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An ab Initio MO and MM Study of Homogeneous Olefin Polymerization with Silylene-Bridged Zirconocene Catalyst and Its Regio- and Stereoselectivity

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Abstract: The olefin polymerization reaction by silylene-bridged zirconocene catalysts has been investigated theoretically. With the ab initio molecular orbital (MO) method the structure and energetics of the reactants, the π-complex, the transition state, and the product for insertion of ethylene into $(SiH_2Cp_2)ZrCH_3^+$ have been determined. The nearly C_s-symmetric transition state has a low activation barrier (about 6.0 kcal/mol from the π-complex). The product shows a strong C^β–H agostic interaction. Based on the above transition state structure, molecular mechanics (MM) calculations have been carried out to investigate the effects of alkyl substituents on olefins and methyl groups and other substituents on the Cp rings as well as the effects of the alkyl group on Zr, a model polymer chain end. The regioselectivity in propylene polymerization, that the primary insertion is preferred to the secondary insertion, is reproduced well by the energy difference at the transition state but not by that of the π-complex. As to the stereoselectivity in isotactic polymerization of propylene by $SiH_2(CpMe_n)_2ZrR^+$, the substituents on the Cp rings have been found to determine the conformation of the polymer chain end, and the fixed polymer chain end conformation in turn determines the stereochemistry of olefin insertion at the transition state. The direct steric effect of the Cp methyl groups on the olefin insertion stereochemistry is negligibly small. The same direct control mechanism is operational also in syndiotactic polymerization of propylene and 4-methyl-1-pentene.

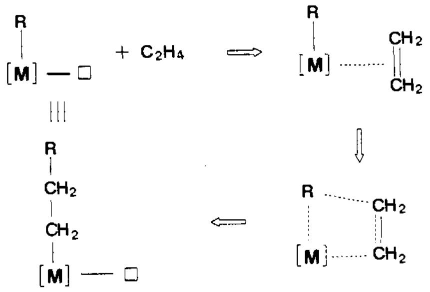
I. Introduction

Traditional catalysts used for Ziegler–Natta olefin polymerization are heterogeneous catalysts: transition metal halides with cocatalysts such as alkylaluminum compounds and electron donors. With the discovery of highly active homogeneous metallocene catalysts with methylaluminoxane by Kaminsky and co-workers,[1] the homogeneous Ziegler–Natta catalyst has become a center of focus of new activities in this field, and many research projects have been carried out for the analysis, development, and identification of active species of these catalysts.[2] To be noted in particular, Marks and co-workers have shown evidence of the direct abstractive role of an organo-Lewis acid in the stoichiometric conversion of a zirconocene dialkyl, Cp_2ZrR_2, to the zirconocene monoalkyl, Cp_2ZrR^+, which has a high activity in homogeneous α-olefin polymerization,[3a] and Jordan et al. have observed that the benzyl species, $Cp_2Zr(CH_2Ph)^+$ can catalyze the polymerization of ethylene.[3b]

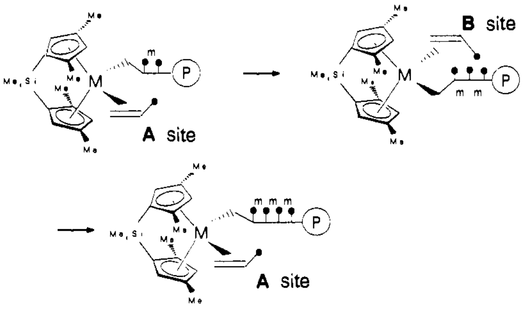
For the generic mechanism of olefin insertion the Cossee mechanism,[4] as illustrated in Scheme I, has been accepted widely as the most plausible. Many studies have been carried out on model reactants, intermediates, and products with molecular orbital methods.[5] Marynick and co-workers have reported using an approximate MO method, PRDDO, as well as a full ab initio molecular orbital method to show that this (eq 1, X = Cp, R = H) is indeed a viable mechanism for homogeneous Ziegler–Natta polymerization.[5j,k] We have studied the model insertion reaction (eq 1, X = Cl, R = H) with the ab initio MO method to determine the optimized structures and the potential energy profile including the correlation effect and have reached the same conclusion.[6]

$$CH_3TiX_2^+ + CH_2{=}CHR \rightarrow CH_3TiX_2(CH_2{=}CHR)^+ \rightarrow (\text{transition state}) \rightarrow C_3H_6RTiX_2^+ \quad (1)$$

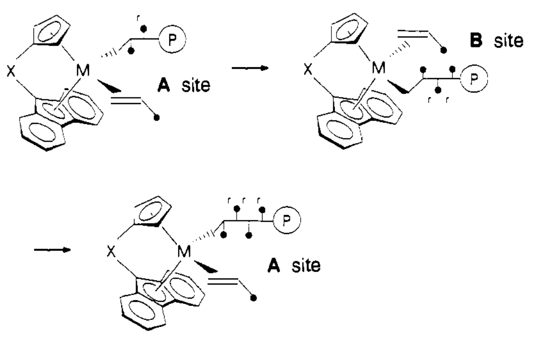
Scheme I. Cossee Mechanism



Scheme II. Isospecific Propagation



Scheme III. Syndiospecific Propagation



The stereoregulation in α-olefin polymerization is one of the most important capabilities of Ziegler–Natta catalysts. Heterogeneous catalysts, $TiCl_3$ + cocatalysts, can produce very highly isotactic polyolefins, whose isotacticity is sufficient for commercial use.[2a-d] On the other hand, for homogeneous catalysts where cyclopentadienyl anions are typically used for ligands, some stereorigid chiral compounds consisting of zirconium or hafnium metallocenes in the presence of methylaluminoxane are good catalysts for isospecific[7-10] or syndiospecific[11] polymerization of 1-alkenes. For example, Ewen has reported that chiral catalysts derived from the racemic enantiomers of ethylene-bridged indenyl

