

Influence of the Counterion $\text{MeB}(\text{C}_6\text{F}_5)_3^-$ and Solvent Effects on Ethylene Polymerization Catalyzed by $[(\text{CpSiMe}_2\text{NR})\text{TiMe}]^+$: A Combined Density Functional Theory and Molecular Mechanism Study

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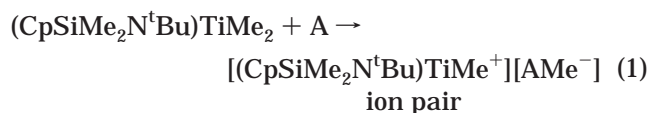
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A combined density functional theory and molecular mechanism (QM/MM) method has been used to study the first ($R = \text{Me}$) and the second ($R = \text{propyl}$) insertion of the ethylene monomer into the $\text{Ti}-\text{R}$ bond of $(\text{CpSiMe}_2\text{N}^t\text{Bu})(\text{R})\text{Ti}-\mu\text{-MeB}(\text{C}_6\text{F}_5)_3$. The present extensive theoretical investigation provides a comprehensive analysis of the chain propagation process for ethylene polymerization catalyzed by CGC in the presence of the counterion $\text{MeB}(\text{C}_6\text{F}_5)_3^-$. Both the counterion and solvent effects play important roles in the first and second ethylene propagations and therefore cannot be ignored in the mechanistic study. The influence of the counterion and the solvent not only changes the reaction barriers but also alters the rate-determining step for the chain propagation, from insertion to uptake. The *cis* approach is preferred over the *trans* approach for the second ethylene propagation in the gas phase as well as in solution. The total reaction barrier for the first ethylene propagation has been calculated to be slightly higher than that for the second ethylene propagation, in general agreement with experimental findings. The total barriers in solution are 11.7 and 8.5 kcal/mol for the first and second ethylene propagations, respectively. These barriers are comparable to the activation energy (13.3 kcal/mol) found experimentally for the same catalyst (CGC).

Introduction

The single-site “constrained-geometry catalyst” (CGC) $[(\text{CpSiMe}_2\text{N}^t\text{Bu})\text{TiR}]^+$ has been used extensively for olefin polymerization in industry.¹ It produces polymers with a narrow molecular weight distribution and linear long-chain branches. This kind of polymer has desirable mechanical properties and possesses at the same time an acceptable processibility.² It has further been found that the constrained-geometry catalyst is useful for copolymerization of ethylene with bulky α -olefins.^{1b,3} Given its importance, it is understandable that the CGC system has been the subject of numerous studies during the past decade.^{1,4,5}

The active species in CGC is assumed to be the cation $[(\text{CpSiMe}_2\text{N}^t\text{Bu})\text{TiMe}]^+$, formed from the reaction of $(\text{CpSiMe}_2\text{N}^t\text{Bu})\text{TiMe}_2$ with a Lewis acid (A) according to



In early theoretical calculations,⁴ it has been customary to consider the ion pair in eq 1 as completely dissociated and describe the polymerization process solely in terms of the cation according to Figure 1. However, recent experimental^{6,7} and theoretical^{1b,c,5,8,9} works have shown that the ion pair of eq 1 is far from dissociated under normal polymerization conditions. It is as a consequence necessary to include the anion in the description of the polymerization process, as has been done first by Lanza et al.^{8a-c} for the CGC system.

The purpose of the present study has been to provide a comprehensive understanding of the chain propagation process for ethylene polymerization catalyzed by CGC in the presence of the counterion AME^- , where the

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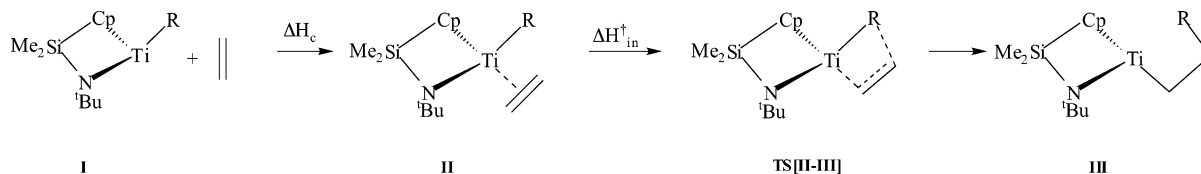


Figure 1. Ethylene insertion process for the naked CGC cation.

often employed activator $B(C_6F_5)_3$ has been used as the Lewis acid A in eq 1. A similar study for the simplified CGC system $(CpSiH_2N^tBu)(R)Ti-\mu-MeB(C_6F_5)_3$ has recently been reported by Lanza et al.,^{8c} focusing primarily on the first ethylene insertion, with a rudimentary discussion of the second ethylene insertion. Our study differs from that of Lanza et al.^{8c} in that we will focus on the second ethylene insertion into the Ti–C $_{\alpha}$ bond of $(CpSiMe_2N^tBu)(R)Ti-\mu-MeB(C_6F_5)_3$ (retaining the two Me groups on the Si atom), where C $_{\alpha}$ denotes the α -carbon of the polymer chain R. The first ethylene insertion will also be explored in order to compare our approach to that of Lanza et al.^{8c} The influence of the counterion will be assessed by comparing ethylene insertions with and without the counterion, $MeB(C_6F_5)_3^-$, while the influence of the solvent will be investigated by comparing gas-phase energies with the corresponding values in solution. The present study provides to date the most extensive theoretical investigation of the second ethylene insertion step involving CGC with the counterion present.

Computational Details

Density functional theory (DFT) calculations were carried out on the basis of the Amsterdam Density Functional (ADF) program version 2000.01, developed by Baerends et al.¹⁰ and vectorized by Ravenek.¹¹ The numerical integration scheme applied was developed by te Velde et al.,¹² and the geometry optimization procedure was based on the method of Verslius and Ziegler.¹³ Geometry optimizations were carried out using

the local exchange-correlation potential of Vosko et al.¹⁴ without any symmetry constraints. The electronic configurations of the atoms were described by a triple- ζ basis set on titanium ($n = 3$) and zirconium ($n = 4$) for the ns , np , nd , and $(n + 1)s$ shells, augmented with a single $(n + 1)p$ polarization function. A double- ζ STO ns and np basis was used for C ($n = 2$), N ($n = 2$), Si ($n = 3$), and P ($n = 3$) augmented with a single 3d polarization function. For hydrogen, a double- ζ 1s basis was used, augmented by a 2p polarization function. Shells of lower energy were treated by the frozen-core approximation. A set of auxiliary s, p, d, f, and g STO functions centered on all nuclei was used to fit the molecular density and represent Coulomb and exchange potentials accurately in each SCF cycle.¹⁵ The gas-phase energy differences were calculated by augmenting the local density approximation energy with Perdew and Wang's nonlocal correlation correction and Becke's exchange corrections (PWB91).¹⁶ The solvation energies based on gas-phase geometries were calculated by the conductor-like screening model (COSMO)¹⁷ with a dielectric constant of 2.023 to represent cyclohexane as the solvent. The radii used for the atoms in Å were as follows: C, 2.0; H, 1.16; B, 1.15; N, 1.5; F, 1.2; Ti, 2.3; Si, 2.2. The enthalpies (ΔH) reported in the following sections are potential energy differences without zero-point or vibrational finite temperature corrections. The insertion barriers were obtained from linear transit calculations with the C $_{\alpha}$ –C $_{Et}$ distance between one C of the ethylene and the α -carbon of the CH $_3$ or CH $_2$ CH $_2$ CH $_3$ growing chain. On the other hand, the uptake barriers were obtained from linear transit calculations with Ti–X (X is the midpoint of the C=C double bond) as the reaction coordinate. A validated QM/MM model⁹ for the counterion has been used in our calculations. In this model, the QM part of $B(C_6F_5)_3Me^-$ is represented by $MeBCl_3^-$. The remaining part is described by molecular mechanics (MM) using the SYBYL/TRIPOS 5.2 force field constants,¹⁸ without electrostatic interactions. QM/MM atoms were also used to model the *tert*-butyl group (tBu) of the $(CpSiMe_2N^tBu)TiMe^+$ cation, with a hydrogen used as the capping atom—hence the QM portion of the cation was $CpSiMe_2NHTiMe^+$. Solvent effects were taken into account by single-point full QM calculations based on the structures optimized by the QM/MM model. The code for QM/MM in ADF has been implemented by Woo et al.¹⁹

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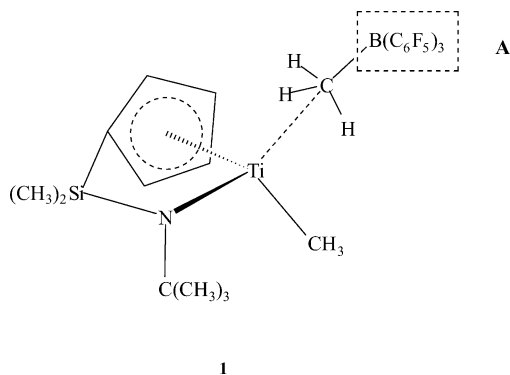


Figure 2. Structure of the contact ion pair $(\text{CpSiMe}_2\text{N}^t\text{-Bu})(\text{Me})\text{Ti}-\mu\text{-MeB}(\text{C}_6\text{F}_5)_3$.

Results and Discussion

I. First Ethylene Insertion. Lanza et al.^{8c} have recently questioned our findings in a previous study,^{8j} where we used an ethyl group ($R = \text{CH}_3\text{CH}_2$) as a growing chain. In this study, we found that the ethylene uptake has a higher barrier than the internal insertion. In contrast, Lanza et al. found that, with a methyl group as the growing chain, the barrier of ethylene uptake is smaller than the insertion. They attributed the differences to “the tendency of DFT approaches to underestimate insertion barriers in this class of reactions”.^{8c} We shall now show that, for $R = \text{CH}_3$, our DFT method for the ethylene insertion is, indeed, in very good agreement with the results obtained by Lanza for the same system.

