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The Influence of the Counter-ion $MeB(C_6F_5)_3^-$ and Solvent Effects on Ethylene Polymerization Catalyzed by $[(CpSiMe_2NR)TiMe]^+$: A Combined Density Functional Theory and Molecular Mechanism Study

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Summary: A combined density functional theory and molecular mechanism (QM/MM) method has been used to study the first (R = Me) and the second (R = propyl) insertion of the ethylene monomer into the Ti-R bond of $(CpSiMe_2N^tBu)(R)Ti\text{-}m\text{-}MeB(C_6F_5)_3$. The computational results, in agreement with experimental findings, show the influence of the counter-ion and the solvent not only changes the reaction barriers, but also alters the rate-determining step for the second ethylene propagation, from insertion to uptake. 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 results. The total barriers in solution are 11.7 kcal/mol and 10.5 kcal/mol for the first and second ethylene insertions, respectively. These insertion barriers are comparable to the activation energy (13.3 kcal/mol) found experimentally for the same catalyst (CGC).

Keywords: counter-ion; homogeneous catalyst; olefin polymerization; QM/MM modeling; reaction mechanism; solvent effect

Introduction

The "constrained geometry catalyst" (CGC) $[(CpSiMe_2N^tBu)TiR^+]$ has been the first commercialized single site catalyst for olefin polymerization[1] and has stimulated intensive investigations in recent years.[2-8] The active species in CGC has usually [3,4] been assumed to be the cation $[(CpSiMe_2N^tBu)TiMe^+]$ formed from the reaction of

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$(CpSiMe_2N^tBu)TiMe_2$ with a Lewis acid (A) according to

$$(CpSiMe_2N^tBu)TiMe_2 + A \rightarrow \underset{\text{ion-pair}}{[(CpSiMe_2N^tBu)TiMe^+][AMe^-]} \qquad (1)$$

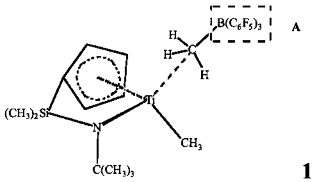
Theoretical studies on the naked cationic systems have provided useful information to further the understanding of the reaction mechanism of catalytic processes.[2b,3] However, these studies could only provide a limited understanding, since it has come to be well known that the counter-ion and solvent effects can significantly influence the catalytic activity and properties of the product polymers.[2b,9] Recent experimental [5,6] and theoretical [2b,3,4,7,8] works have shown that the ion-pair of Eq. (1) is far from dissociated under normal polymerization conditions. Therefore, it is necessary to include the anion in the description of the polymerization process as has been done first by Lanza et al [7a,b,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 counter-ion AMe^-, where the often employed activator $B(C_6F_5)_3$ has been used as the Lewis acid A in Eq. (1). We will focus on the second ethylene insertion into the Ti-C_α bond of $(CpSiMe_2N^tBu)(R)Ti$-μ-$MeB(C6F_5)_3$, to model the chain propagation step, where C_α presents the a carbon of the polymer chain R. The first ethylene insertion will also be explored for the purpose of comparison. The influence of the counter-ion will be assessed by comparing ethylene insertions with and without the counter-ion, $MeB(C6F_5)_3^-$, 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 counter-ion present.

Computational Details

Density functional theory (DFT) calculations were carried out based on the Amsterdam Density Functional (ADF) program version 2000.01, developed by Baerends *et al.*[10] and vectorized by Ravenek.[11] The gas phase energy differences were calculated by augmenting the local density approximation energy with Perdew and Wang's non-local correlation correction and Becke's exchange corrections (PWB91).[12] The solvation energies based on gas phase geometries were calculated by the Conductor-like Screening Model (COSMO)[13] with a dielectric constant of 2.023 to represent cyclohexane as the solvent. The insertion barriers were obtained from linear transit calculations with the C_α-C_{Et} distance between one C of the ethylene and the a-carbon of the CH_3 or $CH_2CH_2CH_3$ growing chain. On the other hand, the uptake barriers were obtained from linear transit calculations with the Ti-X distance (X is the midpoint of the C=C double bond) as reaction coordinate. A validated QM/MM model for the counter-ion has been used in our calculations.[8a] 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,[14] without electrostatic interactions. QM/MM atoms were also used to model the tertiary butyl group (^{t}Bu) 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.*[15]

Results and Discussions

I. First Ethylene insertion



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Previous studies have shown that, the contact ion-pair **1** is undissociated in cyclohexane and other solvents employed in polymerization.[4,7] In principle, an ethylene monomer can approach the ion-pair from any direction. However, in order to insert into the Ti-C_α 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 1, the ethylene molecule can approach the metal center from the direction *trans* (opposite) to the counter-ion, or *cis* to the counter-ion (A).

