Regular article

Ab initio MO study of ethylene insertion into the Sm—C bond of H$_2$SiCp$_2$SmCH$_3$*

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Abstract. Ethylene insertion into the Sm—C bond of H$_2$SiCp$_2$SmCH$_3$, a model reaction of an olefin polymerization propagation step, has been studied by ab initio molecular orbital methods. The small electronegativity of the Sm atom makes the Sm—C bond ionic, the methyl group being negatively charged by −0.75. The reaction passes through a loose ethylene complex with a binding energy of 15 kcal/mol and then a tight four-centered transition state with an agostic interaction between the Sm atom and one of the methyl CH bonds. A small activation energy of 14 kcal/mol is required to pass through this transition state, indicating that this is an easy reaction. Compared with the reactions with group 4 cationic silylene-bridged metallocenes the activation energy is higher and the reaction is less exothermic. The origin of these differences is discussed. The results of molecular mechanics calculations on regio- and stereo-selectivities in the insertion reaction of propylene are also reported.
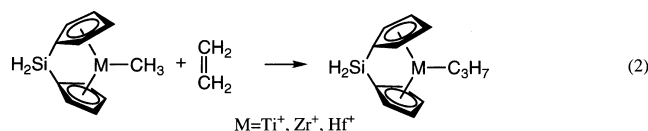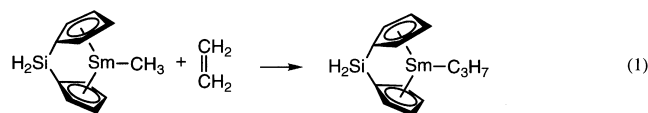
Key words: Ethylene insertion – ab initio MO calculations – Sm complexes – Polymerization

1 Introduction

Lanthanide reagents have become widely used in organic synthesis in the last decade [1, 2], because they give characteristic reactions as well as better efficiency compared with reagents of main-block elements and *d*-block transition metals [1, 3]. One of the most important reagents is SmI$_2$, found by Girard et al. in 1980 [4]. This conducts important reactions in organic chemistry such as reduction of functional groups and reductive coupling of halides with π bonds [5]. On the other hand, organolanthanide complexes act as catalysts

for polymerization of olefin, diene, alkyne, and so forth [6–9]. Some of them have shown different characteristics from the traditional Ziegler-Natta-type [10] and newer homogeneous Kaminsky-type [11] catalysts. Thus theoretical comparison of reaction profiles of lanthanide complexes with those of *d*-block transition metal complexes is of interest.

In this paper, we report the results of ab initio molecular orbital (MO) calculations for the following model reaction (Eq. 1) of the olefin polymerization propagation step catalyzed by a Sm complex, and its potential energy profile is compared with those of the reactions of group 4 cationic complexes (Eq. 2).

$$H_2Si \overset{}{\underset{}{\diagdown}} Sm-CH_3 + \overset{CH_2}{\underset{CH_2}{\|}} \longrightarrow H_2Si \overset{}{\underset{}{\diagdown}} Sm-C_3H_7 \qquad (1)$$

$$H_2Si \overset{}{\underset{}{\diagdown}} M-CH_3 + \overset{CH_2}{\underset{CH_2}{\|}} \longrightarrow H_2Si \overset{}{\underset{}{\diagdown}} M-C_3H_7 \qquad (2)$$

$$M=Ti^+, Zr^+, Hf^+$$

Yasuda and coworkers [9] have designed alkyl Sm complexes with silylene-bridged cyclopendadienyl ligands which catalyze olefin polymerization. It has been demonstrated experimentally that the complex shown below, for instance, conducts ethylene polymerization to give high molecular weight polymers with narrow molecular weight distributions. Equation (1) is a model of such polymerizations.

$$Me_2Si \overset{R \diagdown \diagup R}{\underset{R \diagdown \diagup R}{\diagdown}} Sm-CHR_2 \qquad R=SiMe_3$$
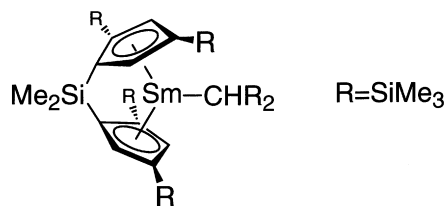
Theoretical studies of model reactions of an olefin polymerization propagation step by Kaminsky-type cationic group 4 metallocenes [12], olefin insertion into

a metal-alkyl bond, have been reported by us [13] as well as others [14]. We have carried out ab initio MO calculations of the model elementary step (Eq. 2) with silylene-bridged cationic group 4 metallocenes [13] and found that activation energies for all the group 4 metals are low and that the activity decreases in the order $Zr \geq Hf > Ti$ [13].

