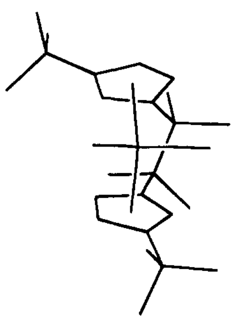
The final two complexes in Table 6 are silicon strapped metallocenes which as a class are of some current interest. The structures of the [Ti(Me$_2$Si(C$_5$H$_4$)$_2$)Cl$_2$][30] and [Zr(Me$_2$Si(C$_5$H$_4$)$_2$)Cl$_2$][30] complexes have been reported and the hydrogen atoms were located. Aside from the methyl group hydrogen atoms which are not reproduced in either structure, the remaining coordinates of the two molecules are calculated with high precision. Both molecules are C_2 symmetric.

5. Structures of Diastereomeric Strapped Metallocenes

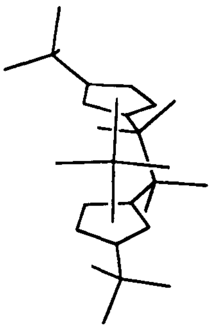
Table 7 contains superimposed structures and salient geometric parameters for the three strapped metallocenes, *meso*-[Ti(Me$_4$C$_2$(3-t-BuC$_5$H$_3$)$_2$)Cl$_2$],[31] *meso*-[Ti(Me$_4$C$_2$(3-TMSC$_5$H$_3$)$_2$)Cl$_2$][32] (where TMS is trimethylsilyl), and *rac*-[Zr(Me$_2$Si(3-t-Bu-5-MeC$_5$H$_2$)$_2$)Cl$_2$].[33] The hydrogen atoms were located in the first and third but not in the second of these molecules. The observed and calculated structures are generally in excellent agreement.

Aside from an interest in reproducing the structures of the molecules contained in Table 7, molecular mechanics provides the possibility of estimating the difference in energy between the racemic and meso forms of the complexes. It has been commonly assumed that by judiciously placing bulky substituents such as t-Bu or TMS on the Cp′ ring of strapped metallocenes might lead to a preference for the generally desired racemic form. This supposition is based on the assumption that in the meso isomer the bulky substituents will experience greater steric interaction than in the racemic form because, in the former, the bulky substituents are positioned adjacent to each other unlike the case of the racemic isomer where these groups are oriented away from each other. Our calculations indicate that VDW interactions are not decisive. The sum of bond stretch, angle bend, and torsional energy terms adds more to the energy difference than do nonbonded interactions. No term is decisive.

Table 8 lists the energy differences (racemic − meso) for all terms for the three complexes. It should be noted that the racemic forms of the two-carbon strapped metallocenes can exist in two diastereomeric forms for one absolute configuration of the Cp′ binding modes. These arise from the (chiral) puckering of the two-carbon strap which can be δ or λ. An example of the two diastereomers is shown in **9** and **10** for the two minimized structures of [Ti(Me$_4$C$_2$(3-t-BuC$_5$H$_3$)$_2$)Cl$_2$] in the R,R absolute configuration of the Cp′ binding. For both the [Ti(Me$_4$C$_2$(3-t-BuC$_5$H$_3$)$_2$)Cl$_2$] and the [Ti(Me$_4$C$_2$(3-TMSC$_5$H$_3$)$_2$)Cl$_2$] complexes we find that the λ-R,R isomer is more stable than the δ-R,R form by 1.3 and 0.9 kcal/mol, respectively (note λ-R,R = δ-S,S and δ-R,R = λ-S,S). The differences in Table 8 refer to the difference between the meso forms and the most stable racemic isomer, λ-R,R or the mirror image δ-S,S. Inspection of the energy terms in Table 8 confirms the supposition that the nonbonded interactions are less for the racemic isomer, but the differences are small and are generally of the same magnitude as the other terms which can be positive or negative. For the two titanium complexes, the meso isomer is slightly more stable, whereas the reverse is true for the zirconium compound for which the racemic isomer is strongly favored. It is not possible to compare these calculated ratios with experiment because formation of these titanium and zirconium complexes is kinetically controlled and no method has yet been found for establishing thermodynamic equilibrium of the isomers. Preparatively, a racemic to meso ratio of 1:4 was found for the [Ti(Me$_4$C$_2$(3-t-BuC$_5$H$_4$)$_2$)Cl$_2$] complex,[31] a ratio of 1.8:1 for [Ti(Me$_4$C$_2$(3-TMSC$_5$H$_4$)$_2$)Cl$_2$],[32] and a ratio of 2:1 for [Zr(Me$_2$Si(3-t-Bu-5-MeC$_5$H$_2$)$_2$)Cl$_2$].[33] The observed ratio for the last complex clearly indicates that, despite the significant thermodynamic preference of the ligand for forming the racemic isomer, the kinetics of formation of the isomers does not reflect this thermodynamic preference to any strong degree.



λ-R,R
9



δ-R,R
10

The related molecule *rac*-[Ti(C$_2$H$_4$(3-t-BuC$_5$H$_3$)$_2$)Cl$_2$] crystallizes in monoclinic and tetragonal forms, and the structure of the molecule in each crystal habit has been determined.[34] The hydrogen atoms were located for the tetragonal but not for the monoclinic crystals. The molecules have different rotamer conformations in the two forms although the puckering of the strap is the same, namely, λ-S,S or δ-R,R. The three superimposed structures with hydrogen atoms deleted for clarity and the relevant geometric parameters are contained in Table 9, where it will be noted that the calculated and the two observed structures correspond geometrically except that the calculated torsional twist of the strap, $B_{Cl}-Ti-D_{Cp'}-C_{Cp'}$, is braced by the two observed structures. We have previously asserted that discrepancies in the observed and calculated structures, par-

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(29) Smith, J. A.; Von Seyerl, J.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1979**, *173*, 175.