We shall thus start our study by first considering the insertion where the growing chain is represented by a methyl group, corresponding to the initiation step in olefin polymerization.

1. Without the Counterion. When the influence of the counterion is ignored, the insertion of an ethylene monomer into the $\text{Ti}-\text{C}$ bond of the constrained-geometry catalyst (CGC) has usually been described as a two-step process:^{1a,4} monomer uptake and insertion (see Figure 1). The uptake involves π complexation of ethylene to the metal center. The insertion goes through a transition state with a four-membered-ring structure.

Our calculations show that, for the $(\text{CpSiMe}_2\text{N}^t\text{-Bu})\text{-TiMe}^+$ cation, the complexation energy (ΔH_c) and internal insertion barrier ($\Delta H_{\text{in}}^{\ddagger}$) are -22.0 and 1.0 kcal/mol, respectively. These values are slightly different from those of the generic CGC model ($(\text{CpSiH}_2\text{NH})\text{-TiMe}^+$) of -20.8 and 3.8 kcal/mol, respectively, reported recently.^{4e} We shall in the following see how the highly exothermic value of ΔH_c and modest value of $\Delta H_{\text{in}}^{\ddagger}$ are modified by the presence of the counterion.

2. In the Presence of the Counterion. Previous studies have shown that the contact ion pair in Figure 2 is undissociated in cyclohexane and other solvents employed in polymerization.^{5b} This means that the catalyst, at least before the first insertion step, lacks an empty coordination site for complexation of an ethylene monomer. In this case, the insertion of the ethylene monomer into the $\text{Ti}-\text{C}_\alpha$ bond may not be a straightforward process. Therefore, the mechanism of ethylene insertion should be modified accordingly, compared to the mechanism shown in Figure 1. In principle, an ethylene monomer can approach the ion

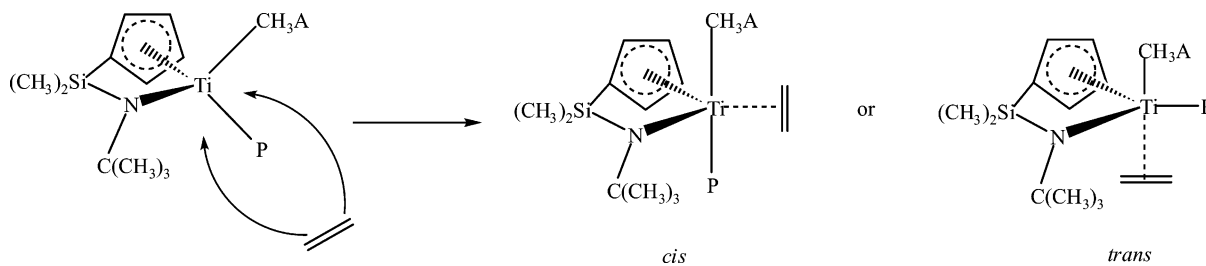
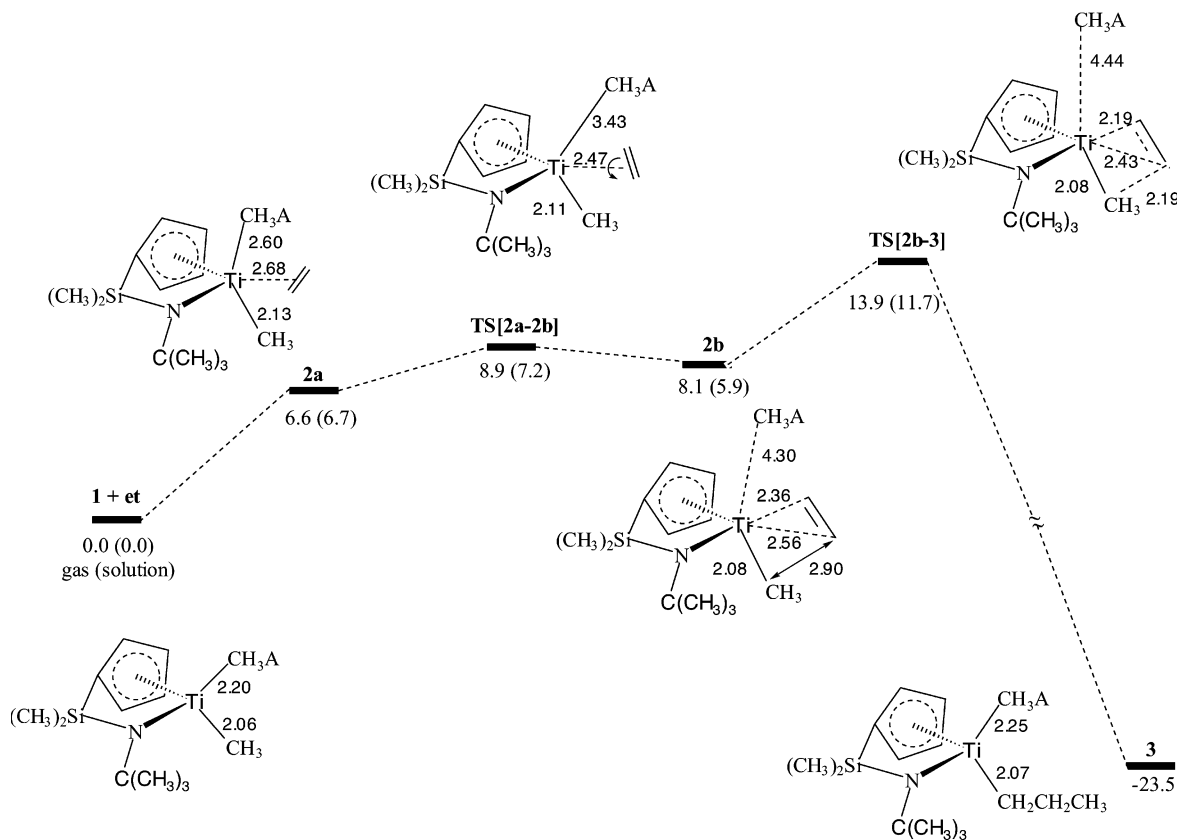
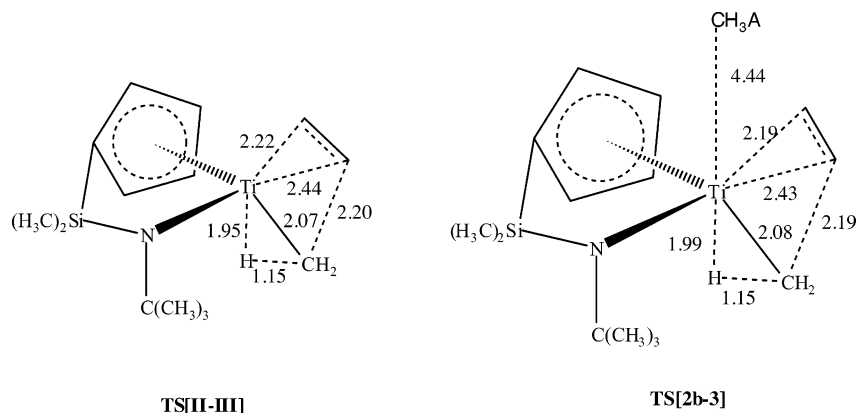
pair from any direction. However, to insert into the $\text{Ti}-\text{C}_\alpha$ bond, the ethylene monomer should finally be close to the α -carbon of the polymer chain. Thus, two possible pathways are considered in our study. As shown in Figure 3, the ethylene molecule can approach the metal center from the direction opposite (trans) to the counterion or cis to the counterion (A), corresponding to pathways A and C, respectively, in the work by Lanza et al.^{8c}

a. Cis Approach. Within the cis approach (Figure 3), we first tried to find a complex, as an analogue to the π complex found in the case of the naked cation, by bringing the ethylene molecule close to the metal center of the ion pair. A weak π complex (**2a**) was found in our geometry optimization with a $\text{Ti}-\text{X}$ distance of 2.68 \AA (X = the midpoint of the $\text{C}=\text{C}$ bond; see Figure 4). This encounter complex is 6.6 kcal/mol higher in energy than the separated species of the reactants but does represent a minimum point on the potential surface. The destabilization of the system is due to the displacement (0.40 \AA) of the counterion from the metal center, indicated by an elongation of the $\text{Ti}-\mu\text{-Me}$ bond from 2.20 \AA in **1** to 2.60 \AA in **2a** (see Figure 4). In this weak π complex, the monomer is situated in a position between the counterion and the methyl group (polymer chain), while the $\text{C}=\text{C}$ bond is oriented almost perpendicular to the $\text{Me}-\text{Ti}-\mu\text{-Me}$ plane.

In order for the insertion to take place, the ethylene molecule must be closer to the metal center so as to form a new $\text{Ti}-\text{C}$ bond, while the $\text{C}=\text{C}$ vector must be rotated so that one of its carbon atoms can approach the methyl group to form a new $\text{C}-\text{C}$ bond. When the $\text{C}=\text{C}$ bond is rotated and, further, the ethylene is brought closer to the metal center, a transition state (**TS[2a-2b]**) for the ethylene uptake was found with a barrier of 8.9 kcal/mol. In this structure (**TS[2a-2b]**), the $\text{Ti}-\text{X}$ distance is 2.47 \AA (Figure 4). It is interesting that the counterion is significantly displaced from the Ti center, indicated by the long $\text{Ti}-\mu\text{-Me}$ distance of 3.43 \AA .

After **TS[2-3]**, a real π complex (**2b**) was located in our geometrical optimization (Figure 4). Although a typical metal- π -bonding interaction (indicated by the short $\text{Ti}-\text{X}$ distance of 2.37 \AA) has been formed in this π complex, the large displacement of the counterion from the metal center ($\text{Ti}-\mu\text{-Me} = 4.30 \text{ \AA}$) still destabilizes the system to be 8.1 kcal/mol higher in energy than the separated species of the reactants. Thus, in contrast to the bare cation case, π complexation of the ion pair here is an endothermic process.