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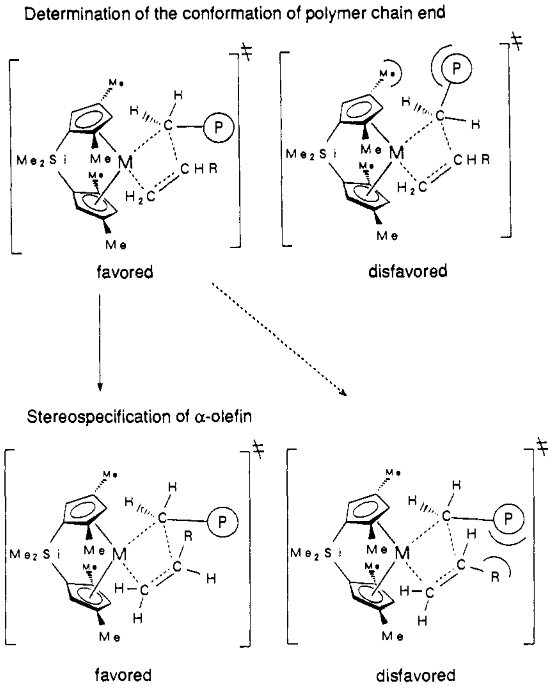
Scheme IV. Model Mechanism of Isospecific Propagation



derivatives are the first metallocene catalysts to form isotactic polypropylene with the conventional structure predicted by an enantiomorphic-site stereochemical control model.[7] Yamazaki and co-workers have found that more highly isotactic polypropylene can be produced with C_2-symmetric silylene-bridged metallocene catalysts.[9] In such isotactic propagation the stereochemistry of monomer insertion can be illustrated by Scheme II. Monomer insertion is to take place on two active sites on the metal center alternately, and the stereochemistry on one site must be the same as that on the other site. Brintzinger and collaborators have suggested that the entering olefin is steered into the correct enantiofacial orientation both by the repulsive interaction with the ring substituent groups and by the preferred trans configuration of the CH_3 group of propylene and the polymer chain end groups in the four-center transition state.[10]

Highly syndiotactic polypropylene has been obtained with the isopropyl(cyclopentadienyl-1-fluorenyl) metallocene by Ewen and co-workers.[11] In syndiotactic polymerization as shown in Scheme III, the stereochemistry of monomer insertion has to change from one site to the other; if the chirality with respect to the local C_2 symmetry is R, when propylene attacks from the A site, the chirality has to be S on the B site, or vice versa. Ewen et al. have proposed that the fluorenyl group directly controls the steric behavior of propylene in syndiotactic propagation.[11] Recently Corradini and co-workers have suggested, however, that the syndiotactic selectivity is "indirectly" controlled by the fluorenyl group.[12] They have carried out a conformational analysis based on nonbonded interactions[12,13] and suggest that the chiral environment of the metal atom forces the growing chain to choose one of two chiral orientations, prior to each addition; this chiral orientation in turn allows the chain to discriminate between the insertion of an *re* and an *si* coordinated monomer as shown in Scheme IV. They have also concluded that the origin of enantioselectivity for the stereorigid models (isospecific, syndiospecific, or hemiisospecific) considered in their work is essentially the same.[12] The model of the catalytic site for the insertion they assumed, however, looks more like an olefin π-complex intermediate than the transition state (vide infra). As mentioned later, we have found with our theoretical calculations that the regio- and stereoselectivity in propylene insertion with metallocene catalysts is determined at the transition state, not at the π-complex. Therefore a more realistic model of the transition state is required for discussion of the small energy difference involved in regio- and stereochemistry in α-olefin polymerization.

The ab initio molecular orbital (MO) method serves this purpose. In our previous study on the propylene insertion reaction (eq 1, X = Cl, R = CH_3), we used the transition state determined for ethylene insertion (R = H) and evaluated and analyzed the activation barrier for propylene insertion. We have found in our energy decomposition analysis that the steric repulsion between the monomer and the methyl group, a model of a polymer chain end, is the most important factor in determining the stereochemistry in propylene insertion. It is not realistic, however, to apply the ab initio MO method to very large catalyst systems. Therefore we will be using an approach which mixes the MO method with the molecular mechanics (MM)[14] method in the present study of the regio- and stereoselectivities. Houk and co-workers have already applied this kind of approach to organic reactions such as intramolecular radical addition[15] and hydrogen abstractions.[16] They first determined the transition state for a

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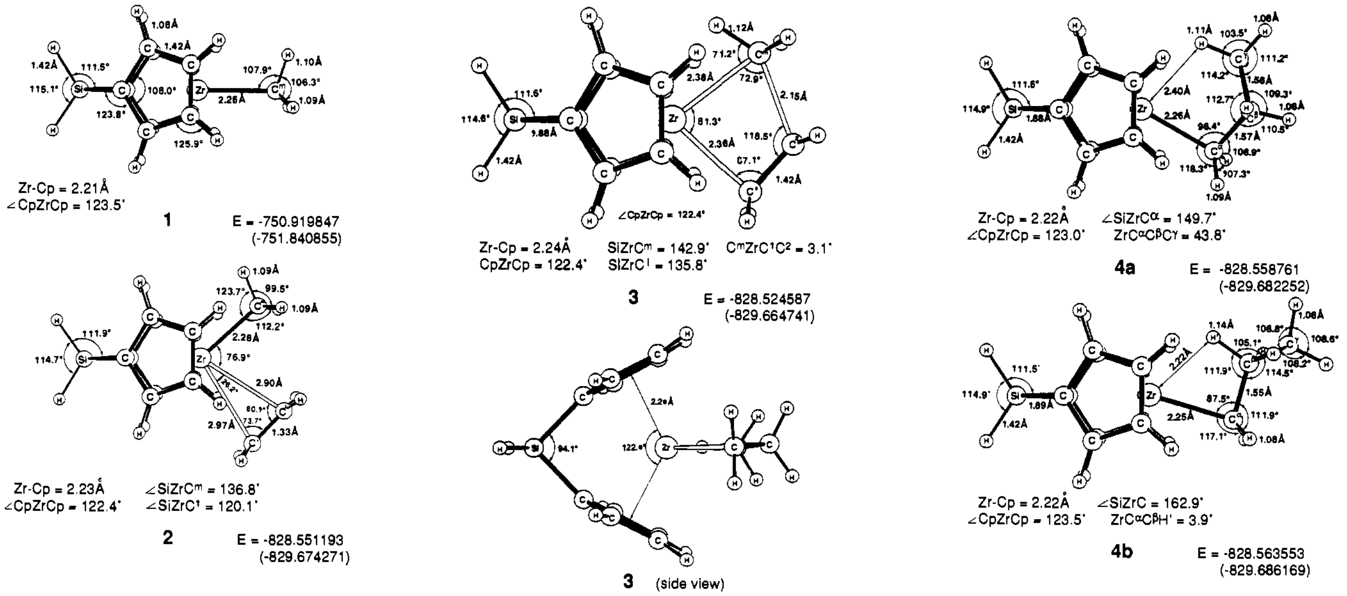

Figure 1. RHF optimized geometries (in Å and deg) of the reactants, **1**, the ethylene π-complex, **2**, the transition state, **3**, and the products, **4a** and **4b**, for ethylene insertion into the Zr–CH$_3$ bond of (SiH$_2$Cp$_2$)ZrCH$_3$$^+$. The total energies *E* at the RHF and the RMP2 level (in parentheses) are also shown.