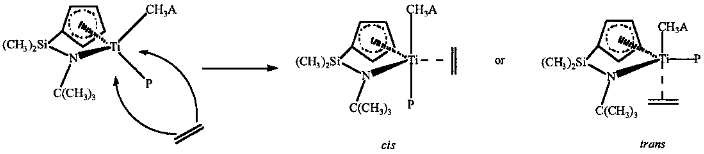


Figure 1. The *cis* and *trans* approaches

a. cis approach

Figure 2 shows the energy profile calculated for the *cis* approach of the first ethylene insertion into the $Ti\text{-}C_{Me}$ bond of $(CpSiMe_2N^tBu)(Me)Ti\text{-}\mu\text{-}MeB(C6F_5)_3$ (CGC). One sees here that, the ethylene insertion can still be described as a two-step process: monomer uptake and insertion, as in the cationic system studied previously.[2a] However, the π-complexation is now an exothermic process with a low uptake barrier of 8.9 kcal/mol in gas phase. The insertion process is the rate-determining step with a total barrier of 13.9 kcal/mol in gas phase. When solvent effects are included, the barrier is reduced to 11.7 kcal/mol. These results are in good agreement with the MP2 results found by Lanza *et al.*[7c] where the uptake and insertion barriers in gas phase are 7 and 15 kcal/mol, respectively.

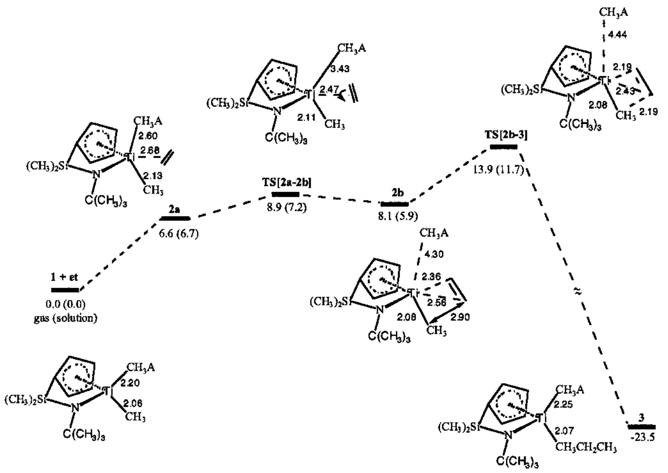


Figure 2. The energy profile for the *cis* approach of the first ethylene insertion for CGC system in gap phase and solution (values in parentheses)

b. trans approach

The energy profile for the *trans* approach of the first ethylene insertion into the Ti-C_{Me} bond of $(CpSiMe_2N^tBu)(Me)Ti$-μ-$MeB(C6F_5)_3$ (CGC) is shown in Figure 3. In gas phase, the total insertion barrier found here (15.8 kcal/mol) is only marginally higher than the uptake barrier (15.0 kcal/mol). It is interesting 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 to 2.67 Å) varies by less than 2 kcal/mol, and in solution the uptake barrier become marginally higher in our DFT approach. The total insertion barrier found here is again in good agreement with the corresponding value, 13 kcal/mol, determined by Lanza *et al.* for their corresponding pathway A.