Olefin insertion into a metal-alkyl bond creating a new CC bond is also one of the most important elementary reactions in organometallic chemistry. Fukui and Inagaki [15] have demonstrated that interaction of an alkyl ligand with olefin is assisted by a d orbital of a transition metal by considering orbital interaction among the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbitals (LUMOs) of three fragments as shown below.
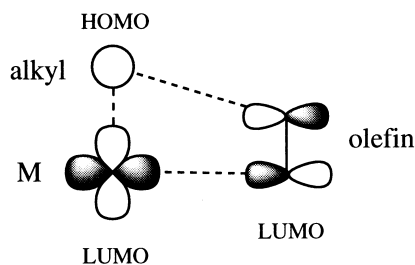
Therefore, energy profiles would be favorable for reactions 1 and 2 to a similar extent, and the difference would be small. Nevertheless, comparison of energy profiles between these reactions is expected to give information on features of the reactions of organolanthanides.

Computational methods used in this study are presented in Sect. 2. The structure of the methyl complex, $H_2SiCp_2SmCH_3$, and its $Sm-CH_3$ bond is discussed in Sect. 3. The computational results for ethylene insertion are discussed in Sect. 4. Concluding remarks are in Sect. 5.

2 Computational details

In theoretical calculations of compounds with heavy metal atoms relativistic effective core potentials (ECPs) are usually used to replace core electrons in order to save computer time and to take relativistic effects into account. Several ECPs have so far been reported for lanthanide atoms. While the ground state of Sm is [Kr] $4d^{10}5s^25p^64f^66s^2$, the primary difference among the ECPs is in choosing the core orbitals to be replaced by ECPs. Since $4f$ orbitals are much smaller than $6s$ and $5d$ orbitals, it can be reasonably assumed that $4f$ orbitals are not responsible for chemical bonds. Accordingly, Dolg et al. [16] developed the ECP replacing the [Kr] $4d^{10}4f^6$ or the [Kr] $4d^{10}4f^5$ core. Since the Sm atom is usually di- or trivalent in organometallic compounds and there are six $4f$ electrons for Sm (II) and five for Sm (III), Dolg et al. prepared the ECPs for both states separately. With the ECP of Cundari and Stevens [17] [Kr] $4d^{10}$ shells are treated as a fixed core. Ross et al. [18] have reported the ECP with which the [Kr] $4d^{10}5s^25p^6$ core is replaced. While Dolg et al. [19] have

also reported a small core ECP by treating $4s$ and $4p$ electrons as well as $4f$ electrons explicitly, in the present study we mainly used their larger core ECP mentioned above for Sm (III) together with their valence basis functions $(7s6p5d)/[5s4p3d]$ [16]. An ECP of this type replacing $4f$ orbitals was successfully used in calculations of the structures of lanthanide metallocenes [20] and of the olefin hydroboration reaction catalyzed by a Sm complex [21]. Treating partially filled $4f$ orbitals explicitly, we have to calculate the electronic structure of open-shell molecules, whereas Sm complexes having only closed shells by replacing $4f$ orbitals with the ECP are computationally much easier. For comparison, energy calculations were also performed with the ECPs of Cundari and Stevens and of Ross et al. together with their basis functions for the Sm atom as well as basis set I for the ligands shown below (latter called basis sets Ia and Ib, respectively). The spin state in these calculations is sextet.

For the representation of ligands and other reactants three different basis sets, called I, II, and III, were used. Basis set I, our previous standard small basis set, consists of STO-3G basis functions [22] for the spectator ligand, H_2SiCp_2, and 3-21G basis functions [23] for the active methyl and ethylene fragments. In basis set II we used the $(8s5p1d)/[3s2p1d]$ and $(4s)/[2s]$ basis functions [24, 25] for the methyl group and ethylene and the 3-21G functions for H_2SiCp_2. In basis set III we modified basis set II by replacing the 3-21G basis functions for the H_2SiCp_2 ligand with $(8s5p)/[3s2p]$ for C, $(4s)/[2s]$ for H, and $(11s8p1d)/[4s3p1d]$ for Si. As shown later the $Sm-CH_3$ bond is ionic. In our previous calculations of the reaction of a methyl complex with formaldehyde the effect of anion functions on the methyl carbon is small [26], and thus in the present calculations anion basis functions were not used.