reference compound with an ab initio method and used this structure and the MM method to further optimize and calculate energies of transition states of compounds of interest. They report that their results agree with the available experimental data, and predictions of relative rate constants have been made for related reactions. A mixed MO–MM approach may be useful for the analysis of stereoselectivity caused by steric repulsion. At least it should be much better than any analysis made in the past without knowledge of the transition state for the stereoselectivity in Ziegler–Natta polymerization. The purpose of the present study is 2-fold. First, with the ab initio MO method we will determine the structures and energies of the ethylene insertion reaction, eq 2, into (SiH$_2$Cp)$_2$ZrCH$_3$$^+$, a model of Yamazaki's catalyst,[9] and we will compare the results with those for CH$_3$TiCl$_2$$^+$ and CH$_3$ZrCl$_2$$^+$.[6,17] Then, starting with these geometries of the

$$\underset{\mathbf{1}}{(\mathrm{SiH_2Cp_2})\mathrm{ZrCH_3}^+} + \mathrm{C_2H_4} \rightarrow \underset{\mathbf{2}}{(\mathrm{SiH_2Cp_2})\mathrm{ZrCH_3(C_2H_4)}^+} \rightarrow \underset{\mathbf{3}}{(\text{transition state})} \rightarrow \underset{\mathbf{4}}{(\mathrm{SiH_2Cp_2})\mathrm{ZrC_3H_7}^+} \quad (2)$$

transition state and intermediate, we will examine with the MM method the effect of the CH$_3$ group in olefins and that of CH$_3$ substituents on the Cp rings as well as the effect of alkyl group assumed as a polymer chain end and elucidate the detailed mechanism of regio- and stereoselectivity in polymerization.

II. Computational Method

We used for geometry optimization the ab initio restricted Hartree–Fock (RHF) energy gradient technique.[18] A single basis set was adopted throughout the paper. For Zr, the effective core potentials were used for the core orbitals, 1s, 2s, 3s, 2p, 3p, and 3d,[19] with the valence basis functions of split valence contraction (311/311/31).[19] For Si, C, and H atoms of the bridged cyclopentadienyl ligands which are spectators of reaction, we used the STO-3G basis functions,[20,21] and for other C and H atoms the 3-21G basis functions.[22]

As is well-known, minimal basis functions such as STO-3G give a large basis set superposition error (BSSE), which results in overestimation of dissociation energy. Accordingly, if the SiH$_2$Cp$_2$ fragment dissociates during a reaction, the STO-3G basis functions cannot be used. However, the SiH$_2$Cp$_2$ fragment is a spectator ligand and does not directly participate in the present reaction. For such spectator ligands we have been using the minimal basis functions to obtain reasonable results.[23]

During all optimizations with the MO method, each Zr–Cp moiety was assumed to maintain local C_{5v} symmetry and the (SiH$_2$Cp$_2$)Zr fragment local C_s symmetry. For an estimation of correlation effect and better energetics, the restricted second-order Møller–Plesset perturbation (RMP2) calculations[24] were carried out, involving all double excitations of the valence electrons including Zr 4s and 4p electrons.

In molecular mechanics (MM) calculations, we used the MM2 program.[14] The parameters for the alkyl carbons on the zirconium atom were parameters of the sp^3 carbon, and the parameters for the ethylene carbons were those of the sp^2 carbon. Zirconium was treated as a dummy atom, and parameters for the others were standard values. In the MM calculation, we optimized only the coordinates of the substituents, i.e., the methyl groups on the cyclopentadienyl ligands and propylene and the alkyl group on the methyl ligand as a polymer chain end. In the last case, there are three hydrogens on the methyl ligand and thus three conformations are possible upon substitution. Consequently, we carried out optimization for each conformation and compared the resultant energy among them to find the most stable conformation.

III. Results and Discussions

III-1. Ab Initio Calculation for Insertion of Ethylene into (SiH$_2$Cp$_2$)ZrCH$_3$$^+$.

In this section, we report the results of ab initio calculations for the ethylene insertion reaction in eq 2.

A. Reactant: (SiH$_2$Cp$_2$)ZrCH$_3$$^+$. The optimized geometry of reactant **1**, shown in Figure 1, was obtained under the C_s symmetry constraint. A small distortion on **1** destroying the C_s symmetry gave a force which serves to restore the C_s symmetry. Therefore the C_s optimized structure can be considered to be the equilibrium

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structure. The optimized structure may be compared with the recently determined experimental X-ray structure of $[1,2\text{-}Me_2Cp]_2ZrCH_3^{+}\cdot CH_3B(C_6F_5)_3^{-}$, **5**.[3a] The zirconium–methyl carbon C^m distance of 2.26 Å agrees well with the experimental value of 2.25 Å. The Zr–C(Cp) distances, which are all the same due to the local C_{5v} symmetry constraint, of 2.53 Å and the ring centroid–Zr–ring centroid angle of 123.5° are in reasonable agreement with the experimental values of 2.50 Å (average) and 131.3°. A remarkable difference is seen in the direction of the methyl group; while the experiment for **5** gives a "bent-sandwich" cation fragment, the calculated structure has a $SiZrC^m$ angle of 180°, that is to say, the centroids of the cyclopentadienyl rings, the zirconium atom, and C^m are all in the same plane. Of course, our calculation is for a free cation, while the experiment for **5** shows that the counterion $CH_3B(C_6F_5)_3^{-}$ is nearby. In order to assess the flexibility of the cation for an in-plane bend of $Zr–CH_3$, we set the $SiZrC^m$ angle to 135° to find its energy to be only less than 2 kcal/mol higher than the optimized structure, **1**, at the RHF level. This indicates that this bending is rather soft; $Zr–CH_3$ can easily be moved away from the equilibrium position, for instance, by the influence of a counterion, an observation consistent with the experiment. An additional ligand can also bend the $Zr–CH_3$ axis, as will be shown below for the ethylene complex of **1**. Another point to make in the calculated structure of **1** is that the Zr–C–H angles are larger than 107°, indicating no sign of a strong α-agostic interaction, a similar conclusion to that for $Cl_2ZrCH_3^{+}$.[17]