(30) Bajgur, C. S.; Tikkanen, W. R.; Petersen, J. L. *Inorg. Chem.* **1985**, *24*, 2539.

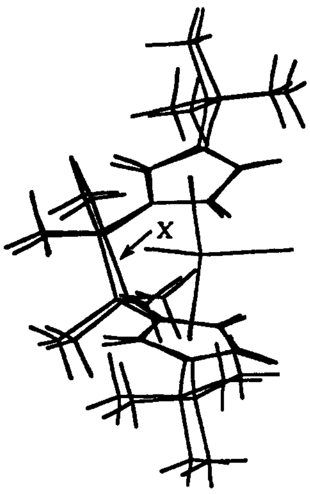
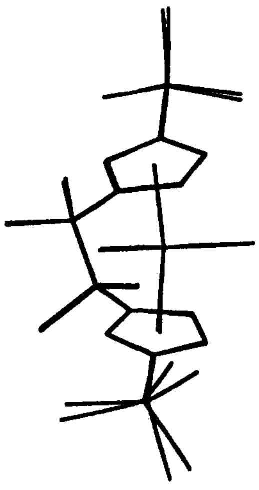
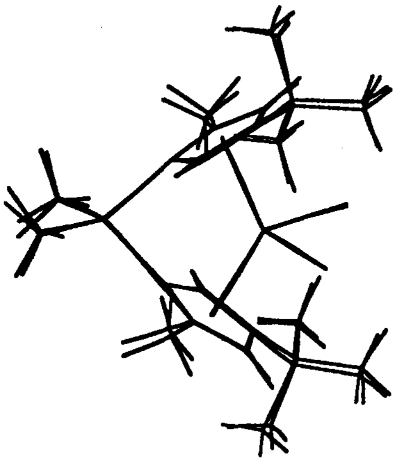
(31) Erickson, M. S.; Fronczek, F. R.; McLaughlin, M. L. *Acta Crystallogr., Sect. C* **1990**, *46*, 1802.

(32) Gutmann, S.; Burger, P.; Hund, H. U.; Hofmann, J.; Brintzinger, H. H. *J. Organomet. Chem.* **1989**, *369*, 343.

(33) Wiesenfeldt, H.; Reinmuth, A.; Barsties, E.; Evertz, K.; Brintzinger, H. H. *J. Organomet. Chem.* **1989**, *369*, 359.

(34) Collins, S.; Hong, Y.; Taylor, N. J. *Organometallics* **1990**, *9*, 2695.

Table 7. Calculated and Observed Structures of Racemic and Meso Strapped Metallocenes[a]

Rigid Fit	Geometry	Calc.	Obs.
 *meso*-$[\mathrm{Ti(Me_4C_2(3\text{-}\mathit{t}\text{-}BuC_5H_3)_2)Cl_2}]$	Ti - $D_{Cp'}$	2.08Å, 2.07Å	2.09Å
	Ti - Cl	2.34Å	2.33Å, 2.36Å
	$D_{Cp'}$-Ti- $D_{Cp'}$	131°	129°
	$D_{Cp'}$-Ti-Cl	106°	107°
	Cl-Ti-Cl	96°	96°
	$D_{Cp'}$-$C_{Cp'}$-C_s	1°, 3°	3°, 2°
	$D_{Cp'}$-Ti- C_{tBu}	11°,12°	10°, 11°
	$C_{Cp'}$- $D_{Cp'}$- $D_{Cp'}$ -$C_{Cp'}$	16°	16°
	$C_{Cp'}$-C_s- C_s-$C_{Cp'}$	33°	36°
	B_{Cl}-Ti- $D_{Cp'}$-$C_{Cp'}$	155°, -141°	162°, -148°
 *meso*-$[\mathrm{Ti(Me_4C_2(3\text{-}TMSC_5H_3)_2)Cl_2}]$	Ti - $D_{Cp'}$	2.06Å, 2.07Å	2.07Å, 2.08Å
	Ti - Cl	2.35Å	2.35Å, 2.34Å
	$D_{Cp'}$-Ti- $D_{Cp'}$	130°	128°
	$D_{Cp'}$-Ti-Cl	107°	107°
	Cl-Ti-Cl	95°	98°
	$D_{Cp'}$-$C_{Cp'}$-C_s	2°, 1°	2°
	$D_{Cp'}$-$C_{Cp'}$-C_{Si}	8°	8°, 10°
	$C_{Cp'}$- $D_{Cp'}$- $D_{Cp'}$-$C_{Cp'}$	15°	14°
	$C_{Cp'}$-C_s- C_s-$C_{Cp'}$	32°	32°
	B_{Cl}-Ti- $D_{Cp'}$-$C_{Cp'}$	-146°, 159°	-146°,159°
 *rac*-$[\mathrm{Zr(Me_2Si(3\text{-}\mathit{t}\text{-}Bu\text{-}5\text{-}MeC_5H_2)_2)Cl_2}]$	Zr - $D_{Cp'}$	2.25Å	2.23Å
	Zr - Cl	2.42Å	2.42Å
	$D_{Cp'}$-Zr- $D_{Cp'}$	125°	127°
	$D_{Cp'}$-Zr-Cl	104°, 112°	104°, 110°
	Cl-Zr-Cl	97°	98°
	$D_{Cp'}$-$C_{Cp'}$-Si	16°	17°
	$C_{Cp'}$-Si-$C_{Cp'}$	95°	94°
	$C_{Cp'}$-Si-C_{Me}	112°, 114°	111°, 115°
	$D_{Cp'}$-$C_{Cp'}$-C_{Me}	1°	3°
	$D_{Cp'}$-$C_{Cp'}$-C_{tBu}	12°	9°
	$C_{Cp'}$- $D_{Cp'}$- $D_{Cp'}$-$C_{Cp'}$	3°	6°
	B_{Cl}-Zr- $D_{Cp'}$-$C_{Cp'}$	179°, 179°	178°, 178°