The structures of stationary points were determined by second-order Møller-Plesset perturbation theory (MP2) as well as by the restricted Hartree-Fock (RHF) method. In the RHF geometry optimizations only basis set I was employed, whereas basis sets I and II were used in the MP2 geometry determinations. In order to obtain more reliable results, we performed energy calculations for the MP2/II structures using Møller-Plesset perturbation theory up to fourth order without triple excitations (MP4SDQ) with basis set III. While there is no overall symmetry constraint in geometry optimizations, to save computer time a local C_{5v} symmetry was assumed for the Cp rings without the constraint of the $Sm-X(Cp$ centroid) axis being perpendicular to the Cp plane. In the reactant methyl complex this assumption gave a structure less stable by only 1.4 kcal/mol at the MP2/I level, compared with the structure determined without any constraint. Since the H_2SiCp_2 fragment is a spectator ligand, the difference of about 1 kcal/mol would result in negligible errors in the activation energy and the energy of reaction as we found previously in calculations of ethane oxidative addition to $CpRhPH_3$ [27]. Therefore the assumption mentioned above is reasonable for determining the structures of the present molecules. All the calculations were carried out using the Gaussian94 program [28].
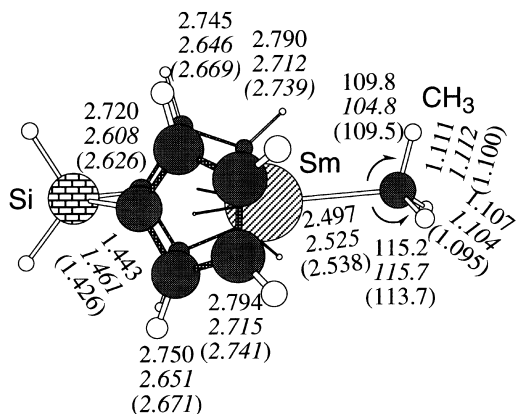
3 H$_2$SiCp$_2$SmCH$_3$ and its Sm─CH$_3$ bond

In this section, the calculated structures of the Sm methyl complex, H$_2$SiCp$_2$SmCH$_3$, and its Sm─C bond are discussed. The structure of H$_2$SiCp$_2$SmCH$_3$ optimized at the MP2 level as well as at the RHF level is shown in Fig. 1. The MP2 calculations with basis sets I and II gave an Sm─C distance of 2.525 and 2.497 Å, respectively. The experimental Sm─C distance in Me$_2$Si (Cp-TMS)$_2$Sm─CH (TMS)$_2$ and Cp*$_2$SmCH$_3$ (THF) is 2.50 and 2.48 Å [9e, 29], respectively, with which the MP2/II distance is in good agreement.

Electron correlation effects shorten the Sm─C bond, showing a contrast to the behavior of covalent bonds which generally become longer when taking correlation effects into consideration. This is presumably due to the ionic character of the Sm─C bond shown later. The bonding interaction between closed-shell fragments would be enhanced by electron correlation effects as in the case of van der Waals complexes. Electron donation from the methyl anion to the H$_2$SiCp$_2$Sm cation certainly makes a contribution to the bond, and such an interaction would be more properly described with correlated wave functions.

The Boys localized molecular orbital (LMO) for the Sm─C bond calculated with the RHF/I wave function is shown in Fig. 2a. It indicates that the bond is quite ionic and consists of the C sp^3 hybrid and the Sm $5d$ orbital mixed with the Sm $6s$ orbital. The natural population analysis shows that there is a negative charge of -0.75 on the CH$_3$ group and that the Sm atom is positively charged by $+2.12$. This large polarization is the result of the large difference in electronegativity between the C and Sm atoms. Note that even if anion sp functions are augmented to the methyl C, the Sm─C bond length shortens by only 0.005 Å.

Furthermore, the LMO calculations were carried out at the restricted open-shell Hartree-Fock (ROHF) level with basis sets Ia and Ib with which the $4f$ orbitals were taken into account explicitly. In these calculations singly occupied orbitals were excluded from the localization
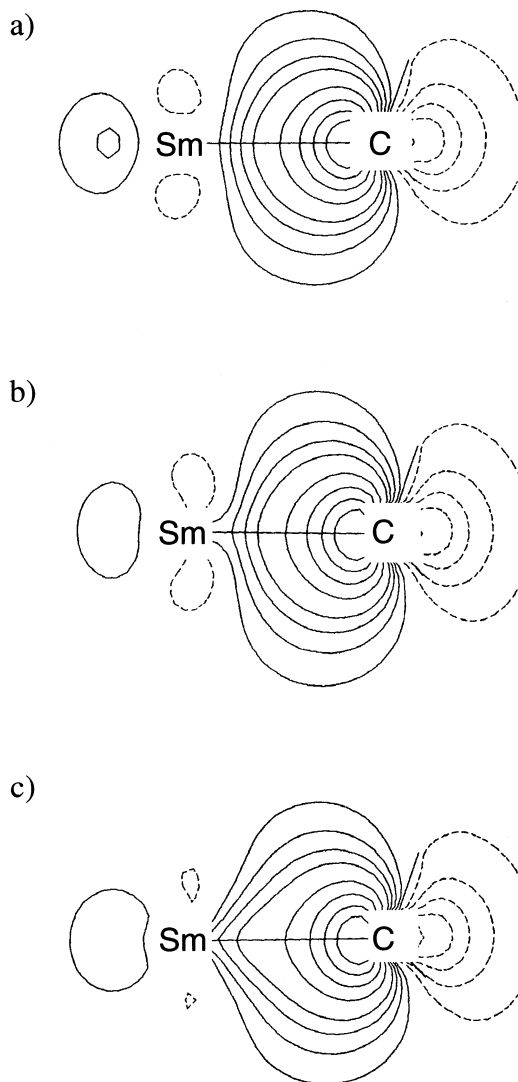
procedure. The calculations showed that the $4f$ orbitals do not make a significant contribution to the Sm─C bond as shown in Fig. 2b and c. Consistent with this, the singly occupied orbitals consist mainly of $4f$ orbitals. One can see a longer tail reaching the Sm atom in the LMO calculated with basis set Ib, suggesting that the ECP used in basis set Ib is too attractive. This is presumably due to the approximation that the outermost $5s$ and $5p$ core orbitals are replaced by the ECP. It is well-known that such orbitals should be treated explicitly [30], and this holds true for the present case.