B. π-Complex: $(SiH_2Cp_2)ZrCH_3(C_2H_4)^{+}$. The geometry of the intermediate, ethylene π-complex **2**, optimized under the C_s symmetry constraint, is also shown in Figure 1. Though the more stable equilibrium structure can be found with C_1 symmetry with an energy less than 0.5 kcal/mol lower than the C_s structure, we will be using the C_s structure for the convenience of analysis. Furthermore, the C_1 structure would be more unstable for propylene and other olefin complexes due to the steric repulsion between the olefin and the Cp rings. In this C_s complex, the $Zr–Cp_2$ moiety has not changed from **1** by ethylene coordination. The methyl group has tilted by 43.2° to the opposite side to allow easy ethylene coordination. As discussed above, this tilt costs less than 2 kcal/mol to gain a substantial stabilization by olefin coordination. The $C^m–Zr–X$ angle, where X is the midpoint between the ethylene $C^1–C^2$ bond, of 90.0° may be compared, though indirectly, with the experimental $C^m–Zr–C^1$ angle of 92.0° in **5**, where C^1 is the CH_3 carbon in the counterion $CH_3B(C_6F_5)_3^{-}$.[3a] The $Zr–C^m$ distance of 2.28 Å is longer than that of 2.26 Å in **1** by 0.02 Å, probably due to the electronic and steric effect of the ethylene ligand. The conformation in which CH_3 is rotated by 180° is higher in energy than **2** by 2.4 kcal/mol and presumably is not an equilibrium geometry. The distances between Zr and olefin carbon atoms in **2**, 2.90 and 2.97 Å, can be compared with the corresponding distances, 2.54 and 3.05 Å in $Cl_2ZrCH_3(C_2H_4)^{+}$, **7**.[17] The ethylene coordination in **2** is more symmetric and weaker than in **7**. In $Cl_2ZrCH_3(C_2H_4)^{+}$ as well as in $Cl_2TiCH_3(C_2H_4)^{+}$,[6] where the central metal is more positively charged as compared with **2**, the olefin is more strongly polarized and is stabilized more strongly by the olefin-to-metal donative interaction as well as by the polarization interaction. This makes the Zr–olefin carbon distances in chloride shorter and more asymmetric than in **2**. In **2**, the steric repulsion between the C^2H_2 hydrogens and C^mH_3 hydrogens as well as that between the C^1H_2 hydrogens and Cp hydrogens might also contribute to the weaker and more symmetric Zr–olefin bonding.

As shown in the energy diagram in Figure 2, the binding energies of ethylene are 19.1 and 33.4 kcal/mol at the RHF and the RMP2 levels, respectively, which are smaller than 41.6 and 42.6 kcal/mol in the chloride **7**, as expected from the structural features.

C. Transition State. The optimized geometry of the transition state, **3**, determined under no overall symmetry constraint is also shown in Figure 1. The C–H bonds of the methyl group are almost eclipsed to the C–H bonds of ethylene in **3**. The four-center transition structure is nearly coplanar, with a $C^m–Zr–C^1–C^2$ torsional angle of only 3.1°, though a larger torsional angle would decrease the steric repulsion due to eclipsing between the methyl group and ethylene. This angle was increased by 0.4°, when chloride ligands were used instead of Cp groups,[17] suggesting that the planarity of the transition state is independent of the kind of ligands. At the transition state for $Cl_2Ti(CH_3)(C_2H_4)^{+}$, we found a larger torsional angle of 10.7°. Presumably, because of more diffuse d orbitals of Zr, the $Zr–C^{\beta}$ interaction is stronger. Compared with the ethylene complex, **2**, the $Zr–C^m$ bond and the $C^1–C^2$ bond of **3** are stretched by 0.1 and 0.09 Å, respectively, as expected. One of the $C^m–H$ bonds is stretched by 0.03 Å, and such a long C–H bond length indicates that there is an α C–H agostic interaction.[10,25]

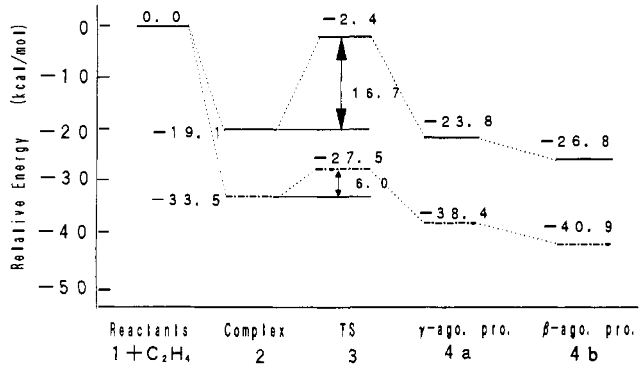

Figure 2. Potential energy profiles of ethylene insertion into the $Zr–CH_3$ bond of $(SiH_2Cp_2)ZrCH_3^{+}$, **1**, at the RHF(—) and the RMP2 (---) level for the RHF optimized geometries.

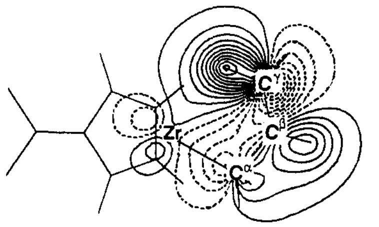

Figure 3. A contour map of the occupied canonical MO 61 of **4a** in the plane $Zr–C^{\alpha}–C^{\beta}–C^{\gamma}$. The contours are for ±0.01, ±0.03, ±0.05, ±0.07, ±0.09, ±0.13, and ±0.17 au, and solid and dotted lines denote positive and negative values, respectively.

Calculated from the energy diagram in Figure 2, the activation energies from the ethylene complex **3** are 16.7 and 6.0 kcal/mol at the RHF and the RMP2 levels, respectively. These calculated barriers with Cp ligands are similar to those with chloride ligands.[17] The more reliable RMP2 barrier is in good agreement with the experimental estimate of the barrier for the propagation step of polymerization, 7.4 kcal/mol.[26]

D. Product: $(SiH_2Cp_2)ZrC_3H_7^{+}$. Our previous results for a propyltitanium complex indicate that structures with an agostic interaction are more stable than stretched structures without an agostic interaction.[6] In this study, we optimized the geometry parameters under no symmetry constraint and confirmed that there is no stable structure without an agostic interaction. For instance, the all-staggered structure is 3.4 kcal/mol higher than the structure **4b** and is a transition state connecting **4b** and its enantiomer. As shown in Figure 1, two equilibrium structures, **4a** with a γ C–H agostic interaction and **4b** with a β C–H agostic interaction, were obtained. All single bonds of the propyl group in **4a** are more or less staggered, whereas **4b** has some eclipsed C–H bonds. One of the $C^{\gamma}–H$ bonds in **4a** is stretched by 0.03 Å and one in **4b** by 0.06 Å, compared with the normal C–H bond, indicating that the β C–H agostic interaction is stronger. The contour map of one of the occupied molecular orbitals in **4a**, given in Figure 3, shows that donative interaction to a Zr d orbital takes place from the

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(25) Piers, W. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 9406.

(26) Chien, J. C. W.; Razavi, A. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 2369.

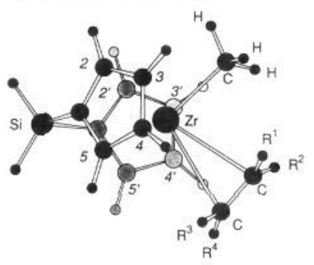
C^{γ}–H σ bond. The Zr–C^{α}–C^{β} angle is larger than 90° in **4a** but smaller in **4b**. In contrast, both angles are smaller than 90° with chloride ligands. The C^{β}–C^{γ} distance of 1.61 Å in the chloride complex corresponding to **4a** is 0.05 Å longer than that in **4a**. This long distance as well as the small Zr–C^{α}–C^{β} angle suggests that the C^{β}–C^{γ} agostic interaction takes place in the chloride complex; the central metal atom is more positively charged and thus the donative interaction from the C^{β}–C^{γ} bond to a Zr d orbital can take place. The larger Zr–C^{α}–C^{β} angle in **4a**, compared to that in the chloride complex, is presumably in part due to the absence of the β C–C agostic interaction mentioned above and in part due to the steric repulsion between C^{β}–H and C–H of Cp; the shortest distance between a C^{β}–H hydrogen atom and one of the Cp hydrogen atoms is 2.8 Å. A smaller Zr–C^{α}–C^{β} angle would decrease the distance and increase the steric repulsion substantially.