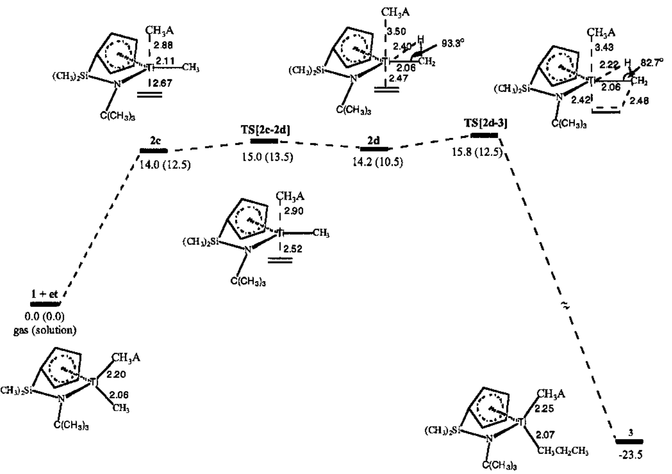


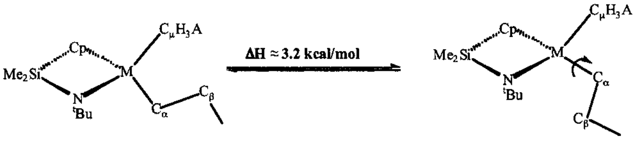
Figure 3. The energy profile for the *trans* approach of first ethylene insertion for CGC system in gap phase and solution (values in parentheses)

For the first ethylene insertion, we shall finally mention that the MP2 method employed by Lanza *et al.* 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 diminish 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:

The product of the first ethylene insertion into the Ti-Me bond of the (CpSiMe$_2$N^{t}Bu)(Me)Ti-μ-MeB(C6F$_5$)$_3$ system is a new ion-pair in which the counter-ion is *re-associated* with the Ti center (Figure 2 and 3) and the methyl group is converted to a propyl chain. 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.

1. resting state of the ion-pair:



3a

$\angle C_\mu\text{-M-}C_\alpha\text{-}C_\beta \approx -40°$

3b

$\angle C_\mu\text{-M-}C_\alpha\text{-}C_\beta \approx 180°$

Scheme 1

It follows from our calculation that the new ion-pair has two stable conformations in which the CH_2CH_3 end group of the propyl chain points either away, **3a** ($\angle C_\mu\text{-Ti-}C_\alpha\text{-}C_\beta \approx -40°$), or toward, **3b** ($\angle C_\mu\text{-Ti-}C_\alpha\text{-}C_\beta \approx 180°$), the anions CH_3A^- (see Scheme 1). Actually, **3a** is the product of the first ethylene insertion from the *trans* approach while **3b** is the product from the *cis* approach. The **3b** conformation is more stable than **3a** by 1.7 kcal/mol. These two structures interconvert by rotating the CH_2CH_3 end group around the Ti-C_α bond with a rotational barrier of only 3.2 kcal/mol,[16] indicating 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 conformations of the ion-pair, and both *cis* and *trans* approaches have to be considered.

2. second ethylene insertion process in the presence of the counter-ion

a. cis approach

Figure 4 shows our calculation results for the *cis* approach of the second ethylene insertion into the Ti-C_α bond of $(CpSiMe_2N^tBu)(propyl)Ti\text{-}\mu\text{-}MeB(C6F_5)_3$. Four p-complexes with different conformations have been found in our calculations. **4a** and **4a'** have α-agostic interactions between the electrophilic Ti center and one of the two a-H atoms of the propyl chain while **4b** and **4b'** have β-agostic interactions between the electrophilic Ti center and one of the two b-H atoms of the propyl chain. **4a** and **4b** differ from **4a'** and **4b'** by having the CH_2CH_3 or CH_3 end group of the propyl chain either pointing to the Cp side or the N side, respectively. A reaction pathway, C_α, C_α', C_β or C_β', refers to the process connecting a certain conformation (**4a, 4a', 4b** or **4b'**) of the p-complex formed during the reaction, with the direct uptake transition state to the reactants and the related insertion transition states to the product.

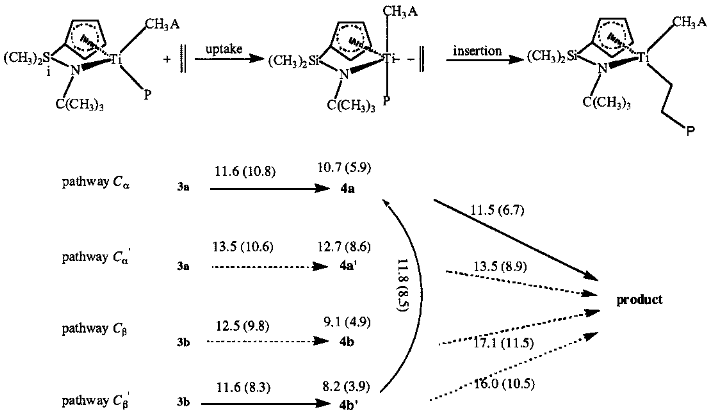


Figure 4. The calculation results for the *cis* approach of the second ethylene insertion in gap phase and solution (values in parentheses)