4 Ethylene insertion into the Sm─C bond of H$_2$SiCp$_2$SmCH$_3$

4.1 Optimized structures and potential energy profile

In the study of the reaction of ethylene with H$_2$SiCp$_2$SmCH$_3$, Eq. (1), we followed the widely-

Fig. 1. MP2/II optimized structures of H$_2$SiCp$_2$SmCH$_3$ in Å and degrees. The distances between the Sm atom and the Cp carbons as well as the structural parameters for the SmCH$_3$ fragment are shown. The numbers in *italics* and *parentheses* are those for MP2/I and RHF/I structures

Fig. 2a–c. Boys localized orbitals for the Sm─C bond of H$_2$SiCp$_2$SmCH$_3$ calculated using **a** RHF/I, **b** ROHF/Ia, and **c** ROHF/Ib molecular orbitals

accepted Cossee mechanism, [31] i.e., ethylene insertion into a metal-carbon bond following ethylene coordination. In this section, first, discussions are made based on the MP4SDQ/III energies calculated at the MP2/II structures. Comparisons among ECPs at the HF level will be made later in this section. The MP2/II optimized structures of stationary points are shown in Fig. 3, and the relative energies calculated up to the MP4SDQ/III level are summarized in Table 1.

In the first step of the reaction ethylene coordinates to the Sm atom with a binding energy of 15.1 kcal/mol. Since $5d$ and $6s$ orbitals of the Sm atom are formally vacant, electron donation from the ethylene π orbital is responsible for this coordination. Without back-donation to the π^* orbital, the C=C bond is not stretched so much; in the present ethylene complex the C=C length is only 0.007 Å longer than that in free ethylene. The Sm—CH$_3$ bond length is also almost unchanged upon coordination. The Sm—C lengths are much longer than those in the transition state (TS) and product, showing the loose structure of this ethylene complex.

The reaction passes through a four-centered TS with a small activation energy of 13.9 kcal/mol relative to the ethylene complex, indicating an easy insertion. Though contribution of the Sm d orbital to the Sm—C bond is small as shown in Fig. 2a, the positively charged Sm atom polarizes the CC π bond to facilitate interaction between the methyl anion and the positively charged C^β atom as shown below.
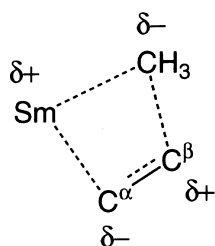
At this TS the length of the Sm—CH$_3$ bond to be broken is only 0.02 Å longer than that of the ethylene complex, and the newly forming C—C bond length is still 0.63 Å longer than that in the product. Though these structural features suggest the TS is located early on the potential energy surface, formation of the newly forming Sm—C bond is almost complete, judging from its length. This asynchronousity of bond exchange has