One might have expected that the internal barrier of insertion for the current system should be similar to that of the free cation, since the anion is partially dissociated in **2b**. However, our calculations show that the internal barrier (5.7 kcal/mol) for the insertion process is higher than that found in the case of the free cation (1.0 kcal/mol). Figure 5 displays the structures and selected geometrical parameters of the transition states with (**TS[2b-3]**) and without (**TS[II-III]**) the counterion. When these two structures are compared, it is evident that the $\text{C}_\alpha-\text{C}_{\text{Et}}$ distances, which were taken as the reaction coordinates during the insertion, are quite similar to each other ($\Delta R(\text{C}_\alpha-\text{C}_{\text{Et}}) = 0.01 \text{ \AA}$). The $\text{Ti}-\text{C}_{\text{Et}}$ distances are also quite similar in these two structures ($\Delta R(\text{Ti}-\text{C}_{\text{Et}}) = 0.02 \text{ \AA}$). However, the $\text{Ti}-\text{H}_\alpha$


Figure 3. Cis and trans approaches.

Figure 4. Energy profile for the cis approach of first ethylene insertion for the CGC system.

Figure 5. Transition state structures of the first ethylene insertion with and without counterion.

and Ti-C_α distances in **TS[2b-3]** (1.99 and 2.08 Å, respectively) are longer than those in **TS[II-III]** (1.95 and 2.07 Å, respectively), suggesting a weaker α-agostic interaction and larger dissociation of the Ti-C_α bond in **TS[2b-3]** compared to **TS[II-III]**. The weaker α-agostic interaction and larger dissociation of the Ti-C_α bond in **TS[2b-3]** indicates that the counterion is still sufficiently close (Ti-μ-Me = 4.44 Å) to compete for

coordination. This further rationalizes the higher internal barrier.

After the insertion, a new ion pair was found as the stable product with an energy that is -23.5 kcal/mol lower than that of the separated reactants. In the new ion-pair structure, the counterion is reassociated to the Ti center (Figure 4). Thus, in the subsequent insertion step, ethylene will again have to displace the counterion.

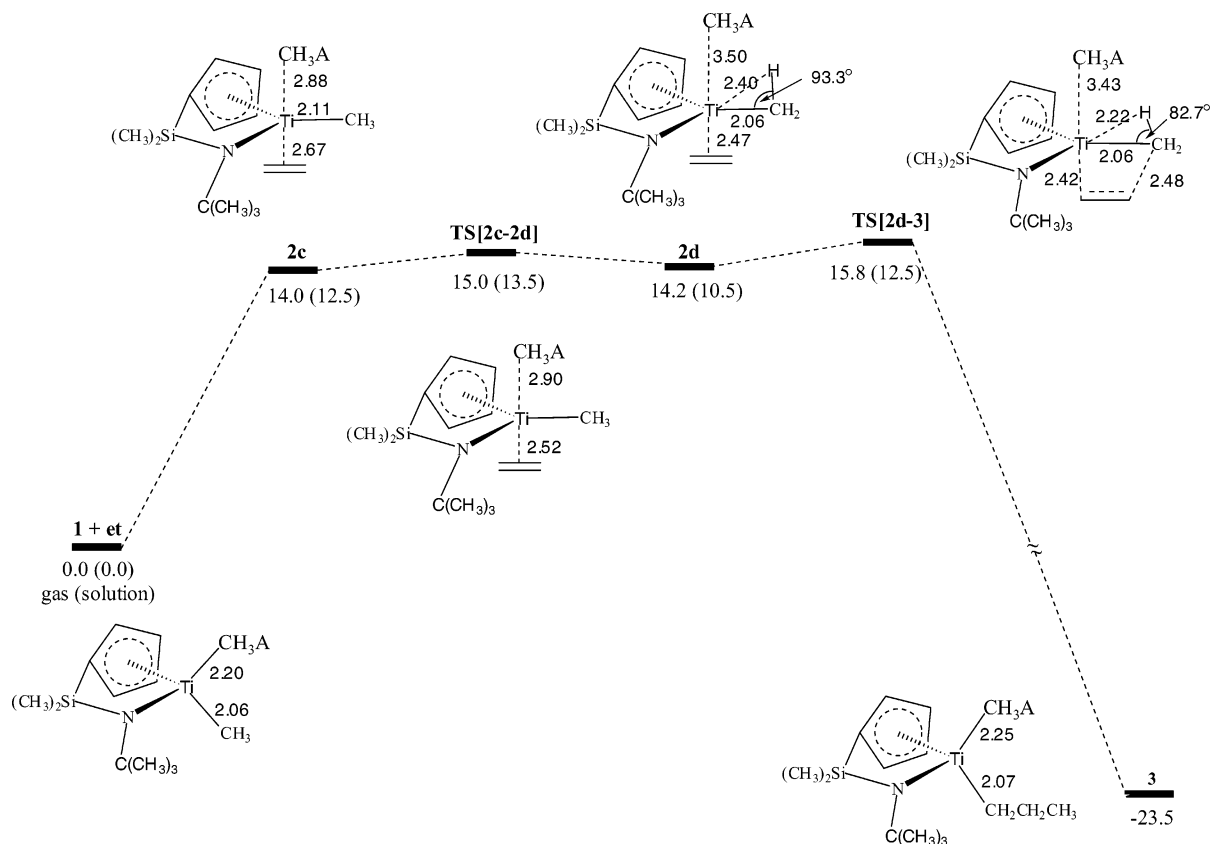


Figure 6. Energy profile for the trans approach of first ethylene insertion for the CGC system.

The total barrier for this reaction path is 13.9 kcal/mol. The insertion process is thus the rate-determining step for the cis approach. The barrier is reduced to 11.7 kcal/mol when solvent effects are included. The decrease in the reaction barrier by solution is due to the large ion-pair separation in **TS[2b-3]**.

It is clear from Figure 4 that our DFT approach indeed finds the barrier of uptake to be lower than that of insertion for the cis approach, in agreement with Lanza et al.^{8c} Moreover, our gas-phase barrier of uptake (8.9 kcal/mol) is in agreement with their value of 7 kcal/mol. A similar good agreement exists between our gas-phase insertion barrier of 13.9 kcal/mol and their value of 15 kcal/mol. We must thus conclude that the MP2 approach by Lanza et al.^{8c} and our DFT method afford quite similar results when use is made of the same growing chain.

b. Trans Approach. In the trans approach, by situating the ethylene monomer closed to the Ti center, a weak π complex (**2c**) was located, with a Ti–X distance of 2.67 Å (Figure 6). In this weak π complex, the Ti center is coordinated in a pseudo-trigonal-bipyramidal environment with ethylene and the counterion in the axial positions while the ancillary ligand (CpSiMe₂N^t-Bu) and the methyl group are in the equatorial plane. The weak π complex is 14.0 kcal/mol higher in energy than the separated reactants and much higher in energy than its analogue in the cis case (**2a**). The destabilization of the system is in the first place due to the displacement of the counterion from the Ti center (Ti– μ -Me = 2.88 Å). It is further caused by the strong trans-like influence between the CH₃ group and the ancillary ligands (CpSiMe₂N^t-Bu) in the equatorial plane.

To form a real π complex, the ethylene monomer is pushed closer to the Ti center, as in the case of the cis approach. A transition state (**TS[2c-2d]**) for the ethylene uptake with a small internal barrier (1.0 kcal/mol higher than **2a**) was located at a Ti–X distance of 2.52 Å. It is interesting that the counterion in **TS[2c-2d]** (Ti– μ -Me = 2.90 Å, Figure 6) is not displaced from the Ti center as far as in **TS[2a-2b]** (Ti– μ -Me = 3.43 Å), although **TS[2a-2b]** is much more stable than **TS[2c-2d]** (8.9 vs 15.0 kcal/mol). It suggests that the trans influence between the CH₃ group and ancillary ligands (CpSiMe₂N^t-Bu) in **TS[2c-2d]** may play an important role in destabilizing the system.

A real π complex (**2d**) was found after the uptake transition state (**TS[2c-2d]**, Figure 6). The ethylene in **2d** is closer to the Ti center (Ti–X = 2.47 Å) than in **2c**. This real π complex is slightly more stable (0.8 kcal/mol) than **TS[2c-2d]**, most likely due to the α -agostic interaction between Ti and the methyl group indicated by the short Ti–H _{α} distance (2.40 Å) and small T–C _{α} –H _{α} angle (93.3°). The structure of **2d** is characterized by a significant displacement of the counterion from the Ti center. However, the Ti– μ -Me distance in **2d** (3.50 Å) is still shorter than that in **2b** (4.30 Å), suggesting again that the trans-like influence between the CH₃ group and the ancillary ligands (CpSiMe₂N^t-Bu) play an important role in destabilizing the system.