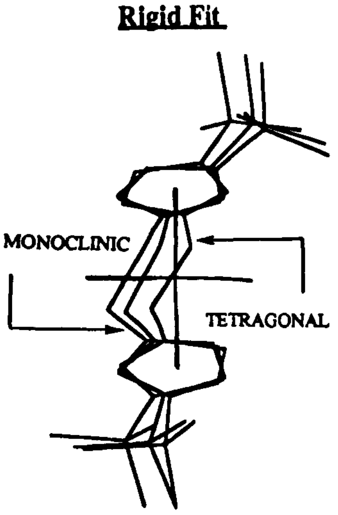
[a] X indicates the structure determined by X-ray diffraction.

ticularly discrepancies involving the twist of the strap, could be accounted for, at least in part, by the effects of crystal packing. Since the hydrogen atom coordinates of the tetragonal form of $[\mathrm{Ti(C_2H_4(3\text{-}t\text{-}BuC_5H_3)_2)Cl_2}]$ are known, we are in a

Table 8. Difference in Energy (Racemic − Meso) for the Various Molecular Mechanics Terms

complex	energy terms (kcal/mol) bonds	angles	torsions	VdW	total
$[Ti(Me_4C_2(3\text{-t-BuC}_5H_3)_2)Cl_2]$	−0.46	0.58	0.52	−0.35	0.29
$[Ti(Me_4C_2(3\text{-TMSC}_5H_3)_2)Cl_2]$	−0.04	0.51	0.24	−0.26	0.45
$[Zr(Me_2Si(3\text{-t-Bu-5-MeC}_5H_2)_2)Cl_2]$	−0.47	−1.23	−2.30	−0.66	−4.66

Table 9. Calculated and Observed Structures of a Chiral Strapped Metallocene

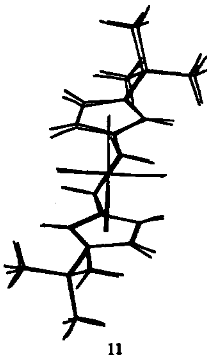


$rac\text{-}[Ti(C_2H_4(3\text{-}t\text{-BuC}_5H_3)_2)Cl_2]$

Geometry	Calc.	Obs. monoclinic	tetragonal
Ti - $D_{Cp'}$	2.09Å, 2.08Å	2.10Å, 2.09Å	2.11Å, 2.10Å
Ti - Cl	2.35Å, 2.32Å	2.35Å,2.32Å	2.38Å,2.33Å
$D_{Cp'}$-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_{tBu}	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°
B_{Cl}-Ti- $D_{Cp'}$-$C_{Cp'}$	-171°, 155°	-164°, 147°	175°, 166°

position to test this assertion by minimizing the structure in its crystal environment.

The packing calculation was performed to a good degree of accuracy as follows. The selected molecule was minimized in the presence of 16 of its rigidly positioned crystal nearest neighbors. This included all surrounding molecules for which the titanium atoms were within 12.5 Å of the titanium atom of the molecule of interest. Upon minimization the external coordinates of the minimized molecule did not change, but its internal coordinates adjusted to the nonbonding interactions emanating from its neighbors. This minimized structure and the structure of the molecule in the tetragonal crystal are shown in **11**, where the hydrogen atoms are now shown. The correspondence between the two structures supports our earlier assertion that crystal packing forces can have a significant effect on the twisting of the ligand about the metal. The only significant discrepancy in the calculated and observed structures is that one of the calculated Ti−Cl bond lengths is 0.06 Å shorter than that reported for the crystal structure. Crystal packing can also affect the conformation of the strap. For the racemic $[Ti(C_2H_4(3\text{-t-BuC}_5H_3)_2)Cl_2]$ complex, we find that the λ-S,S (or δ-R,R) isomer found in both monoclinic and tetragonal crystals is less stable by about 1 kcal/mol than the δ-S,S (or λ-R,R) conformation of the strap. This energy difference between the two isomers is small, and the preference for the less stable λ-S,S (or δ-R,R) isomer in the crystal is presumably a consequence of crystal packing. The small energy difference between the two conformational forms and the considerable twist displacements observed in the two crystal forms suggest that these types of molecules can undergo considerable low-energy twisting and conformational interconversion in solution. This structural mobility may be of importance when these types of molecules are employed in stereoselective reactions. We find that the difference in energy between the more stable δ-S,S isomer and the meso (R,S) isomer is 0.61 kcal/mol in favor of the meso form. The preparation of this compound gives a 2:1 meso:rac ratio of isomers.[35]