usually been observed in TSs of insertion reactions [32]. Also, these structural features indicate that the TS is tight as well. At the TS one of the CH bonds of the
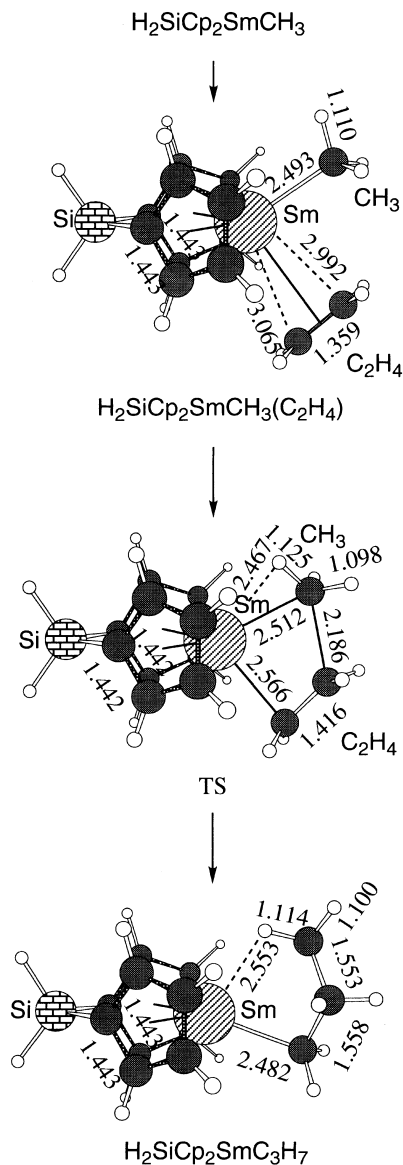
Fig. 3. MP2/II optimized structures, in Å, of stationary points in the reaction of ethylene insertion into the Sm—C bond of H$_2$SiCp$_2$SmCH$_3$

Table 1. Energies (in kcal/mol) of stationary points for ethylene insertion into the Sm—C bond of H$_2$SiCp$_2$SmCH$_3$ relative to H$_2$SiCp$_2$SmCH$_3$ + C$_2$H$_4$

Method	Reactants	Ethylene complex	Transition state	Product
RHF/I//RHF/I	0.0	−9.6	10.8	−20.8
ROHF/Ia//RHF/I	0.0	−7.7	12.4	−19.4
ROHF/Ib//RHF/I	0.0	−14.4	−14.4	
UHF/Ib//RHF/I	0.0	−15.2	−14.5	
MP2/III//RHF/I	0.0	−17.5	−8.8	−30.0
MP2/I//MP2/I	0.0	−20.2	−11.2	−30.3
MP2/II//MP2/II	0.0	−17.3	−8.9	−30.5
RHF/III//MP2/II	0.0	−5.3	19.1	−15.5
MP2/III//MP2/II	0.0	−17.9	−8.8	−30.2
MP3/III//MP2/II	0.0	−15.1	−0.7	−26.5
MP4SDQ/III//MP2/II	0.0	−15.1	−1.2	−26.5

methyl group is 1.125 Å long, 0.03 Å longer than the other CH bonds of the same methyl group. The distance of the H atom from the central metal is 2.467 Å, only 1.15 times longer than the Sm—H bond length in H_2SiCp_2SmH, which is 2.151 Å at the same level of calculation. These structural features indicate that interaction of the CH bond with the central Sm atom, called agostic interaction, takes place [33].

This interaction remains in the product of a propyl complex as an agostic interaction between the γ CH bond and the Sm atom, called γ CH agostic interaction. The length of the interacting CH bond is 1.114 Å. This is only 0.01 Å longer than the standard distance, and therefore this interaction is not so strong as that in the TS. The product is 11.4 kcal/mol more stable than the ethylene complex, and the overall energy of reaction is −26.5 kcal/mol.

The relative energies calculated at several levels given in Table 1 show that the MP3 and MP4SDQ energy profiles are almost parallel, the perturbation series converging quickly, and that even the MP2 energy profile is not very different from the MP4SDQ one. These results are similar to those for reaction 2 with $M = Zr^+$ and Hf^+, in which we found that the MP3 and MP4SDQ results are quite similar to the QCISD energetics [13b]. The structures of the TS and product for $M = Sm$ determined at the RHF/I level are presented in Fig. 4, and are qualitatively the same as those at the MP2 level. Also, the MP2/III energy calculations at the RHF/I structures gave similar energy profiles to those for the MP2/II structures, indicating that single-reference methods are qualitatively reliable, although

the MP2 calculations slightly underestimate the activation barrier.

In order to evaluate the approximation of replacing partially occupied 4f orbitals by the ECP, we performed the energy calculations for the RHF/I structures at the ROHF or unrestricted HF (UHF) levels as shown in Table 1. With basis set Ia in which 4f orbitals as well as 5s and 5p orbitals are treated explicitly we obtained a similar energy profile to that at the RHF/I level, indicating that in theoretical calculations of such organometallic reactions of Sm complexes 4f orbitals can be replaced by the ECP, as long as oxidation or reduction processes in which an electron is removed from or added to one of 4f orbitals are not included. On the other hand, using basis set Ib in which the 5s and 5p electrons are replaced by the ECP, and 4f orbitals are in the valence space, the calculations gave a small activation energy of 0.0 and 0.7 kcal/mol at the ROHF and UHF levels, respectively. Such outermost core orbitals should be treated explicitly as discussed in Sect. 3.