As shown in the energy diagram in Figure 2, **4b** with the β C–H agostic interaction is more stable than **4a** with the γ agostic interaction by 3.0 and 2.5 kcal/mol at the RHF and the RMP2 levels, respectively. This order is opposite to what was found with chloride ligands;[17] the structure with the β C–H agostic interaction was less stable than the structure with the γ C–H agostic interaction by 3.2 and 6.4 kcal/mol at the RHF and RMP2 levels, respectively. The fact that the Zr···H distances in γ agostic species are similar, 2.40 Å in **4a** and 2.41 Å in the corresponding chloride, suggests that their agostic interaction energies are similar. Likewise, the fact that the Zr···H distances in β agostic species are similar, 2.22 Å in **4b** and 2.20 Å in the corresponding chloride, suggests that their agostic interaction energies are similar. Therefore, the difference in the order of the stability between Cp compounds and chlorides may be attributed to the absence of β C–C agostic interaction in **4a** and a larger steric repulsion in **4a** than in **4b**. An examination of the optimized geometries reveals that **4a** has six distances which are smaller than 3.0 Å between the Cp hydrogen atoms and the propyl hydrogen atoms, while **4b** has only three. The larger stability of the alkyl complex with the β C–H agostic interaction may be related to the experimental suggestion that the β-H elimination can take place in α-olefin polymerization using a metallocene catalyst under the low concentration of aluminoxane.[27]

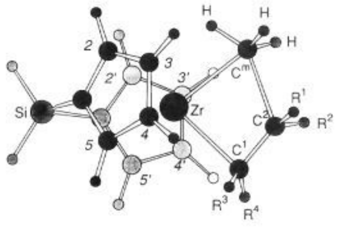
One notices that the distance between the Cp rings and the zirconium atom and the Cp–Zr–Cp angle, however, are nearly unchanged from the reactant through the π-complex and the transition state to the product. Cp rings tend to change the Cp–M–Cp angle by several degrees upon moving from the reactant to the products, as seen in hydrozirconation,[28] the present tightness of these Cp ligands is presumably caused by the bridged structure with an SiR_2 group.

III-2. Molecular Mechanics Calculation of Regio- and Stereoselectivity. A. Regioselectivity in Propylene Polymerization. As the first step in studying the role of methyl substituents on Cp rings in the regioselectivity of propylene polymerization, we replaced, in the ethylene complex **2** and in the transition state **3**, one of the C_2H_4 hydrogen atoms by a methyl group, and zero, two (at 3 and 4′), or four (at 3, 5, 2′ and 4′) hydrogen atoms of the Cp rings by methyl groups.[29] 2P*n* and 3P*n* denote the propylene π complex and the transition state, respectively, having a total of *n* methyl groups on the Cp rings. The positions of methyl groups on the Cp rings and the position of methyl group of propylene are shown in Scheme V. The Cp methyl positions are taken from those catalysts which experimentally give highly isotactic polypropylene.[9] With MM2 calculations we optimized all the geometrical parameters (including methyl–C distance) of the methyl groups on the Cp rings as well as those of methyl group of propylene. The alkyl group bonded to the Zr atom in 2P*n* and 3P*n* is CH_3. Additionally, in order to estimate the effect of the chain end group on the steric energy, one of the hydrogen atoms of the CH_3 group bonded to Zr was replaced by an alkyl group whose geometrical parameters were also optimized with MM2 calculations.

Scheme V. Models for MM Calculation



2Pn
(Propylene Complex)



3Pn
(Transition State)

Table I. MM Steric Energies[a] of π-Complexes and Transition States for Propylene Insertion into the Zr–R′ Bond of $[SiH_2(CpMe_n)_2]ZrR^+$, Where R′ = Me, Relative to Primary Insertion with R^1 = Me

	primary		secondary	
R′ = Me	R^1 = Me	R^2 = Me	R^3 = Me	R^4 = Me
π-complex				
2P0	0.0	0.0	−1.2	−1.2
2P2 (3,4′-Me_2)	0.0	1.1	−1.3	1.8
2P4 (3,5,2′,4′-Me_4)	0.0	1.2	2.4	1.7
transition state				
3P0	0.0	0.1	3.4	3.0
3P2 (3,4′-Me_2)	0.0	0.9	2.6	11.4
3P4 (3,5,2′,4′-Me_4)	0.0	0.9	4.2	11.3

[a] In kilocalories/mole.

The relative energies of propylene complexes and transition states, where the chain end is a methyl group, are summarized in Table I. Because the transition state for ethylene insertion, **3**, nearly maintains the C_s symmetry, the two transition states for primary insertion of propylene, 3P0 with R^1 = Me and that with R^2 = Me, have nearly the same geometry, as is also true for secondary insertion, R^3 = Me and R^4 = Me. The primary insertion, represented by the lower energy R^1 = Me transition state, is more favorable by 3.0 kcal/mol than the secondary insertion, represented by R^4 = Me. This is in agreement with the experimental facts that primary insertion is dominant in the system modeled by the present calculation.[2] An energy decomposition analysis (EDA) for the transition state for propylene insertion into the Ti–CH_3 bond in $CH_3TiCl_2^+$ has shown that the preference of the primary insertion over the secondary insertion is determined by both larger electrostatic stabilization and smaller exchange repulsion.[6] The present MM calculation takes both interactions into account empirically. The instability in the secondary transition states comes from a steric repulsion due to a close contact made between a methyl hydrogen and a Cp hydrogen atom, 2.00 Å between the 4-hydrogen and R^3 or 2.01 Å between the 4′-hydrogen and R^4. No such contact exists for primary insertion.

An introduction of 3,4′-Me_2 makes the 4′-R^4 contact more serious, putting the R^4 = Me transition state much higher in energy, as seen for 3P2 in Table I. However, the R^3 = Me

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[27] Mise, T.; Kagayama, A.; Miya, S.; Yamazaki, H. *Chem. Lett.* **1991**, 1525.

[28] Endo, J.; Koga, N.; Morokuma, K. To be submitted.

[29] Since the transition state **3** is slightly out of the C_s symmetry, the alternative positions of Cp methyl groups, 4,3′ and 2,4,3′,5′, have to be taken into account as well. However, the steric energies of these species are always higher by several kcal/mol than those in the text and will be omitted from the discussion without losing the generality of our results and discussions.