11

Although the meso to racemic preference for these two-carbon strap systems is generally small by our calculations, large differences are calculated when the strap is extended to three carbons. The analogous complex, $[Ti(C_3H_6(3\text{-t-BuC}_5H_3)_2)Cl_2]$, has been prepared[35] but its crystal structure has not been reported. It is isolated exclusively as the racemic form and it is found to be C_2 symmetric on an ^1H NMR time scale. We find that the difference in energy between the minimized meso and racemic forms is 4.6 kcal/mol in favor of the racemic isomer. This large difference is consistent with experimental results.[35] In both the minimized meso and racemic forms the three-carbon strap is in the boat **7** rather than in the chair **8** conformation, and the structure of the racemic form is not C_2 symmetric. We find, however, that the difference in energy between the boat and chair conformations is small, 1.7 kcal/mol for the racemic isomer and 1.0 kcal/mol for the meso form. Assuming that the fluxional interconversion, which leads to

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(35) Schnutenhaus, H.; Brintzinger, H. H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 777.

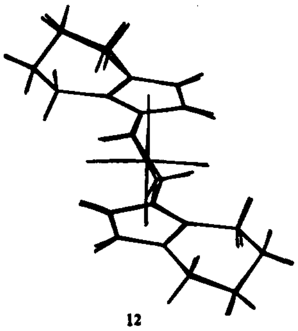
apparent C_2 symmetry on an ^{1}H NMR time scale for the racemic isomer, involves traversing conformations resembling the boat and chair forms, the present calculations suggest that the process is facile as is observed.

6. Structure of Diastereomeric Strapped 1,1′-Bis(tetrahydroindenyl) Complexes

Because their derivatives have the ability to promote stereoselective transformations, the [M(ethylene-1,1′-bis(tetrahydroindenyl)Cl$_2$] ([M(C$_2$H$_4$(THIND)$_2$)Cl$_2$]) complexes are of special current interest. Table 10 lists the calculated and observed structures and selected geometric parameters in the now familiar format. A crystal structure analysis of [Ti(C$_2$H$_4$(THIND)$_2$)Cl$_2$] located the hydrogen atoms and found that the molecule was C_2 symmetric.[36a] This molecule possesses three dissymmetric components: the face binding of each of the 1-tetrahydroindenyl units, designated as R or S; the conformation of the strap, labeled as δ or λ; and the puckering of each reduced part of the tetrahydroindenyl groups, also given the δ and λ designations. Thus the absolute configuration of the molecule [Ti(C$_2$H$_4$(THIND)$_2$)Cl$_2$] as the diastereomer illustrated in Table 10 would be written as (*R,R*)-[Ti(δ-C$_2$H$_4$(λ-THIND)$_2$)Cl$_2$] or is designated simply as the sequence δ-R,R-λ,λ. The δ and λ labeling is based on the convention used for the chiral conformations of chelate rings[37] and the R and S labeling for π-ligand to metal chirality is that commonly used.[36b,38] The rigid fit of the (*R,R*)-[Ti(δ-C$_2$H$_4$(λ-THIND)$_2$Cl$_2$] molecule was based on the minimization of this diastereomer. It will be noted that the fit is good but that the minimized structure is rotated relative to the crystal structure. When these metallocenes bear two or more atoms for the strap, rotated non-C_2 symmetric structures are usually observed in the calculations. This rotation serves to alleviate strain which is present when the strap span is larger than the distance between the two Cp′ carbon atoms bearing the strap. A single silicon strap generally gives structures where the silicon bisects the Cl−M−Cl angle; with dimethylene straps, the strap span is almost strain free and the amount of ligand rotation depends on subtle factors including the metal radius. With trimethylene or greater strap spans, the ligand is always rotated relative to the Cl−M−Cl bisector. Since the dimethylene strap in [Ti(C$_2$H$_4$(THIND)$_2$)Cl$_2$] is nearly ideal for this system, we might anticipate that the C_2 symmetric structure will be close in energy to the rotated minimized structure and that crystal packing could account for the difference.

A crystal packing calculation was performed on the (*R,R*)-[Ti(δ-C$_2$H$_4$(λ-THIND)$_2$)Cl$_2$] molecule where the molecule of interest was allowed to interact with its 11 nearest neighbors which included all molecules, the titanium atoms of which, were within 11 Å of the titanium atom of the molecule of interest. The result of the packing calculation is shown in **12**.

After investigating all of the possible diastereomeric conformations of [Ti(C$_2$H$_4$(THIND)$_2$)Cl$_2$], we find that the δ-R,R-λ,λ or the enantiomer λ-S,S-δ,δ diastereomer found in the crystal is not the most stable conformer. The λ-R,R-δ,δ or δ-S,S-λ,λ diastereomer is 3 kcal/mol more stable than the δ-R,R-λ,λ (λ-S,S-δ,δ) isomer found in the crystal. Further, the λ-R,R-δ,δ isomer is found to minimize to a C_2 symmetric structure. Taking the λ-R,R-δ,δ diastereomer as a zero energy reference, Table 11 lists the energies of the possible racemic conformations of [Ti(C$_2$H$_4$(THIND)$_2$)Cl$_2$]. Given the small energy differences between the diastereomers and that the activation energy of the interconversion is likely to be small, it is probable that this system is undergoing rapid conformational interconversion involving the strap and tetrahydroindenyl fragments, and as a consequence of these interconversions the ligand will engage in oscillating rotations about the C_2 axis. Because of this flexibility, stereoselective reactions promoted by derivatives of the complex are likely to be sterically controlled by conformations which accommodate the reacting substrate rather than by the crystal conformation as has sometimes been supposed.