Starting from the real π complex, the ethylene insertion easily takes place by reducing the C _{α} –C_{Et} distance, leading to a transition state (**TS[2d-3]**) that is 15.8 kcal/mol higher in energy than the separated reactants. The internal barrier is only 1.6 kcal/mol. This transition state is much earlier than in the cases of the cis

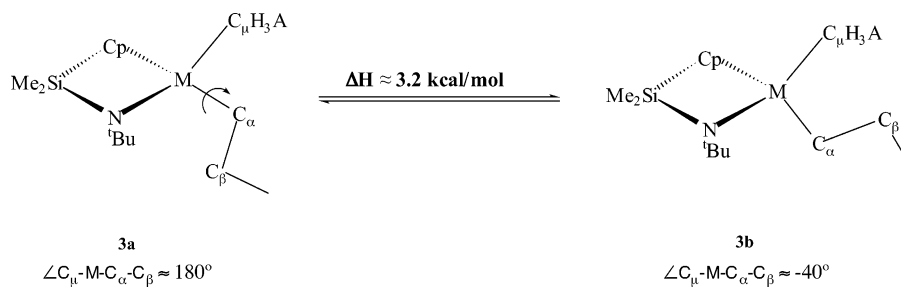


Figure 7. Resting states of the new ion pair (CpSiMe₂NtBu)(propyl)Ti- μ -MeB(C₆F₅)₃.

approach and the free cation, as can be seen by the long C_α-C_{Et} and Ti-C_{Et} distances (2.48 and 2.42 Å, respectively). The Ti- μ -Me distance (3.43 Å) in **TS[2d-3]** is much shorter than that in **TS[2b-3]** (4.44 Å) and even slightly shorter than in **2d** (3.50 Å). The small Ti-C_α-H_α angle (82.7°) suggests that the α -agostic interaction between the Ti center and the methyl group is still present in **TS[2d-3]**, although it is much weaker (Ti-H_α = 2.22 Å) than in both **TS[2b-3]** and **TS[II-III]**.

The gas-phase insertion barrier found here of 15.8 kcal/mol for the trans approach is again in good agreement with the corresponding value (13 kcal/mol) determined by Lanza et al.^{8c} for their corresponding pathway A, again confirming that the two methods afford quite similar energetics.

A problematic point in the study of systems as complex as the catalysts treated here is the employment of fixed (arbitrary) reaction coordinates. Ideally, use should be made of the intrinsic reaction coordinate (IRC) introduced by Fukui.²⁰ Unfortunately, the IRC method would be too expensive to apply for the systems treated here. Instead, Lanza et al.^{8c} have adopted two different reaction coordinates for the cis (pathway C) and trans (pathway A) approaches, respectively, consisting of the distances for the emerging Ti-C (pathway C) and C-C bonds (pathway A). We have on the other hand adopted two coordinates for both processes (see Computational Details), where the first describes the displacement of the anion (uptake) and the second the formation of the C-C bond (insertion). We attribute the different choices of reaction coordinates to the fact that the insertion transition state found in the trans approach (**TS[2d-3]**) is much different from that found by Lanza et al.^{8c} in their pathway A. The short Ti-C_{Et} distance in the transition state found by Lanza et al. (2.14 Å) indicates somehow an already formed Ti-C bond in this structure, while both the long Ti-C_{Et} and C_α-C_{Et} distances (2.42 and 2.48 Å, respectively) in **TS[2d-3]** suggest that **TS[2d-3]** is an earlier transition state in the insertion process. It is in this respect important to note that the energy of the system within a wide range of Ti- μ -Me (2.88 to 3.43 Å) and Ti-X distances (2.47–2.67 Å) varies by less than 2 kcal/mol. A similar shallow potential surface was found by Lanza et al.^{8c} around the transition state for their pathway A.

Another minor point related to the nature of the potential surface around the insertion transition state for the trans approach is the fact that in the gas phase we find a shallow minimum corresponding to a π complex that separates barriers of uptake and insertion of the same magnitude, whereas Lanza et al. find only

a single barrier without a π complex. However, with solvent effects included both studies find a “two barrier profile”. Interestingly, in solution the uptake barrier now becomes marginally larger in our DFT approach.

We shall finally mention that the MP2 method employed by Lanza et al.^{8c} in the gas phase favors the trans approach over the cis attack by 2 kcal/mol, whereas our DFT scheme as well as the DFT calculations (B3LYP) employed by Lanza find the reverse preference by a small margin of 1–2 kcal/mol. Adding solvent effects diminishes in all cases the preference between the two approaches. Thus, it is not possible with certainty to say if there exists a clear preference for either approach in the first insertion as far as the CGC system is concerned. We shall now turn to a discussion of the second insertion.

II. Second Ethylene Insertion. We have discussed the first ethylene insertion into the Ti-Me bond of the (CpSiMe₂N^tBu)(Me)Ti- μ -MeB(C₆F₅)₃ system in the previous section. The product of the first ethylene insertion is a new ion pair in which the counterion is *reassociated* with the Ti center (Figure 4) and the methyl group is converted to a propyl chain. Lanza et al.^{8c} have recently reported a rudimentary discussion on the second ethylene insertion into the Ti-C_α bond of (CpSiH₂N^tBu)-(propyl)Ti- μ -MeB(C₆F₅)₃. They studied the insertion step and the related π complex by choosing only one possible reaction channel. We do agree with them that carrying out a full analysis of all possible reaction channels for second ethylene insertion is impractical. However, we shall in the following try to discuss the chain propagation, represented by the second ethylene insertion, more comprehensively, by considering both uptake and insertion steps as well as the conformational problems of the propyl group.

1. Resting State of the Ion Pair. As mentioned above, the product from the first ethylene insertion is an ion pair with a propyl chain attached to the Ti center. It is likely that the orientation of the propyl chain will influence the approach of the second ethylene toward the Ti catalyst. Therefore, it is necessary to look at the possible conformations of the propyl chain in the ion pair so as to determine the resting state of the catalyst.

It follows from our calculation that the new ion pair has two stable conformations in which the CH₂CH₃ end group of the propyl chain points either away (**3a**; $\angle C_{\mu}-Ti-C_{\alpha}-C_{\beta} \approx 180^{\circ}$) or toward (**3b**; $\angle C_{\mu}-Ti-C_{\alpha}-C_{\beta} \approx -40^{\circ}$) the anions CH₃A⁻ (see Figure 7). Actually, **3a** is the product of the first ethylene insertion from the cis approach, while **3b** is the product from the trans approach. The **3a** conformation is more stable than **3b** by 1.7 kcal/mol. These two structures interconvert by

(20) Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363.

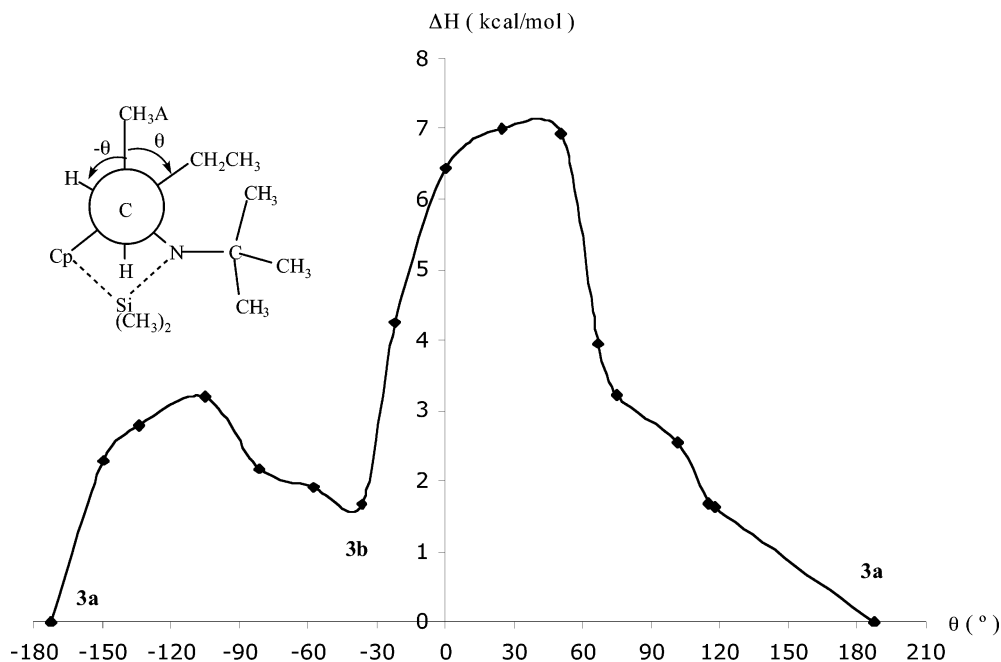


Figure 8. Energy profile for the rotation of the CH_2CH_3 end group along the $\text{Ti}-\text{C}_\alpha$ bond in $(\text{CpSiMe}_2\text{NtBu})(\text{propyl})\text{Ti}-\mu\text{-MeB}(\text{C}_6\text{F}_5)_3$.

rotating the CH_2CH_3 end group around the $\text{Ti}-\text{C}_\alpha$ bond. The rotational barrier is only 3.2 when the CH_2CH_3 end group rotates counterclockwise toward the Cp ligand (starting from **3a**), although the clockwise rotation toward N (see Figure 8) has to overcome a slightly higher barrier (7.0 kcal/mol), due to the greater steric repulsion between the CH_2CH_3 end group and the bulky $\text{C}(\text{CH}_3)_3$ group on the N atom. Overall, the low rotational barriers indicate that the CH_2CH_3 end group can freely rotate under normal polymerization conditions (140 °C). Therefore, the second ethylene insertion can start from either conformation of the ion-pair, and both cis and trans approaches have to be considered, as in the case of the first ethylene insertion.

2. Second Ethylene Insertion Process in the Presence of the Counterion. In the following discussion, a reaction pathway refers to the process connecting a certain conformation of the π complex formed during the reaction, with the direct uptake transition state to the reactants and the related insertion transition states to the product.

a. Cis Approach. (i) Pathway C_β and C_β' . With the most stable conformation **3a** of the ion pair as the starting point, the cis approach of the second ethylene toward titanium can displace the counterion from the metal center (Figure 9). Two possible pathways, C_β and C_β' , have been explored. They differ by having the CH_3 end group of the propyl chain pointing to either the N side or the Cp side. The uptake barriers for these two pathways were calculated to be 11.6 and 12.5 kcal/mol (compared to the most stable reactants) for C_β and C_β' , respectively. The uptake barriers here are significantly higher than that found in the case of the cis approach of the first ethylene uptake (8.9 kcal/mol). The long $\text{Ti}-\mu\text{-Me}$ distances in **TS[3a-4a]** and **TS[3a-4a']** (4.41 and 4.48 Å; compared with that in **TS[2a-2b]**, 3.43 Å) along with the increasing steric bulk of the propyl chain are responsible for the high uptake barriers.