Table II. MM Steric Energies[a] of the Transition State for Propylene Insertion into the Zr–R′ Bond of $[SiH_2(CpMe_n)_2]ZrR'^+$, Where R′ = Ethyl and 2-Methylbutyl, Relative to the Primary Insertion with R^1 = Me

	primary		secondary	
	R^1 = Me	R^2 = Me	R^3 = Me	R^4 = Me
R′ = Et				
3PE0	0.0	3.1	5.1	4.5
3PE2 (3,4′-Me_2)	0.0	4.0	4.8	16.3
3PE4 (3,5,2′,4′-Me_4)	0.0	3.9	9.6	19.6
R′ = 2-methylbutyl				
3PM0	0.0	5.5	4.3	3.1
3PM2 (3,4′-Me_2)	0.0	7.2	3.2	21.0
3PM4 (3,5,2′,4′-Me_4)	0.0	9.4	9.0	25.2

[a] In kilocalories/mole.

secondary transition state is unaffected by these substituents, and the difference in the transition state energies between the primary and secondary insertions remains small, 2.6 kcal/mol. Further introduction of 2′,5-Me_2 increases the primary–secondary difference of the transition state energy to 4.2 kcal/mol. Based on their experimental facts Brintzinger and co-workers have proposed that 2,5′-methyl substituents suppress 1–3 misinsertion, i.e., secondary insertion, of the α-olefin into the methyl–polymer bond.[10] Our theoretical results above provide a support to this proposal.

As for the stability of propylene π-complex, 2P0, Table I shows the primary coordination is slightly less favored than the secondary coordination, the trend opposite to that of the transition state. We emphasize here that it is therefore essential to use a correct transition state geometry, not a guess[12,13] which looks like a π-complex, for reliable discussion of regio- and stereoselectivity in propylene insertion.

In order to assess the effect of a polymer chain end on the regioselectivity, we have replaced the methyl group on Zr by an ethyl and a 2-methylbutyl group, as shown in Table II. Though the larger polymer chain end seems to enhance the preference of primary insertion over secondary insertion, especially when Cp rings have methyl substituents, the overall picture of regioselectivity remains unchanged.

B. Isotacticity in Propylene Polymerization. Now we turn our attention to stereoselectivity in propylene polymerization. In the present model, the stereoregularity of polymerization is to be controlled by the energy difference between two transition states for primary insertion, one with R^1 = Me and other with R^2 = Me. Table I shows that when a methyl group is used as the polymer chain end and the Cp groups have no substituent, the steric energy of 3P0 (R^1 = Me) is almost the same as that of 3P0 (R^2 = Me), because the transition state **3** nearly retains a C_s symmetry. Even when two or four methyl groups are introduced on Cp rings, the transition state energy difference between R^1 = Me and R^2 = Me remains small (0.9 kcal/mol). This small energy difference can be regarded as the *direct* steric energy due to the methyl substituents that control stereochemistry, in contrast to the *indirect* steric control energy to be discussed later, but it does not appear to be large enough for good stereochemical control.

In order to obtain a reasonable estimate of the steric energy between the polymer chain end and the olefin at the transition state, we replaced the methyl group on Zr by an ethyl and a 2-methylbutyl group as models of polymer chain ends. The MM2 optimized energies and C^1–Zr–C^m–C^n torsional angles φ are shown in Tables II and III, respectively. The relative energetics for R′ = Et and R′ = 2-methylbutyl are similar, with somewhat larger differences in the latter. In 3PE0, without methyl groups on Cp rings, the transition state with R^1 = Me is lower in energy than that with R^2 = Me by 3.1 kcal/mol (5.5 kcal/mol for 3PM0).[30] This is due to the direct steric interaction between the polymer chain end and the olefin. However, the catalyst $(SiH_2Cp_2)ZrR'^+$ without methyl groups on Cp rings is not chiral, and therefore this difference cannot cause stereoregularity.

Table III. MM Optimized Torsional Angles φ[a] of C^1–Zr–C^m–C^n of the Transition State for Propylene Insertion into the Zr–R′ Bond of $[SiH_2(CpMe_n)_2]ZrR'^+$

	primary		secondary	
	R^1 = Me	R^2 = Me	R^3 = Me	R^4 = Me
R′ = Et				
3PE0	93.1	103.7	92.9	92.9
3PE2 (3,4′-Me_2)	93.1	102.8	92.9	92.9
3PE4 (3,5,2′,4′-Me_4)	93.1	102.8	92.9	92.9
R′ = 2-methylbutyl				
3PM0	95.8	105.3	95.4	95.4
3PM2 (3,4′-Me_2)	95.8	105.2	95.4	95.4
3PM4 (3,5,2′,4′-Me_4)	95.3	114.2	94.9	94.8

[a] In degrees.

Table IV. Relative MM Steric Energies[a] and Torsional Angles φ[b] for Three Ethyl Conformations at the Transition State for Ethylene Insertion into the Zr–R′ Bond of $[SiH_2(CpMe_n)_2]ZrR'^+$

R′ = Et			
3PE0	0.0 (92.8°)	0.3 (−94.0°)	11.7 (−175.6°)
3PE2 (3,4′-Me_2)	0.0 (92.8°)	6.1 (−91.2°)	12.3 (−178.0°)
3PE4 (3,5,2′,4′-Me_4)	0.0 (92.9°)	6.2 (−91.2°)	14.3 (−176.7°)

[a] In kilocalories/mole. [b] In degrees, in parentheses. The torsional angle C^1–Zr–C^m–C^n, where C^n is the terminal C of R′ = Et and others are shown in 3P*n* of Scheme V.

When 3,4′-Me_2 or 3,5,2′,4′-Me_4 are introduced onto Cp rings, the catalyst becomes chiral and can actually cause stereoregularity. The energy difference between R^1 = Me and R^2 = Me in Table II, 3.9–9.4 kcal/mol, is the difference in the activation energy between isotactic chiral growth and atactic growth. One can see that this difference does not change by going from 3,4′-Me_2 to 3,5,2′,4′-Me_4; the effect of 2′,5-methyl groups is very small. The difference increases substantially, however, when the chain end becomes larger (from R′ = Et to R′ = 2-methylbutyl), indicating that the steric interaction between the chain end and the olefin becomes larger as the chain grows. In order to assess the direct steric interaction between the methyl groups on Cp rings with the polymer chain end at the transition state, we compared the steric energy for ethylene insertion with R′ = Et in Table IV. It clearly shows that methyl groups on the Cp rings determine the conformation of the polymer chain end by the steric energy difference of several (~6) kcal/mol. The results in Table II have already indicated that this fixed conformation of the polymer chain end favors one transition state (R^1 = Me) over the other (R^2 = Me) by several (7–9) kcal/mol.