12

The meso isomer (*R,S*)-[Ti(C$_2$H$_4$(THIND)$_2$)Cl$_2$] has been isolated and its crystal structure was determined, but the hydrogen atoms were not located.[36b] The superimposed structure is shown in Table 10 where the parameters indicate a good fit but the ligand is rotated further from the Cl−M−Cl bisector in the minimized structure than it is in the crystal. The crystal conformation is δ-R,S-λ,λ, and we find that it is the global minimum (Table 12). But there is a cluster of conformations of similar energy. Since in the meso isomer the two tetrahydroindenyl groups are not in the same chemical environment, one being closer to the chloro ligand than the other, the δ-R,S-δ,λ and δ-R,S-λ,δ conformers are energetically different. Given the low-energy differences between the various conformations, the meso isomer is expected to be conformationally mobile like its racemic analogue as is observed experimentally.

The crystal structure of racemic [Zr(C$_2$H$_4$(THIND)$_2$)Cl$_2$] has been reported and the hydrogen atoms were located.[36a] In the crystal the λ-S,S-δ,δ (shown) or the δ-R,R-λ,λ isomer is observed. The calculated structure of this conformer is in excellent agreement with the X-ray structure (Table 10). It will be noted that the minimized structure is C_2 symmetric, probably because of the longer bond lengths of zirconium compared to titanium. As in the case of the titanium analogue, this is not the lowest energy conformer, but rather the δ-S,S-λ,λ or λ-R,R-δ,δ isomer is the most stable. Table 11 lists the difference in energy for each of the racemic isomers relative to the most stable conformer, λ-R,R-δ,δ. The energetic hierarchy is similar to that found for the titanium analogue, and we draw the same conclusion about the conformational mobility of the system.

No structure of the meso (*R,S*)-[Zr(C$_2$H$_4$(THIND)$_2$)Cl$_2$] has been reported. Our calculations predict that the most stable conformation should be δ-R,S-δ,λ, but the δ-R,S-λ,λ conformer is almost the same energy (Table 12). The low-energy differences between the various conformations indicates, as in the titanium analogue, that they readily interconvert.

As for the titanium and zirconium complexes, the racemic [Hf(C$_2$H$_4$(THIND)$_2$)Cl$_2$] crystallizes in the δ-R,R-λ,λ or λ-S,S-δ,δ form; the minimization of this form compared to the X-ray structure[39] is shown in Table 10. The most stable conformer is λ-R,R-δ,δ as is the case for titanium and zirconium, and,

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(36) (a) Collins, S.; Kuntz, B. A.; Taylor, N. J.; Ward, D. G. *J. Organomet. Chem.* **1988**, *342*, 21. (b) Wild, F. R. W. P.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1982**, *232*, 233.

(37) *Inorg. Chem.* **1970**, *9*, 1.

(38) Schlögl, K. *Top. Stereochem.* **1967**, *1*, 39.

(39) Ewen, J. A.; Haspeslagh, L.; Atwood, J. L.; Zhang, H. *J. Am. Chem. Soc.* **1987**, *109*, 6544.

Table 10. Calculated and Observed Structures of Strapped Tetrahydroindenyl Complexes[a]