After the uptake process, two real π complexes (**4a** and **4a'**) have been found in our geometry optimizations.

The $\text{Ti}-\text{X}$ distances in **4a** and **4a'** are 2.35 and 2.38 Å, respectively (Figure 9). It follows from our calculations that β -agostic interactions between the electrophilic Ti center and one of the two β -H atoms of the propyl chain can be observed in both **4a** and **4a'**, as evidenced by the shorter $\text{Ti}-\text{H}_\beta$ distances (1.97 and 1.93 Å). Although the counterions were further displaced from the metal centers in these two structures ($R_{\text{Ti}-\mu\text{-Me}} = 4.76, 4.73$ Å), the systems were stabilized by stronger β -agostic interactions. The stabilities of the two real π complexes, **4a** (8.2 kcal/mol) and **4a'** (9.1 kcal/mol), are similar to that of **2b** found in the case of first insertion.

The second ethylene insertion takes place when the $\text{C}_\alpha-\text{C}_{\text{Et}}$ distances are further reduced. At the transition states (**TS[4a-5]** and **TS[4a'-5]**), the $\text{C}_\alpha-\text{C}_{\text{Et}}$ distance is about 2.01 Å. Although the $\text{C}_\alpha-\text{C}_{\text{Et}}$ distances in **TS[4a-5]** and **TS[4a'-5]** are significantly shorter than that found for the cis approach of the first ethylene insertion (**TS[2b-3]**), the internal insertion barriers of 7.8 kcal/mol (**TS[4a-5]**) and 8.0 kcal/mol (**TS[4a'-5]**) are still higher than that (5.7 kcal/mol) found for the first ethylene insertion. The total insertion barriers are 16.0 and 17.1 kcal/mol for **TS[4a-5]** and **TS[4a'-5]**, respectively. The high insertion barriers are due to the significant displacement of the α -carbons on the propyl chains from the metal centers, as indicated by the long $\text{Ti}-\text{C}_\alpha$ distances, 2.26 and 2.27 Å, in **TS[4a-5]** and **TS[4a'-5]** (compared to 2.08 Å of **TS[2b-3]**). We note that β -agostic interactions are still present in both **TS[4a-5]** and **TS[4a'-5]**. It is also worth noting that the $\text{Ti}-\mu\text{-Me}$ distances in **TS[4a-5]** and **TS[4a'-5]** (4.61 and 4.50 Å) are remarkably shorter than those in the real π complexes **4a** and **4a'** (4.76 and 4.73 Å). This means that the counterions have started to reassociate to the metal centers before the ethylene insertion is finished.

For the second ethylene insertion, the rate-determining steps along pathways C_β and C_β' have to overcome a barrier in the gas phase higher than for the first insertion. However, our calculations show that solvent effects significantly reduce the insertion barriers, to 10.5

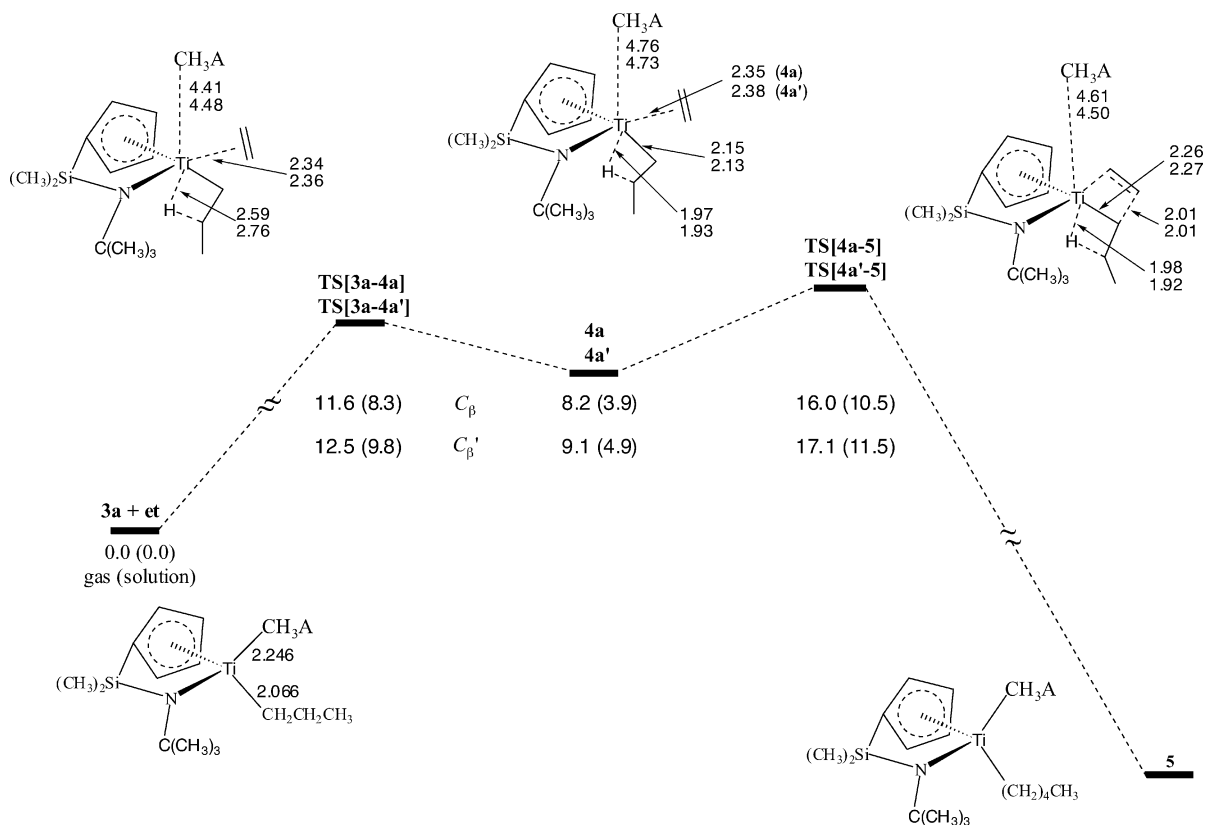


Figure 9. Energy profile for the second ethylene insertion through pathways C_β and C_β' .

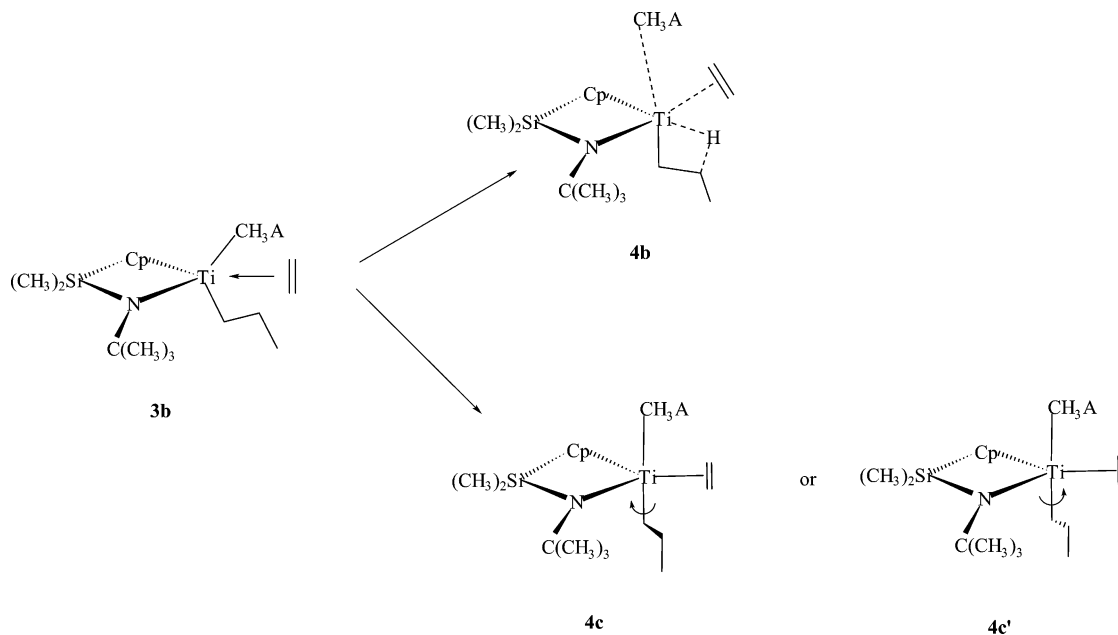


Figure 10. Cis approach of the second ethylene to the Ti center of the less stable confirmation **3b**.

and 11.5 kcal/mol for C_β and C_β' , respectively. The total barriers become even lower than that found for the first ethylene insertion (11.7 kcal/mol).

We turn next to the cis approach of the second ethylene to the Ti center of the less stable confirmation **3b**. This approach can either displace the counterion from the Ti center or force the propyl chain to rotate around the Ti– C_α bond (see Figure 10). Our computational results show that the displacement of the counterion results in the formation of an ethylene π complex (**4b**) with a β -agostic interaction between the electro-

philic metal center and the propyl group (Figure 10). Such a β -agostic interaction will resist the ethylene monomer approaching the α -carbon of the polymer chain, and thus, the ethylene insertion barrier will be prohibitively high. Thus, we shall in the following only discuss the lower path of Figure 10 involving **4c** and **4c'**.