The conclusion of the present section is that, in the isotactic polymerization by $SiH_2(CpMe_n)_2ZrR^+$, *the substituents on the Cp rings determine the conformation of the polymer chain end, and the fixed polymer chain end conformation in turn determines the stereochemistry of olefin insertion at the transition state* (*indirect steric control*). The direct steric effect of the Cp methyl groups on the stereochemistry of olefin insertion is very small, and is not enough to control the stereochemistry. The model of isotactic polymerization we arrive at is the same as that shown in Scheme IV recently proposed by Corradini et al., based on a π-complex like model.[12,13] We emphasize, however, the importance of using a realistic transition state model, which we have obtained by an ab initio MO calculation. The steric energy depends very critically on the structure of the transition state, and its behavior is quite different from that of the propylene π-complex, as we have shown for regioselectivity in the early part of this section.

In order to further ascertain the reliability of our conclusions, we have calculated energies of some π-complexes and transition states, 2P0, 2P2, 3P2, and 3PE2, with the ab initio MO method using the geometries obtained by MM optimization. As shown in Table V, all the relative energy profiles are in semiquantitative agreement with those obtained by the MM steric energy calculations in Table I and II. This agreement suggests that the energy differences between various transition states of the present system

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[30] Actually there is another set of conformations with φ values of −94° to −103° for every R^i. However, its energy is higher by several kcal/mol and need not be considered explicitly.

Table V. Energies[a] by MO Calculation of the π-Complex and Transition States for Propylene Insertion into the Zr–R′ Bond of $[SiH_2(CpMe_n)_2]ZrR'^+$, Relative to Primary Insertion with R^1 = Me[b]

	primary		secondary	
	R^1 = Me	R^2 = Me	R^3 = Me	R^4 = Me
		R′ = Me		
π complex				
2P0	0.0	0.0	–0.3	–0.3
2P2 (3,4′-Me_2)	0.0	1.8	–0.5	6.3
transition state				
3P2 (3,4′-Me_2)	0.0	–0.5	5.8	14.9
		R′ = Et		
transition state				
3PE2 (3,4′-Me_2)	0.0	7.6	8.9	21.5

[a] In kilocalories/mole. [b] At the MM optimized geometries.

are determined mainly by the steric effect and also demonstrates that the assumptions in the present MM calculations are reasonable.

C. Syndiotacticity in Propylene and 4-Methyl-1-pentene Polymerization. As discussed in the Introduction, in syndiotactic polymerization, monomer insertion takes place on two active sites on the metal center alternately and the stereochemistry of insertion has to change from one site to the other.[31] In order to achieve this alternation of stereochemistry in the present metallocene catalysts, one has to make the steric environment of two Cp rings quite different from each other.

For this purpose we used two model catalysts having Cp on one side of SiH_2 and a larger ligand L on the other side. They are $[SiH_2(C_5Me_4)Cp]ZrR'^+$ and $[SiH_2(FluCp)]ZrR'^+$, where Flu = fluorenyl group. We calculated the MM steric energies at the transition states of propylene or 4-methyl-1-pentene insertion, using the methyl, ethyl, or 2-methylbutyl group as the polymer chain end, starting with the ab initio transition state **3** as in the preceding subsections. In Table VI, we summarize the results of MM calculations.

At first we discuss propylene polymerization with L = C_5Me_4. As discussed for isotactic polymerization, the energy difference between R^1 = Me and R^2 = Me for the chain end group R′ = Me represents the direct stereocontrol of propylene conformation by the ligand. For the bulky L = C_5Me_4, this is quite large (4.8 kcal/mol) and is larger than for L = fluorenyl. When R′ is replaced by an ethyl group, the bulky ligand determines the conformation of the ethyl group. In the optimized conformation, the distance between the terminal CH_3 of the ethyl group and the propylene CH_3 becomes shortest and the steric repulsion is increased by about 3.0 kcal/mol for R^1 = Me in comparison with other R^i = Me. Therefore, the steric energy difference between the primary and the secondary insertion becomes very small (0.1 kcal/mol), so does the energy difference between R^1 = Me and R^2 = Me that controls the stereoregularity (1.8 kcal/mol). When R′ = 2-methylbutyl is used, further destabilization of R^1 = Me takes place and, as the results indicate, the secondary insertion becomes more favorable by 2.1 kcal/mol than the primary insertion.[32] The energy difference between R^1 = Me and R^2 = Me is now only 1.3 kcal/mol, not sufficient for good stereoselectivity. Therefore, high regio- or stereoselectivity cannot be expected with this catalyst, $SiH_2(C_5Me_4)CpZrR'^+$.

Now we turn our attention to propylene polymerization with L = fluorenyl. One finds in Table VI that the direct steric control energy, the energy difference between R^1 = Me and R^2 = Me with R′ = Me, is rather small (1.2 kcal/mol). The stereocontrol energy is increased to 1.8 kcal/mol for R′ = Et and to 4.2 kcal/mol for R′ = 2-methylbutyl. The secondary insertion is less favorable than the primary insertion even with R′ = 2-methylbutyl. These results indicate that the indirect control mechanism by the bulky ligand through the conformation of polymer chain end, which we proposed for isotactic polymerization, is in operation also in syndiotactic polymerization.

Table VI. MM Steric Energies[a] of the Transition State for Propylene and 4-Methyl-1-pentene Insertion into the Zr–R′ Bond of $[SiH_2(CpL)]ZrR'^+$, R′ = Me, Et, and 2-Methylbutyl

	primary		secondary	
	R^1 = Me	R^2 = Me	R^3 = Me	R^4 = Me
R′ = Me				
L = C_5 (2′,3′,4′,5′-Me_4)	0.0	4.8	3.0	16.1
L = fluorenyl[b]	0.0	1.2	3.0	22.1
R′ = Et				
L = C_5 (2′,3′,4′,5′-Me_4)	0.0	1.8	0.1	13.2
L = fluorenyl[b]	1.8	0.0	1.9	21.1
R′ = 2-methylbutyl				
L = C_5 (2′,3′,4′,5′-Me_4)	1.3	0.0	−2.1	16.8
L = fluorenyl[b]	4.2	0.0	1.6	11.1
	primary		secondary	
	R^1 = *i*-Bu	R^2 = *i*-Bu	R^3 = *i*-Bu	R^4 = *i*-Bu
R′ = 2-methylbutyl				
L = C_5 (2′,3′,4′,5′-Me_4)	4.8	0.0	6.1	24.8
L = fluorenyl[b]	7.5	0.0	7.4	33.6

[a] In kilocalories/mole. [b] This fluorenyl group is used instead of the lower Cp ring of the transition state model in Scheme V.