4.2 Comparison of the potential energy profile with those for group 4 cationic metallocene catalysts

Ethylene insertion is a model reaction of the propagation step in olefin polymerization. Previously, we have studied theoretically the model reaction of the propagation step catalyzed by silylene-bridged metallocenes of group 4 cations (Ti^+, Zr^+, and Hf^+) [13]. The present potential energy profile can be compared with those as

Fig. 4. Structures of the transition state (*TS*) and product for ethylene insertion into the M—C bond of $H_2SiCp_2MCH_3$ for M = Sm and M = Zr^+ at the MP2/I level. Numbers in parentheses are distances at the RHF/I level
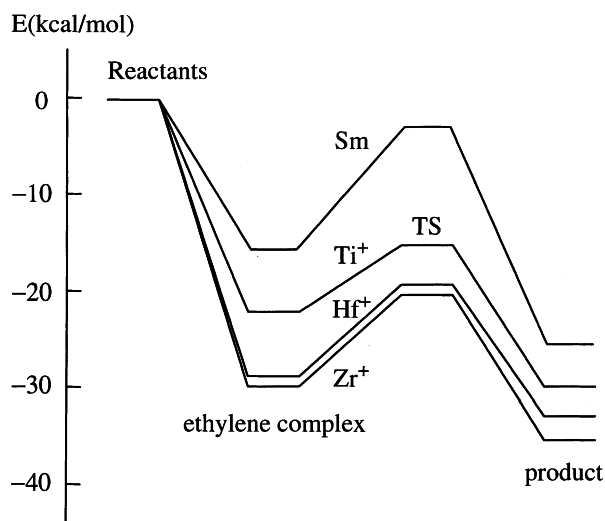
E(kcal/mol)
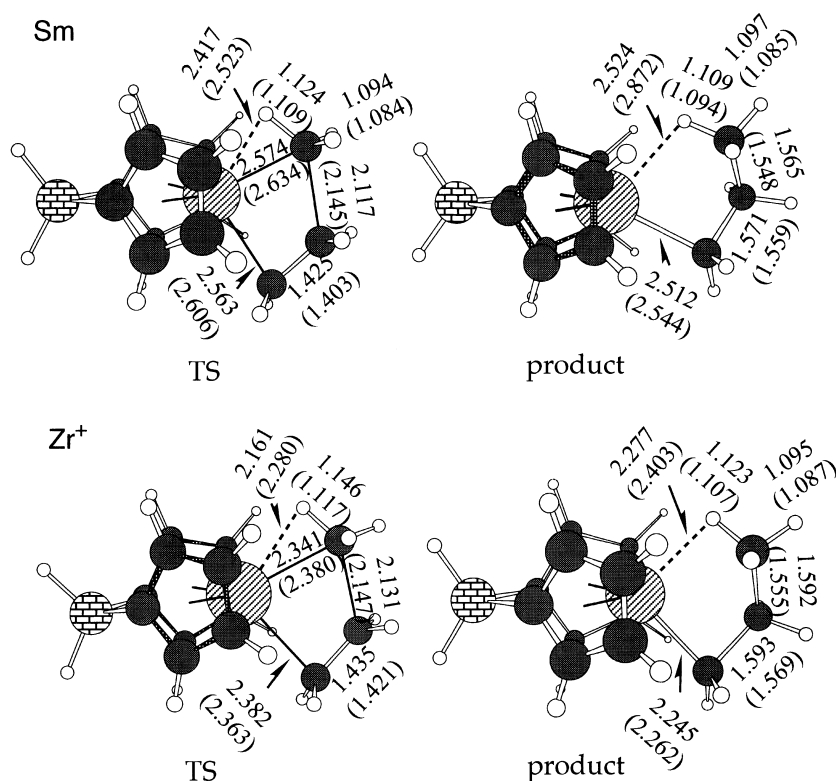
Fig. 5. Potential energy profiles for ethylene insertion into the M—C bond of H$_2$SiCp$_2$MCH$_3$. MP4SDQ profiles for M = Sm, Zr$^+$, and Hf$^+$ and PUMP3 profile for Ti$^+$ are shown. The results for group 4 metal cations were taken from Ref. [13c]

shown in Fig. 5. Though the structural features such as a weak ethylene complex, a four-centered TS with an agostic interaction, and a product with a γ agostic interaction are similar, there are significant differences in the potential energy profiles as discussed below.