(ii) Pathway C_α and C_α' . When the second ethylene is forced close to the Ti center of the less stable confirmation **3b** in the direction cis to the counterion, the propyl chains are rotated around the Ti– C_α bond

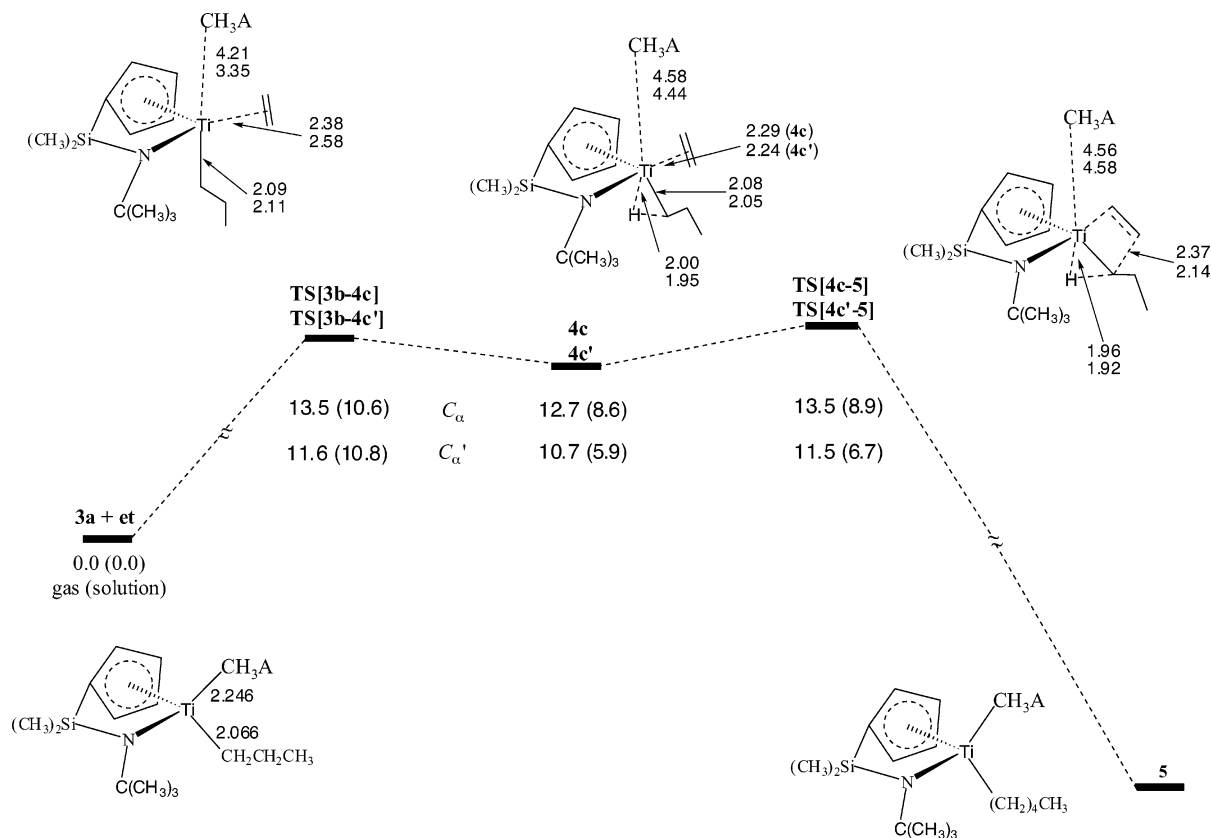


Figure 11. Energy profile for the second ethylene insertion through pathways C_α and $C_{\alpha'}$.

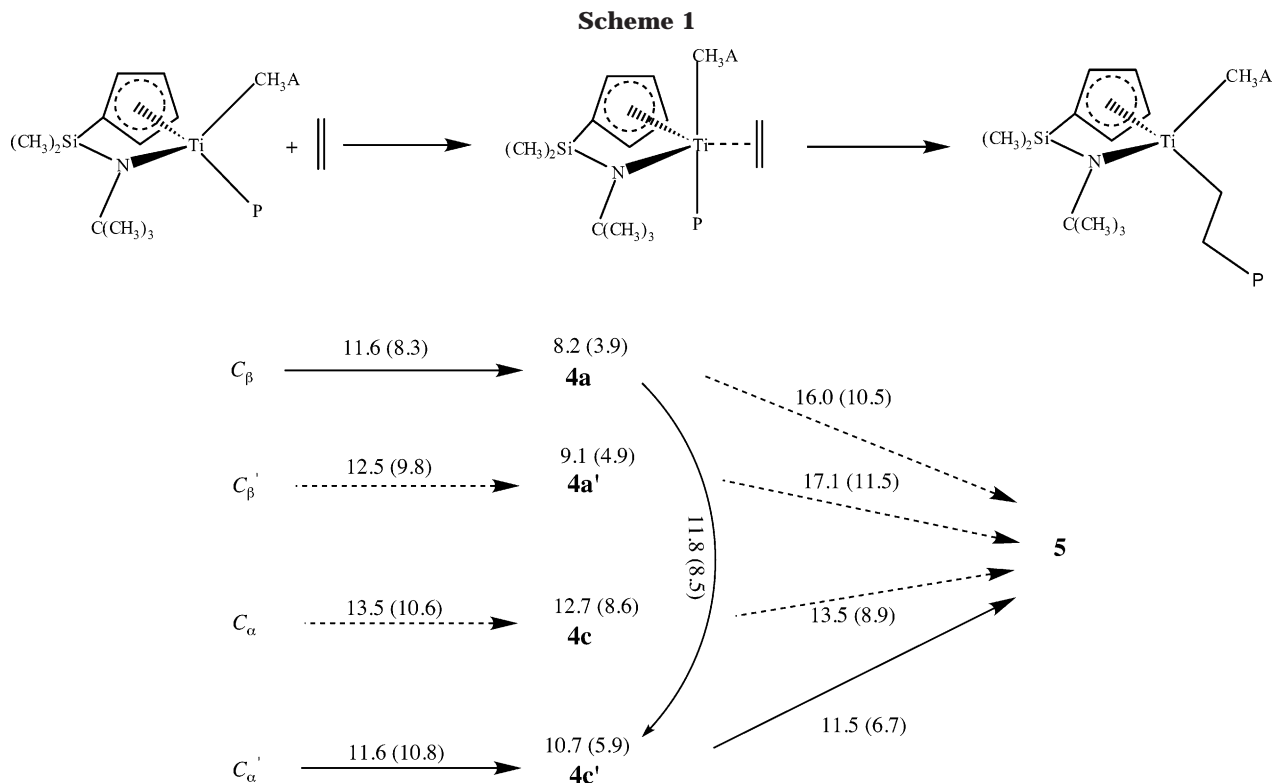
either counterclockwise (the CH_2CH_3 end group pointing to the N side, pathway C_α ; see Figure 10) or clockwise (the CH_2CH_3 end group pointing to the Cp side, pathway $C_{\alpha'}$). As has been found in the cis approach of the first insertion, the ethylene molecule must be brought close enough to the metal center so as to form a new Ti–C bond, while the C=C vector must be rotated so that one of its carbon atoms can approach the methyl group to form a new C–C bond. Our computational results show that the uptake barriers are 13.5 and 11.6 kcal/mol for C_α and $C_{\alpha'}$, respectively (Figure 11). These values are close to those found in pathways C_β and $C_{\beta'}$ and still higher than those found for the first ethylene uptake involving a cis approach (8.9 kcal/mol). The higher uptake barrier for pathway C_α is again due to the larger displacement of the counterion ($R_{\text{Ti}-\mu-\text{Me}} = 4.21 \text{ \AA}$) and the larger steric bulk of the propyl chain in **TS[3b-4c]** when compared with that in **TS[2a-2b]** (3.43 \AA). The larger steric bulk of the propyl chain in **TS[3b-4c']** is responsible for the high uptake barriers for pathway $C_{\beta'}$. The higher uptake barrier (13.5 kcal/mol) for pathway C_α compared to $C_{\alpha'}$ (11.6 kcal/mol) is due to the greater steric repulsion between the CH_2CH_3 end group and the bulky $\text{C}(\text{CH}_3)_3$ group on the N atom. The same steric interaction was found to be responsible for the largest rotational barrier for the propyl chain in Figure 8.

The uptake of the second ethylene gives two π complexes, **4c** and **4c'** (Figure 11). The short Ti–X bond lengths (2.29 and 2.24 \AA) and long Ti– μ -Me distances (4.58 and 4.44 \AA) in **4c** and **4c'** suggest that they are both real π complexes, such as those found previously (**2b**, **4a**, and **4a'**) in the cis approaches for both the first and second ethylene uptakes. They are 12.7 kcal/mol (**4c**) and 10.7 kcal/mol (**4c'**) higher in energy than the

most stable reactants, slightly less stable than the other real π complexes **2b**, **4c**, and **4c'**. The α -agostic interactions between Ti and the propyl chains can be found in both **4c** and **4c'**, as indicated by the short Ti–H α distances (2.00 and 1.95 \AA).

It is interesting that the second ethylene insertion can take place easily (with the internal barriers of less than 1.0 kcal/mol) once the α -agostic π complexes (**4c** and **4c'**) have been formed (Figure 11). This is similar to the case of the trans approach for the first ethylene insertion, where an α -agostic interaction was also found in the π complex **2d**. The total insertion barriers here are 13.5 and 11.5 kcal/mol, related to **TS[4c-5]** and **TS[4c'-5]**, respectively. The insertion barriers are almost identical to the corresponding uptake barriers. The insertion barrier for pathway $C_{\alpha'}$ is almost identical with that found by Lanza et al.^{8c} By comparing the structural parameters, one sees that **TS[4c'-5]** is very similar to the transition structure found by Lanza, indicated by the similar C_α – C_{Et} distances (2.14 and 2.19 \AA , respectively).