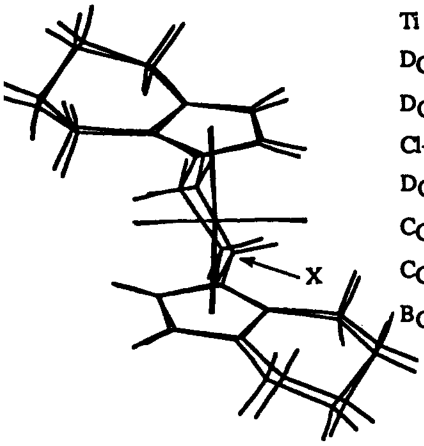
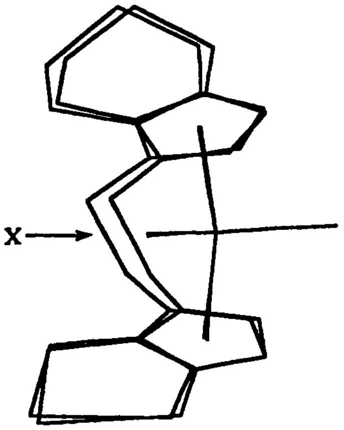
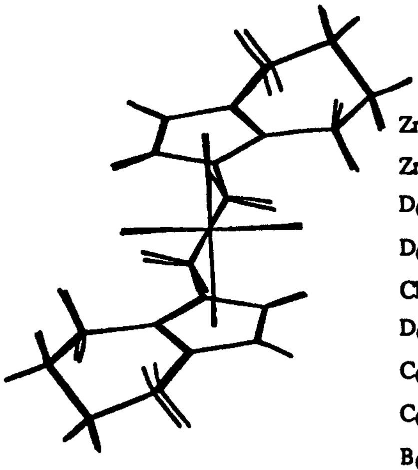
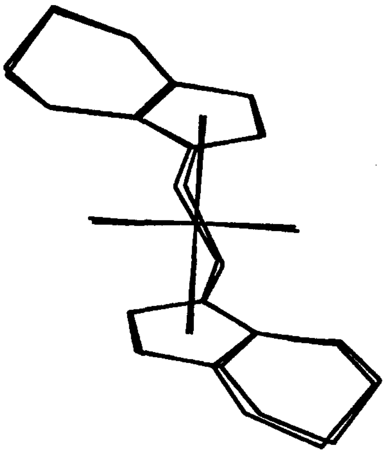
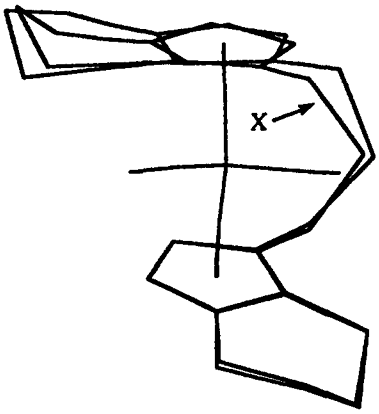
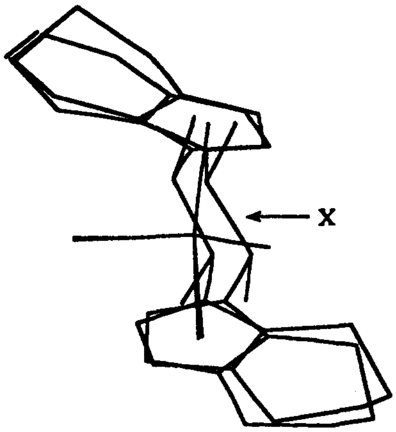
Rigid Fit	Geometry	Calc.	Obs.
	Ti - $D_{Cp'}$	2.09Å	2.10Å
	Ti - Cl	2.34Å	2.35Å
	$D_{Cp'}$-Ti- $D_{Cp'}$	131°	128°
	$D_{Cp'}$-Ti-Cl	106°	107°
	Cl-Ti-Cl	95°	96°
	$D_{Cp'}$-$C_{Cp'}$-C_s	2°	0°
	$C_{Cp'}$- $D_{Cp'}$- $D_{Cp'}$-$C_{Cp'}$	19°	20°
	$C_{Cp'}$-C_s-C_s- $C_{Cp'}$	42°	46°
	B_{Cl}-Ti- $D_{Cp'}$-$C_{Cp'}$	-165°, -177°	-171°, -171°
rac-[Ti(C_2H_4 (THIND)$_2$)Cl_2]			
	Ti - $D_{Cp'}$	2.08Å	2.08A
	Ti - Cl	2.36Å, 2.31Å	2.35Å, 2.34Å
	$D_{Cp'}$-Ti- $D_{Cp'}$	131°	129°
	$D_{Cp'}$-Ti-Cl	107°	107°
	Cl-Ti-Cl	94°	93°
	$D_{Cp'}$-$C_{Cp'}$-C_s	1°	2°
	$C_{Cp'}$- $D_{Cp'}$- $D_{Cp'}$-$C_{Cp'}$	18°	19°
	$C_{Cp'}$-C_s-C_s- $C_{Cp'}$	41°	42°
	B_{Cl}-Ti- $D_{Cp'}$-$C_{Cp'}$	-157°, 173°	-148°, 165°
meso-[Ti(C_2H_4 (THIND)$_2$)Cl_2]			
	Zr - $D_{Cp'}$	2.22Å	2.21Å
	Zr - Cl	2.43Å	2.44Å
	$D_{Cp'}$-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°
	B_{Cl}-Zr- $D_{Cp'}$-$C_{Cp'}$	171°, 171°	171°, 171°
rac-[Zr(C_2H_4 (THIND)$_2$)Cl_2]			

Table 10 (Continued)

Rigid Fit	Geometry	Calc.	Obs.
	Hf - $D_{Cp'}$	2.20Å	2.20Å
	Hf - Cl	2.42Å	2.42Å
	$D_{Cp'}$-Hf-$D_{Cp'}$	126°	126°
	$D_{Cp'}$-Hf-Cl	106°, 110°	107°, 108°
	Cl-Hf-Cl	95°	97°
	$D_{Cp'}$-$C_{Cp'}$-C_s	1°	1°
	$C_{Cp'}$-$D_{Cp'}$-$D_{Cp'}$-$C_{Cp'}$	20°	19°
	$C_{Cp'}$-C_s-C_s-$C_{Cp'}$	45°	49°
	B_{Cl}-Hf-$D_{Cp'}$-$C_{Cp'}$	-174°, -168°	-172°, -172°
rac-C_2H_4 (THIND)$_2$HfCl$_2$			
	Ti - $D_{Cp'}$	2.09Å, 2.07Å	2.07Å
	Ti - Cl	2.35Å, 2.38Å	2.34Å
	$D_{Cp'}$-Ti-$D_{Cp'}$	132°	133°
	$D_{Cp'}$-Ti-Cl	106°	106°
	Cl-Ti-Cl	92°	92°
	$D_{Cp'}$-$C_{Cp'}$-C_s	6°	8°
	$C_{Cp'}$-$D_{Cp'}$-$D_{Cp'}$-$C_{Cp'}$	11°	3°
	B_{Cl}-Ti-$D_{Cp'}$-$C_{Cp'}$	130°, -140°	142°, -139°
rac-[Ti(C$_3$H$_6$(THIND)$_2$)Cl$_2$]			
	Ti - $D_{Cp'}$	2.08Å	2.09Å
	Ti - Cl	2.33Å, 2.35Å	2.34Å
	$D_{Cp'}$-Ti-$D_{Cp'}$	131°	129°
	$D_{Cp'}$-Ti-Cl	106°	107°
	Cl-Ti-Cl	94°	95°
	$D_{Cp'}$-$C_{Cp'}$-C_s	2°	2°, 1°
	$C_{Cp'}$-$D_{Cp'}$-$D_{Cp'}$-$C_{Cp'}$	20°	22°
	$C_{Cp'}$-C_s-C_s-$C_{Cp'}$	41°	42°
	B_{Cl}-Ti-$D_{Cp'}$-$C_{Cp'}$	173°, -155°	-171°, 169°
(R,R)-[Ti(S,S-Chiracene)Cl$_2$]			