The Sm ethylene complex is less stable compared with those of group 4 cations, i.e., the ethylene binding energy is smaller. In all the ethylene complexes discussed here electron donation from ethylene is responsible for the metal-ethylene bonds. The Sm atom is absolutely less electron-withdrawing than the group 4 metal cations, resulting in a less stable ethylene complex. On the other hand, the TSs for group 4 metal cations are much more stable than that for M = Sm, and consequently the activation energies are smaller. This is because of the stronger interaction of the group 4 cations with organic fragments. This can be seen in the difference in the bond length of the methyl agostic CH bond (Fig. 4); at the TS for M = Zr$^+$ determined by the MP2/I method the bond length of the agostic CH bond is 1.146 Å, whereas that for M = Sm is 1.124 Å. We clarified that the agostic interaction at the TS actually lowers the activation energy in the ethylene insertion into the Zr—CH$_3$ bond [34].

This reaction is formally a conversion of an M—CH$_3$ bond and a C=C bond into an M—C$_3$H$_7$ bond and two C—C bonds. The energy of reaction is formally expressed in terms of bond energies as

$$\Delta E(M) = - \left[D(M{-}C_3H_7) + D(MCH_2CH_2{-}CH_3) \right.$$
$$+ \left. D(MCH_2{-}CH_2CH_3) \right]$$
$$+ \left[D(M{-}CH_3) + D(C{=}C) \right] .$$

Using this equation the difference in the energy of reaction between Sm and Zr is

$$\Delta E(Sm) - \Delta E(Zr) = \left[D(Zr{-}C_3H_7) \right.$$
$$- \left. D(Sm{-}C_3H_7) \right]$$
$$- \left[D(Zr{-}CH_3) \right.$$
$$- \left. D(Sm{-}CH_3) \right] .$$

Accordingly, it is expected that the overall energy of reaction for M = Sm is similar to those for group 4 cations. However, the reaction for M = Sm is less exothermic. This suggests that the Zr—C$_3$H$_7$ bond is stronger compared with the Sm—C$_3$H$_7$ bond and in addition the difference in the bond energy is larger than that between the M—CH$_3$ bonds. This characteristic of the Zr—C$_3$H$_7$ bond is induced by the interaction of the Zr cation with the CC and CH bonds of the propyl group due to electron donation from ligand σ orbitals to metal vacant orbitals which stretches the σ bonds. As shown in Fig. 4 the CC bond lengths of the propyl group for M = Zr$^+$ are 1.59 Å at the MP2/I level, whereas the lengths for M = Sm are 1.57 Å. The agostic γ CH bond is also longer in the Zr propyl complex. Such interactions are similar to what we found previously; cationic group 4 metals can induce bonding interaction with ligand σ bonds such as CC and CSi bonds [35].

Positive charges on the group 4 cations induce the stronger bonding interaction at the TSs to lower the activation energies and make the reactions more exothermic as just discussed. This is furthermore supported by calculations of ethylene insertion into the Sc—C bond of neutral H$_2$SiCp$_2$ScCH$_3$ [36]. The Sc atom, a group 3 d-block transition metal is classified into the rare-earth elements as are lanthanides. The profile of the insertion reaction is similar to that of the Sm complex; at the MP4SDQ level the TS for M = Sc is only 4.0 kcal/mol more stable than the reactants, and the activation energy relative to the ethylene complex is 11.7 kcal/mol.

4.3 Molecular mechanics calculations of regio- and stereoselectivities of propylene polymerization

Tacticity control is an important property of metallocene catalysts. It was found in 1985 that substituted zirconocene catalysts can yield highly isotactic propylene. Since then, great attention has been given to ligand effects on stereoregulation for isotacticity as well as syndiotacticity in homogeneous propylene polymerizations, and substantial advances in the design of group 4 metallocenes have been made [37–40]. Employing molecular mechanics (MM) calculations for the TSs with the substituted catalysts (M = Zr$^+$ and Hf$^+$), we have found that an indirect control mechanism is operative [13b, d]. As shown in Scheme 1, in the primary insertion the substituents on the Cp rings determine the conformation of the polymer end, which in turn controls the sense of approach of the propylene monomer. On the other hand, steric interaction with the Cp rings makes methyl substitution on the α C, which would lead to secondary insertion, unfavorable.

Mechanism of Isospecific Propagation

Determination of the Conformation of Polymer Chain End

more favorable
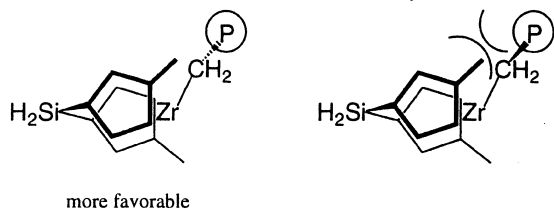
Stereo- and Regiospecification of α-Olefin