It follows from our calculations that pathway C_α has the lowest barrier (11.6 kcal/mol) and therefore is the most favorable reaction path for the cis approaches of the second ethylene insertion in the gas phase. In contrast to our finding for pathways C_α and $C_{\alpha'}$, where the second ethylene insertions are the rate-terminating steps, no matter whether solvent effects are included or not, the second ethylene uptake in pathways C_α and $C_{\alpha'}$ become the rate-determining steps when solvent effects are included in our calculations. The total barriers are 10.6 and 10.8 kcal/mol higher in energy than the most stable reactants (**3a** and ethylene), respectively. The decrease in energy due to the solvent



effects for **TS[3b-4c]** and **TS[3b-4c']** (see Figure 11) are smaller than those for other transition states of the second ethylene uptake and insertions because of the smaller degree of ion-pair separation in both **TS[3b-4c]** and **TS[3b-4c']**.

We have so far discussed the four possible pathways of the cis approach for the second ethylene uptake starting from either **3a** or **3b**. Overall, pathway C_{α}' has been found to be the most favorable reaction path in the gas phase because of the low uptake and insertion barriers. It should be pointed out here that the entire propagation reaction could also take place by combining the uptake of one path with the insertion of another path as long as a facile interconversion is possible between the π -complex associated with the uptake and the π -complex associated with the insertion. Thus, as shown in Scheme 1, one could envision uptake to proceed along path C_{β} leading to the π complex **4a** with an uptake barrier of 8.3 kcal/mol in solution. After that, **4a** might interconvert to **4c'** with an internal barrier of 4.6 kcal/mol (absolute barrier 8.5 kcal/mol). In the final step insertion can proceed along path C_{α}' from **4c'** to **5** with a barrier of 6.7 kcal/mol in solution. The overall barrier of propagation would now be 8.5 kcal/mol and be determined by the complexation process (mainly the uptake step).

Although the overall reaction barrier (11.6 kcal/mol) for the cis approach of the second ethylene insertion in the gas phase is very close to that (11.5 kcal/mol) found by Lanza et al.,^{8c} it is interesting to note that the ethylene uptake and π -complex conversion step (not considered by Lanza) play a more important role in determining the reaction rate of chain propagation. This is especially the case in solution, where we, as already discussed, find ethylene complexation through C_{β} to be rate determining with a barrier of 8.5 kcal/mol. Our results are in general agreement with the recently

published experimental finding by Landis et al.,²¹ where they concluded that "the dramatic effect of cocatalyst on the reaction rate arises from the effect of the counterion on the alkene association equilibrium constant." Nifant'ev et al.⁸ⁱ have also found, from theoretical calculations, that the uptake of the ethylene monomer is the rate-determining step for the $Cp_2ZrEt-MeB(C_6F_5)_3$ system. Therefore, one sees that the influence of counterion and the solvent not only changes the reaction barriers but also alters the rate-determining step, from insertion to uptake.

b. Trans Approach. The trans approach to **3a** can be as in the cis case either displace the counterion or force the propyl chain to rotate around the Ti- C_{α} bond. The displacement of the counterion again results in forming an ethylene π complex (**4d**) with a β -agostic interaction between the electrophilic metal center and the propyl group (see Figure 12). The β -agostic interaction in this case as the cis case hinders the second ethylene insertion. Thus, we shall in the following only consider the approach of ethylene toward **3a**, in which the propyl chain rotates around the Ti- C_{α} bond.

(i) Pathways T_{α} and T_{α}' . When the propyl group is rotated along the Ti- C_{α} bond, our geometry optimizations show that the trans approach of the second ethylene to the metal center results in forming two ethylene π complexes, **4e** and **4e'** (Figure 12). In these two structures, **4e** and **4e'**, the CH_2CH_3 end group orients itself either to the N side (**4e**, pathway T_{α}) or to the Cp side (**4e'**, pathway T_{α}') (see Figures 12 and 13). An α -agostic interaction between the Ti center and the propyl chain can be found in both **4e** and **4e'**, indicated by the short Ti- H_{α} distances (2.45 and 2.43 Å) and small Ti- C_{α} - H_{α} angles (both 92.1°). The counterions

(21) (a) Liu, Z.; Somsook, E.; White, C. B.; Rosaaen, K. A.; Landis, C. R. *J. Am. Chem. Soc.* **2001**, *123*, 1193. (b) Landis, C. R.; Rosaaen, K. A.; Uddin, J. *J. Am. Chem. Soc.* **2002**, *124*, 12062.

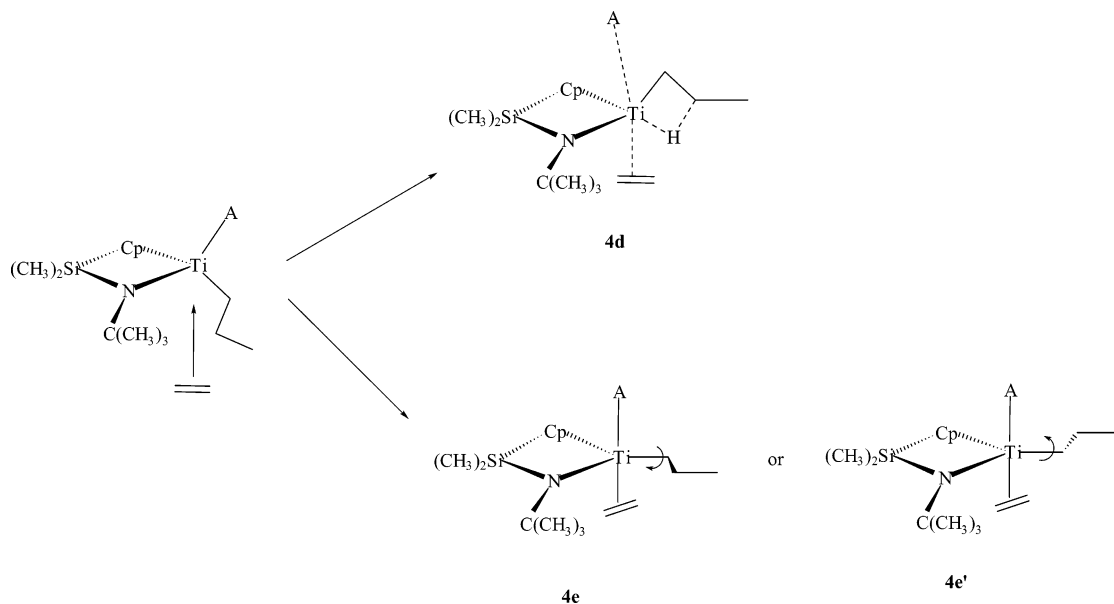


Figure 12. Trans approach of the second ethylene to the Ti center of the most stable confirmation **3a**.

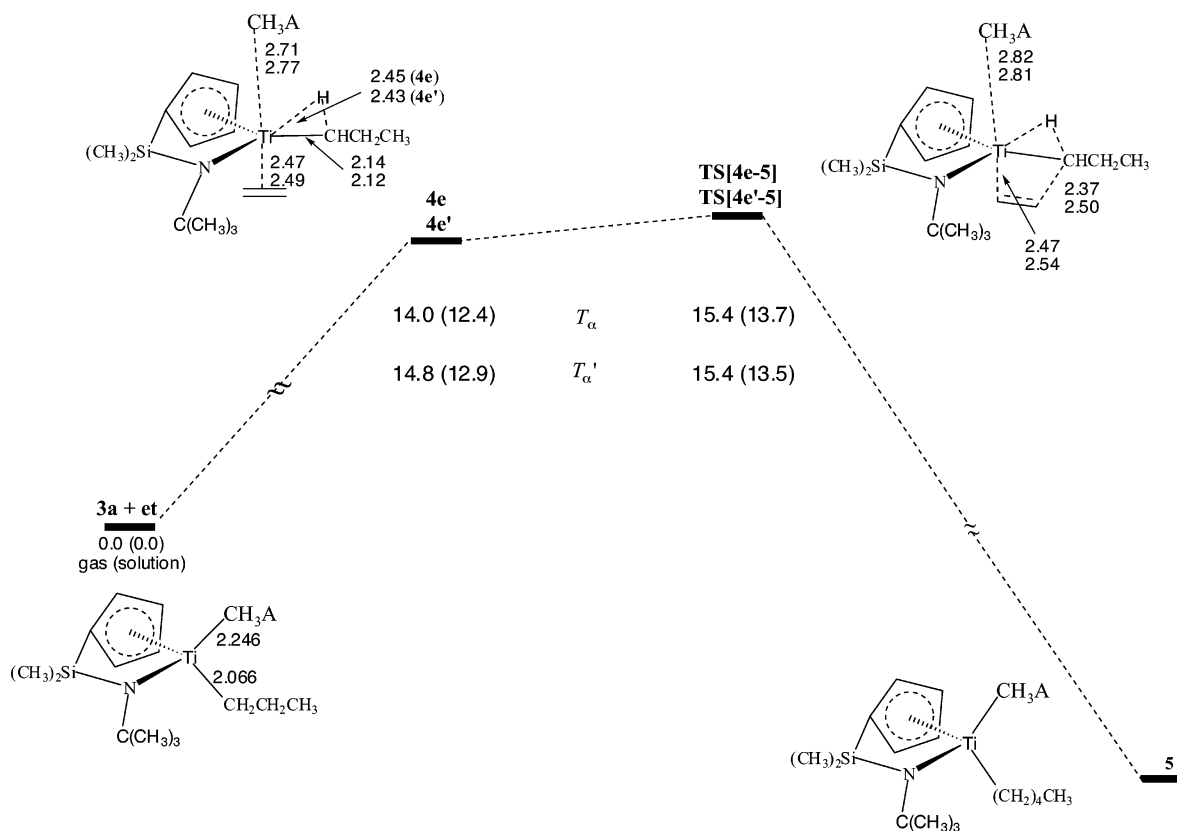


Figure 13. Energy profile for the second ethylene insertion through pathways T_α and $T_{\alpha'}$.

in these two structures are somewhat displaced from the metal centers with Ti- μ -Me distances of 2.71 and 2.77 Å, respectively. The Ti-X distances in the **4e** and **4e'** species are 2.49 and 2.47 Å, respectively, indicating that both **4e** and **4e'** are real π complexes. Interestingly, the short Ti-X distances here are quite similar to that for the real π complex (**2d**) found in the trans approach of the first ethylene insertion, while the Ti- μ -Me distances here are similar to that for the weak π complex (**2c**) (see Figures 6 and 13). The absence of weak π complexes in the present case may be due to

the greater steric repulsive interaction between ethylene and the CH_2CH_3 end group of the propyl chain. The energy of the system increases monotonically before the complexation interactions between ethylene and the Ti center become strong enough to form the real π complexes with energies that are 14.0 kcal/mol (**4e**) and 14.8 kcal/mol (**4e'**) higher than those of the separated reactants. Our computational studies did not reveal any uptake barrier for the olefin complexation process.