In order to make some useful predictions, we have also studied the 4-methyl-1-pentene syndiotactic polymerization, as shown in the bottom of Table VI. Here even with L = $C_5(Me)_4$ as well as with L = fluorenyl, the primary insertion is more favorable than the secondary insertion, mainly due to the steric repulsion between the unsubstituted Cp ligand and the *i*-Bu group of 4-methyl-1-pentene. The steric energy differences between R^1 = *i*-Bu and R^2 = *i*-Bu are 4.8 kcal/mol (L = $C_5(Me)_4$) and 7.5 kcal/mol (L = fluorenyl). Based on these data, we propose that the $SiR_2(FluCp)ZrR'^+$ may be a good catalyst for the synthesis of highly syndiotactic poly(4-methyl-1-pentene). In this connection, it has been reported experimentally that the syndiotactic poly(4-methyl-1-pentene) could be obtained with the $Me_2C(FluCp)ZrCl_2$/MAO catalyst.[33]

IV. Concluding Remarks

We have studied with the ab initio MO method the optimized structures and energy profiles of ethylene insertion into the Zr–CH_3 bond of $(SiH_2Cp_2)ZrCH_3^+$. The binding energy of the ethylene π-complex, 33.4 kcal/mol at the RMP2 level, is smaller than that for $Cl_2ZrCH_3^+ + C_2H_4$. The transition state is four-centered and retains a near C_s symmetry, with a CZrCC dihedral angle of 3.1°. The activation energy from the ethylene π-complex is 6.0 kcal/mol at the RMP2 level, indicating that ethylene insertion can take place easily. In the product, there is a strong C^β–H agostic interaction to the vacant site of Zr.

We have also studied the origin of the regio- and stereoselectivity in isospecific propylene polymerization for models of C_2-symmetric $[SiH_2(CpMe_n)_2]ZrCl_2$ (n = 0, 1, or 2)/methylaluminoxane catalyst with molecular mechanics calculations based on the transition state determined above with the ab initio MO method for ethylene polymerization for the unsubstituted catalyst. The regioselectivity, the preference of primary insertion over secondary insertion, has been found in good agreement with the order of steric energy at the transition state. If π-complexes are used for comparison, however, one finds the trend opposite to that at the transition state. This indicates that adaptation of a realistic transition state model is essential for reliable elucidation of insertion mechanism. Introduction of 2′,5-Me_2 increases the primary–secondary activation

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[31] Ewen, J. A.; Elder, M. J.; Jones, R. L.; Cheng, H. N. Syndiospecific Propylene Polymerizations with iPr[CpFlu]$ZrCl_2$. In *Catalytic Olefin Polymerization*; Keii, T., Soga, K., Eds.; Kodansha-Elsevier: Tokyo, 1990.

[32] The electrostatic energy in favor of the primary insertion as discussed before will reduce this difference.

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energy difference, which gives support to experimental observation and proposal that 2,5'-methyl substituents suppress 1-3 misinsertion.[10]

As to isotactic polymerization, methyl groups on the Cp rings favor one specific conformation of polymer chain end over the others by a margin of several (~6) kcal/mol. This fixed conformation of the polymer chain end in turn favors one primary insertion transition state over the other having opposite site stereochemistry by several (7-9) kcal/mol. This *indirect* stereocontrol mechanism, as illustrated in Scheme IV, is essentially same as that very recently proposed by Corradini and collaborators.[12,13] However, their proposal is based on a guess of transition state, which looks more like our olefin π-complex. As discussed for regioselectivity, the steric requirement of the π-complex is very different from that of the transition state. It is essential that one uses a reasonable transition state structure for comparison of steric energy.

A word of caution is in order even with regard to our transition state model. We have used without modification the main feature of the transition state structure determined for $(SiH_2Cp_2)ZrCH_3^+ + C_2H_4$, the catalyst with unsubstituted Cp rings and with CH_3 as the polymer chain end and the unsubstituted ethylene, and optimized the geometrical parameters of only the substituents on Cp groups, the chain end CH_3, and CH_3 of the olefin. The transition state structure should actually depend on the substituents. This must be the next step of improving our model. Efforts of optimizing the transition state structure in the MO-MM mixed approach have been made,[16] but some arbitrariness in such studies has been pointed out.[34]

Our model for syndiotactic polymerization is essentially the same as that for isotactic polymerization: the indirect control mechanism. We have suggested that SiR_2(FluCp) may be a good ligand for syndiotactic polymerization of propylene and 4-methyl-1-pentene.

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Advancing the Search for Cyclopropenylidenecarbene, the Exocyclic Ring Isomer of Diacetylene

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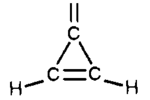
Abstract: Ab initio molecular electronic structure theory is used to determine the structure, harmonic vibrational frequencies, infrared (IR) intensities, rotational constants, and dipole moment of cyclopropenylidenecarbene ($:C{=}CC_2H_2$). These properties are investigated using double-ζ plus polarization (DZP) and triple-ζ plus double polarization function (TZ2P) basis sets at the self-consistent-field (SCF), configuration interaction with single and double excitations (CISD), and coupled cluster with single and double substitutions (CCSD) levels of theory. Based on the IR intensity profile and the large dipole moment (~5 D), we predict that this molecule is a good candidate for an astronomical search and for identification in the laboratory.

Introduction

As the quest for larger, more complex molecules in the interstellar medium continues, reliable information on some exotic species is needed. Carefully chosen theoretical methods provide accurate predictions of the physical observables of these species, thereby expediting the search.

Structural isomers of diacetylene (HC_4H) are currently of interest to astrophysicists. Although the nonpolar diacetylene has not yet been observed in the interstellar medium (ISM), Cernicharo, Gottlieb, Guélin, Killian, Thaddeus, and Vrtilek have used a millimeter-wave spectral survey in the ISM to detect one isomer, butatrienylidene ($:C{=}C{=}C{=}CH_2$),[1] lying 43 kcal mol^{-1} (1.9 eV) above diacetylene.[2] Another isomer, cyclopropenylidenecarbene,



has been estimated to lie 81 kcal mol^{-1} (3.5 eV) above diacetylene and contains a three-membered carbon ring.[1] At present, it has neither been observed in the interstellar medium nor identified in the laboratory.

In 1981, Andrade, Chandrasekhar, and Schleyer obtained an ab initio geometry and energy for this ring isomer at the 6-31G*/SCF level of theory.[3] Although the theoretical results were illuminating, spectroscopists and astrophysicists require more accurate descriptions of the structural and physical properties of their target species. In the present work, high level ab initio methods are used to predict a reliable equilibrium geometry, harmonic vibrational frequencies, infrared (IR) intensities, rotational constants, and the dipole moment of cyclopropenylidenecarbene.

Theoretical Methods

This study investigates the salient physical features of cyclopropenylidenecarbene, using two basis sets and three theoretical methods. The basis set designated DZP is the standard Huzinaga-Dunning double-ζ basis contracted as C(9s5p/4s2p), H(4s/2s),[4,5] augmented by po-

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