We can see from Figure 4 that pathway C_α is the favorable reaction path in gas phase because of the low uptake (11.6 kcal/mol) and insertion (11.5 kcal/mol) barriers. Although the lowest insertion barrier found here (11.6 kcal/mol) in gas phase is very close to that (11.5 kcal/mol) found by Lanza et al, it is important to note that the second ethylene uptake has been found to be the rate-determining step. Interestingly, it follows in our calculations that the energy required to convert **4c'** to **4a** is only 11.8 kcal/mol, almost equals to the related uptake barriers. It means that the ethylene monomer can approach the Ti center through different pathways to form **4a** and then overcome the lowest insertion barrier (11.5 kcal/mol) to finish the chain propagation step. However, the insertion step is still not the rate-determining process. When solvent effects are taken into account, the ethylene uptake through C_β' followed by a conformational conversion and insertion through C_α become the dominant reaction path. The total reaction barrier is reduced to only 8.5 kcal/mol. It is clear that, the ethylene uptake is the rate-determining step for the chain propagation in both gas phase and solutions. Our calculation results are, in general, consistent with the recently published experimental finding by Landis et al.[17], where they concluded that "the dramatic effect of the cocatalyst on the reaction rate arises from the effect of the counterion on the alkene association equilibrium constant." Nifant'ev et al.[7i] have also found, from theoretical calculations, that the uptake of the ethylene monomer is the rate-determining step for the $Cp_2ZrEt\text{-}\mu\text{-}MeB(C_6F_5)_3$ system. Therefore, one sees that the influence of counter-ion and the solvent not only changes the reaction barriers, but also alters the rate-determining step, from insertion to uptake.

b. trans approach

Table 1. The related energies of transition states and p-complexes for the *trans* approaches of the second ethylene to both **3a** and **3b**

Pathway	Uptake		p-complex		Insertion	
	gas	solution	gas	solution	gas	solution
T_β (**3a**)	19.3	16.5	7.8	3.2	10.5	6.0
T_β' (**3a**)	17.9	14.4	11.4	5.8	12.1	6.6
T_α (**3b**)	-	-	14.0	12.4	15.4	13.7
T_α' (**3b**)	-	-	14.8	12.9	15.4	13.5

Table 1 shows the related energies of transition states and p-complexes for the *trans* approaches of the second ethylene to both **3a** and **3b**. The *trans* approach of the second ethylene to **3a** (T_β or T_β') has also been found to be a two-step process, as in the case of the *cis* approach. Although the insertion barriers of both T_β and T_β' (10.5 and 12.1 kcal/mol, respectively) are very similar to that found by Lanza et al as well as in our *cis* approach, the higher uptake barriers (19.3 and 17.9 kcal/mol) here result in much higher total reaction barriers, even when the solvent effects are taken into account. Interestingly, no uptake barriers have been found in the *trans* approach of the second ethylene to **3b** (T_α

or T_α'). However, the insertion barriers are remarkably higher than the total barrier found for the *cis* approach, in both gas phase and solution.

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

Conclusion

We have so far studied the reaction mechanism of ethylene polymerization catalyzed by CGC in the presence of the counter-ion $MeB(C6F_5)_3^-$ using a QM/MM method. The first (R = Me) and second (R = propyl) ethylene insertions into the Ti-R bond of $(CpSiMe_2N^tBu)(R)Ti\text{-}\mu\text{-}MeB(C_6F_5)_3$ (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 counter-ion as well as solvent effects can be summarized as follows.

1) Both the counter-ion 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 propagations. The presence of the counter-ion not only has a significant influence on the internal insertion barriers but, more important, it could also change the rate-determining step of the reaction, from ethylene insertion to ethylene uptake.
2) The *cis* approach is preferred over the *trans* attach for the second ethylene propagation in gas phase as well as in solution.
3) The total reaction barrier for the first ethylene propagation has been calculated to be higher than that for the second ethylene propagation both in gas phase and the solution. This is in general agreement with the most recent experimental[17] and

other theoretical[7i] findings. The total barriers are 11.7 kcal/mol and 8.5 kcal/mol for first and second ethylene propagation, respectively, in solutions. These barriers are comparable to the activation energy (13.3 kcal/mol) found experimentally for the same catalyst.

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