After the real π complexes, **4e** and **4e'**, are formed, the ethylene insertion easily takes place by reducing the

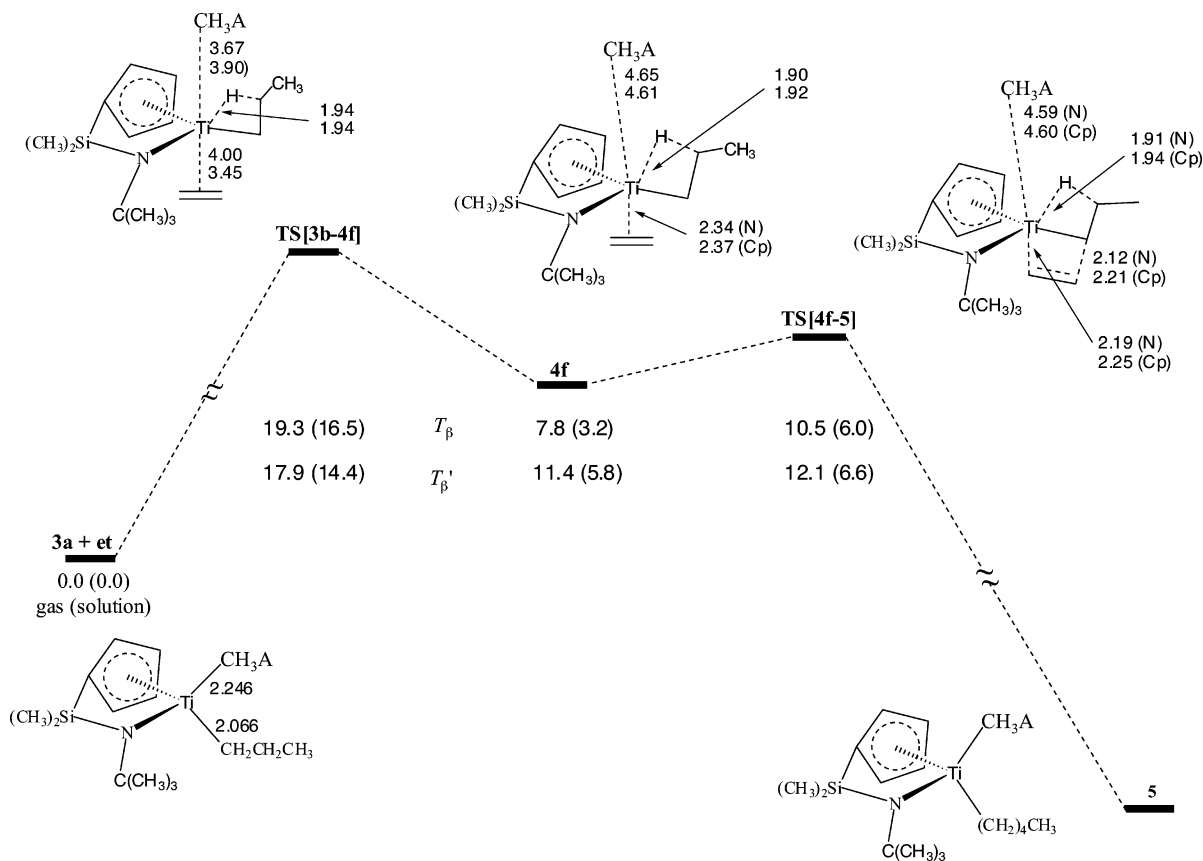


Figure 14. Energy profile for the second ethylene insertion through pathways T_β and T_β' .

C_α - C_{Et} distance, as in the case of the first insertion, giving rise to the two transition structures **TS[4e-5]** and **TS[4e'-5]**, respectively. The α -agostic interactions can be found between the Ti centers and the propyl groups in both structures (see Figure 13). It is worth noting that the counterions have not been displaced as much as found in the case of first ethylene insertion. The Ti- μ -Me distances are only 2.82 and 2.81 Å in **TS[4e-5]** and **TS[4e'-5]**, respectively. However, as already found for the first insertion, the energy of the system does not change significantly within a wide range of Ti- μ -Me distances. Both **TS[4e-5]** and **TS[4e'-5]** are 15.4 kcal/mol higher in energy than the most stable separated species (ethylene and **3a**). The internal insertion barriers here are 1.4 and 0.6 kcal/mol: lower than that found for the first ethylene insertion (1.6 kcal/mol). The total barriers (15.4 kcal/mol) are slightly lower than that found for the first ethylene insertion (15.8 kcal/mol), indicating a marginally easier insertion from the trans approach for the second ethylene insertion. Although solvent effects can slightly reduce insertion barriers, the total barriers for T_α and T_α' (13.7 and 13.5 kcal/mol, respectively) are still the highest so far found for the second ethylene propagation in solution, even higher than that of the first ethylene insertion.

(ii) Pathways T_β and T_β' . We shall finally consider the trans approach of the second ethylene to the metal center in the less stable structure **3b**. Figure 14 shows the energy profile and the structures found for the critical points along this pathway from our calculations. Obviously, the β -agostic interaction between Ti and the propyl group is the common feature for all structures along this pathway. The H atom involved in the β -agostic interaction is situated in the position trans to the

incoming ethylene group, forming a H_β -Ti- C_α plane which is perpendicular to the N-Ti-Cp plane. The CH_3 end group of the propyl chain can orient itself either to the N side or to the Cp side in these structures.

It follows from Figure 14 that, to form a real π complex, the system has to overcome a high barrier related to the displacement of the counterion. Two transition structures, **TS[3b-4f]** (pathway T_β) and **TS[3b-4f']** (pathway T_β'), have been located in our linear transit calculations, in which the displacement of the counterion was described by increasing the Ti- μ -Me distance while the approach of the ethylene group to the Ti center was described by decreasing the Ti-X distance using the reaction coordinate $\Delta R = R(Ti-\mu-Me) - R(Ti-X)$. In **TS[4f-5]** and **TS[4f'-5]**, the counterions are displaced significantly from the metal center, as seen by the long Ti- μ -Me distances (3.67 and 3.90 Å), while the ethylene monomer is still far away from the metal center. The two transition states are 19.3 kcal/mol (**TS[4f-5]**) and 17.9 kcal/mol (**TS[4f'-5]**) higher in energy than the separated stable reactants. The real π complexes, **4f** and **4f'**, found here are more stable (7.8 and 11.4 kcal/mol) than those of pathways T_α and T_α' (14.0 and 14.8 kcal/mol) and in the trans case of the first insertion (14.2 kcal/mol). This is largely the result of the strong β -agostic interactions and complexations in these two structures. After the real π complexes are formed, the ethylene insertion can easily take place, as in the other cases of a trans approach. The transition states (**TS[4f-5]** and **TS[4f'-5]**) in this case are 10.5 and 12.1 kcal/mol higher in energy than the separated most stable reactants. Although the insertion barriers here are lower than those found previously in the trans approaches, the total barrier for this pathway is still

the highest, due to the large uptake barriers. The situation does not change, even when solvent effects are included in our calculations (see Figure 14). Therefore, pathways T_β and T'_β are not preferred for the second ethylene propagation.

In summary, it follows from our calculations as discussed above that the cis approach is preferred over the trans approach for the second ethylene propagation in the gas phase as well as in solution. Different from the first ethylene insertion, the ethylene uptake or π -complex conversion becomes the rate-determining step of chain propagation in ethylene polymerization. The total barriers for the second ethylene propagation are 11.6 and 8.5 kcal/mol in the gas phase and in solution, respectively.

Conclusion

We have so far studied the reaction mechanism of ethylene polymerization catalyzed by CGC in the presence of the counterion $\text{MeB}(\text{C}_6\text{F}_5)_3^-$ using a QM/MM method. The first ($\text{R} = \text{Me}$) and second ($\text{R} = \text{propyl}$) ethylene insertions into the Ti-R bond of $(\text{CpSiMe}_2\text{N}^t\text{-Bu})(\text{R})\text{Ti}-\mu\text{-MeB}(\text{C}_6\text{F}_5)_3$ (CGC) were studied as models for the initialization and propagation steps, respectively, of the polymerization process. The results from the comprehensive study of the influences of the counterion as well as solvent effects can be summarized as follows.

Both the counterion and solvent effects play important roles in the first and the second ethylene propagation and therefore cannot be ignored in the mechanistic study. The solvent effects reduce the reaction barrier significantly for both first and second ethylene propaga-

tion. The presence of the counterion not only has a significant influence on the internal insertion barriers but, more important, could also change the rate-determining step of the reaction, from ethylene insertion to ethylene uptake.

The cis approach is preferred over the trans approach for the second ethylene insertion in the gas phase as well as in solution.

The total reaction barrier for the first ethylene propagation has been calculated to be higher than that for the second ethylene propagation both in the gas phase and in solution. This is in general agreement with the most recent experimental findings by Landis et al.²¹ The total barriers are 11.7 and 8.5 kcal/mol for the first and second ethylene propagations, respectively, in solution. These barriers are comparable to the activation energy (13.3 kcal/mol) found experimentally for the same catalyst.²²

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Supporting Information Available: Tables giving Cartesian coordinates for all structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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