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[a] X indicates the structure determined by X-ray diffraction.

similarly, there exists a cluster of energetically similar conformations (Table 11). For the meso form of [Hf(C_2H_4(THIND)$_2$)Cl$_2$], whose structure is not known, we find that the δ-R,S-λ,λ and δ-R,S-δ,λ forms are of essentially the same energy and are the most stable but are similar in energy to the other forms (Table 12).

The calculations indicate that the lowest energy conformers of the racemic and meso forms of the titanium, zirconium, and hafnium complexes, [M(C_2H_4(THIND)$_2$)Cl$_2$], are similar in energy. The meso form is less stable, by 1.0 kcal/mol for the zirconium and hafnium complexes and by 0.8 kcal/mol for the titanium analogue. An analysis of the various strain and VDW

Table 11. Relative Energies of the Various Conformers of (*R*,*R*)-[M(C$_2$H$_4$(THIND)$_2$)Cl$_2$] Complexes and Symmetries of the Minimized Structures

	ΔE (kcal/mol), M =			symmetry, M =		
conformer	Ti	Zr	Hf	Ti	Zr	Hf
λ-R,R-δ,δ	0	0	0	C_2	C_2	C_2
λ-R,R-λ,δ	1.6	1.5	1.5	C_1	C_1	C_1
δ-R,R-λ,δ	1.8	1.5	1.6	C_1	C_1	C_1
δ-R,R-δ,δ	2.0	1.8	1.8	C_1	C_1	C_1
δ-R,R-λ,λ[a]	3.0	2.2	2.4	C_1	C_2	C_1
λ-R,R-λ,λ	3.4	2.9	3.0	C_2	C_2	C_2

[a] Conformer found by X-ray diffraction analysis.

Table 12. Relative Energies of the Various Conformers of (*R*,*S*)-[M(C$_2$H$_4$(THIND)$_2$)Cl$_2$] Complexes

	ΔE (kcal/mol), M =		
conformer	Ti	Zr	Hf
δ-R,S-λ,λ	0[a]	0[c]	0[c]
δ-R,S-δ,λ[b]	0.4	0[c]	0[c]
δ-R,S-λ,δ	0.5	0.8	0.8
δ-R,S-δ,δ	1.4	1.1	1.1

[a] Conformer found by X-ray diffraction analysis. [b] The R,S sequence is the same as the δ,λ sequence; thus, the R disposed THIND ring bears the δ conformation. [c] Energy differences in the second decimal place which are found for these conformers are not considered significant.

Table 13. Relative Energies of the Various Conformers of *R*,*R*-[Ti(C$_3$H$_6$(THIND)$_2$)Cl$_2$]

conformer	ΔE (kcal/mol)	conformer	ΔE (kcal/mol)
boat-R,R-λ,λ	0	chair-R,R-λ,δ	4.2
boat-R,R-δ,λ[a]	1.4	boat-R,R-δ,δ	4.5
boat-R,R-λ,δ	1.6	chair-R,R-δ,λ	4.8
chair-R,R-λ,λ	3.2	chair-R,R-δ,δ	5.4

[a] Conformer found in the X-ray diffraction analysis of the crystal.

Table 14. Relative Energies (in kcal/mol) of the Various Isomers of [Ti(*S*,*S*-chiracene)Cl$_2$]

conformer[a]	ΔE	conformer[a]	ΔE
δ-R,R-δ,λ	0	δ-S,S-λ,δ	3.4
δ-R,R-δ,δ	0.3	δ-S,S-δ,δ	4.7
δ-R,R-λ,λ	1.4	λ-R,R-δ,δ	6.2
δ-R,S-λ,λ	1.4	λ-R,S-δ,δ	10.0
δ-R,S-δ,λ	1.4	λ-R,S-λ,δ	10.2
δ-S,S-λ,λ	1.6	λ-R,S-δ,λ	12.1
δ-R,S-λ,δ	1.6	λ-S,S-λ,δ	14.6
δ-R,S-δ,δ	2.0	λ-S,S-δ,δ	15.1
		λ-S,S-λ,λ	16.5

[a] The sequence R,S-δ,λ, for example, implies that the R bound THIND group has the δ conformation of the cyclohexenyl group, and S applies to λ.

components of these small differences indicates that there is no dominating contributor to the total energy difference between the meso and racemic forms.