Primary insertion

more favorable

Secondary insertion
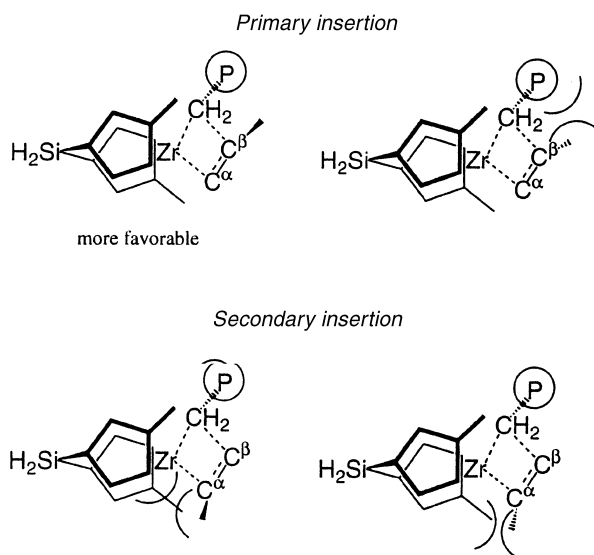
At the TS for M = Sm, however, the situation would be different. Because of the larger size of the Sm atom the polymer end as well as the propylene methyl group would be too far from the Cp rings. Thus, we performed MM calculations using the same procedure as previously to investigate the possibility of regulation for isotacticity with Sm catalysts. Preliminary results are presented in Table 2 in which the steric energies of the four regio- and stereoisomeric TSs are listed with those for one of the zirconocene catalysts we have investigated [13b]. In the MM calculations the following four H atoms of the MP2 optimized geometry of the TS were replaced by methyl groups: the two H atoms at 3,4′ positions of the Cp rings, one of the ethylene H atoms, and one of the H atoms of the methyl group of an model polymer end. The coordinates of the substituents were optimized in the MM calculations, whereas the remaining part of the MP2-optimized structures were frozen. We used the MM2 force field and program [41]. While the sp^3 and sp^2 C parameters were used for methyl and ethylene Cs of the reaction center, the central metal was treated as a dummy atom. For all other atoms, standard parameters were used.

While the primary insertion with R^1 = Me is the most favourable in the reaction of M = Zr^+, the steric energy of the secondary insertion with R^3 = Me is smallest in the reaction of M = Sm. The large Sm atom makes the Sm—Cp distance so long that R^3 is in the least crowded space. For instance, the distance between the C atom at the 4′ position of the Cp ring and the olefin α C atom is 3.14 Å in the Zr TS, whereas that in the Sm TS is 3.66 Å. These results show that in contrast to polymerization with group 4 metallocenes, secondary insertion would take place and more importantly the different mechanism could control tacticity in propylene polymerization catalyzed by Sm complexes. MM calculations to confirm this and to investigate the ability of other ligands to control tacticity are in progress.

5 Concluding remarks

In this paper we have reported the results of ab initio MO calculations on ethylene insertion into the Sm—C bond of $H_2SiCp_2SmCH_3$, a model propagation step of olefin polymerization catalyzed by Sm complexes. The calculations have shown that the reaction takes place through the loose ethylene complex and the tight four-centered TS and that an activation energy of 14 kcal/mol is required to pass through this TS. Comparing the reactions of ethylene with the group 4 cationic metallocene catalysts, the energies of the ethylene complex and TS relative to the isolated reactants are higher. These differences originate from the difference in the ability of the central metal to interact with the ligands. In the reaction of the Sm complex the central atom has a small electronegativity and thus the interaction due to the electron donation from the ligand σ bonds to the vacant metal orbitals is difficult, and consequently the TS and product are less stable. Also in the preliminary MM calculations of the stereoregulation in propylene polymerization catalyzed by substituted Sm complexes we have obtained results which are different from those of group 4 cations, suggesting different control mechanisms could be operational.

Though in the present calculations partially filled $4f$ orbitals were replaced by the ECP, single-point SCF calculations with $4f$ orbitals treated explicitly gave qualitatively similar results, suggesting that in such organometallic reactions without oxidation and/or reduc-

Table 2. Molecular mechanics steric energies (in kcal/mol) for propylene insertion into the M—C bond of $[H_2Si(CpMe)_2]$-MCH_2CH_3 relative to primary insertion with R^1 = CH_3[a]

M	Primary		Secondary	
	R^1 = Me	R^2 = Me	R^3 = Me	R^4 = Me
Zr^+	0.0	4.0	4.8	16.3
Sm	0.0	0.3	−6.4	−0.9

[a] The results for Zr^+ were taken from Ref. [13b]
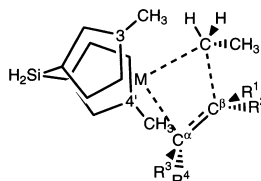
tion partially filled 4*f* orbitals could be replaced by the ECP to obtain qualitative results at less expense.

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