The superimposed structures of the three-carbon strap system racemic [Ti(C$_3$H$_6$(THIND)$_2$)Cl$_2$] is shown in Table 10 where it will be noted that one of the tetrahydroindenyl groups is twisted more in the minimized structure than it is in the crystal.[40] The C−C bond length of the three strap carbon atoms is reported to be 1.52 Å in the crystal. The calculation generates "normal" aliphatic C−C bond lengths (1.56 Å), and the origin of the larger twisting in the minimized structure can be traced to this difference in C−C bond lengths. It will be noted that the two tetrahydroindenyl groups are not symmetrically disposed, that the strap is in the boat conformation, and that the cyclohexenyl fragments are in different conformations; the "top" one is λ and the "bottom" cyclohexenyl is δ. Thus we may write the structure shown as boat-R,R-λ,δ. The observed conformation, boat-R,R-λ,δ or boat-S,S-δ,λ, is found not to be the global minimum. The boat-R,R-λ,λ or boat-S,S-δ,δ is the lowest energy conformer. Table 13 lists the relative energies of the various conformations of the racemic [Ti(C$_3$H$_6$(THIND)$_2$)Cl$_2$] complex where in these conformations, whether chair or boat, one of the tetrahydroindenyl groups is disposed closer to one of the chloro groups than is the other tetrahydroindenyl group (see **6**, **7**, and **8**). The conformation of the cyclohexenyl ring that is closer to the chloro group is designated first. Generally the boat conformation is found to be preferred, but the chair forms are close in energy. Consequently, we expect that in solution most of these conformers will be accessible at room temperature. Although all of these conformers do not possess a C_2 axis, ^{1}H NMR spectra of this complex gives a symmetrical spectrum indicating rapid conformational interconversion, probably via many of these low-energy conformers. The meso isomer of [Ti(C$_3$H$_6$(THIND)$_2$)Cl$_2$] is found to have some 16 conformers with an energy span of 9 kcal/mol and it is probable that this isomer is also conformationally mobile.

In order to avoid resolution of the racemic forms of these complexes, a number of attempts at circumventing optical resolution have been reported. Our attempt involved the use of the *S*,*S*-chiracene ligand where the tetrahydroindenyl groups are joined by a chiral 2,3-butane strap.[41] It was asserted that the strap would adopt a preferred chiral conformation where the methyl groups were equatorially (rather than axially) disposed. This preferred conformation of the strap would then induce the tetrahydroindenyl groups to adopt a preferred absolute configuration because one diastereomer would experience fewer steric interactions than the other. It was also concluded that the racemic form would be more stable than the meso. The net conclusion was that *S*,*S*-chiracene would prefer the R,R configuration of the tetrahydroindenyl binding. The present force field allows us to test these assertions.

The calculated and crystal structures of [Ti(*S*,*S*-chiracene)Cl$_2$] are superimposed in Table 10. It will be noted that the methyl groups of the strap are equatorially disposed, and the overall absolute configuration is R,R as predicted. The crystal structure of the complex of the "bottom" cyclohexenyl group is disordered in the sense that this group is undergoing conformational interconversion so that on the average all of the carbon atoms appear to be in the same plane. It is depicted as planar in Table 10. The X-ray and calculated structures match well except that the minimized ligand structure is rotated relative to that found in the crystal which would be C_2 symmetric if the two cyclohexenyl groups bore the same conformation. We find that the minimized structure is δ-R,R-δ,λ which is 0.3 kcal/mol more stable than the perhaps expected symmetrical conformer δ-R,R-δ,δ.

We calculated the energies of the conformers of the (R,R), (S,S), and (R,S) isomers of [Ti(*S*,*S*-chiracene)Cl$_2$]. These are listed in Table 14. We were unable to find the minimized energies of the (λ-R,R-λ,λ), (λ-R,R-λ,δ), and (λ-R,S-λ,λ) because upon minimization these conformations flipped to more stable forms. The relative energies listed in Table 14 support the expectation that the strap of *S*,*S*-chiracene will prefer to adopt the δ conformation, because in this chirality the methyl groups are equatorially disposed in contrast to the opposite λ conformation where the methyl groups are axially oriented. Further, the

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(40) Röll, W.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1987**, *322*, 65.

(41) Rheingold, A. L.; Robinson, N. P.; Whelan, J.; Bosnich, B. *Organometallics* **1992**, *11*, 1869.

prediction is that the R,R form will be preferred with *S*,*S*-chiracene but not overwhelmingly. Thus the δ-S,S-λ,λ is only 1.6 kcal/mol less stable and the meso form, δ-R,S-λ,λ is 1.4 kcal/mol less stable that the δ-R,R-δ,λ isomer. In the thermodynamic sense, these calculations indicate that the chiracene ligand is not strongly diastereoselective.

Conclusions

The present work demonstrates that the force field derived here can generate structures of $[M(Cp')_2Cl_2]$ complexes which are almost identical with those found by X-ray diffraction. Although the parameters for the Cp′ ligands are transferrable from one system to another to a very good approximation, the generally small Cp′ bond length variation found in the crystals are not reproduced, presumably because of their electronic provenance. These variations can cause small deviations of the Cp′ rotations from those that are calculated by the force field. It was shown that crystal packing forces can also affect the Cp′ rotations as well as fixing conformations of straps, rings, and pendant groups. It was shown that for ethylene-1,1′-bis(tetrahydroindenyl) complexes and for analogous systems with trimethylene straps there exist clusters of energetically closely spaced conformations. These conformations probably undergo facile interconversion. Consequently, stereoselective reactions promoted by derivatives of these complexes are likely to be sterically controlled by conformations which relax to accommodate the reacting substrate. Further, using only the structure of the complex found in the crystal is likely to provide a poor representation of the steric effects emanating from the complex. We expect that this work will provide a basis for assessing the steric interactions which contribute to the stereoselective reactions promoted by derivatives of these complexes.

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