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A Combined Density Functional Theory and Molecular Mechanics (QM/MM) Study of Single Site Ethylene Polymerization Catalyzed by [Cp{NC(^{t}Bu)$_2$}TiR$^+$] in the Presence of the Counterion, $CH_3B(C_6F_5)_3^-$

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Summary: A density functional study was conducted on the approach and insertion of ethylene monomer into the Ti-C_α bond of the catalyst system, CpNC(^{t}Bu)$_2$RTi-μ-Me-B$(C_6F_5)_3$ (R= methyl, propyl). A validated QM/MM model was used to represent the counterion. Solvent effects were incorporated with single point solvent calculations done with cyclohexane (ε = 2.023) as the solvent. For R=Me (the initiation step), approach and insertion of the ethylene was found to be endothermic, with the barrier for insertion being 12.7 kcal/mol for the most favourable case. For R=Pr (the propagation step), the insertion barrier was found to decrease slightly (11.5 kcal/mol for the most favorable case), corroborating experimental evidence of decrease in insertion barrier with increase in chain length. Termination by chain transfer to monomer was also considered, and found to be unfavourable, in comparison to insertion, by 8.6 kcal/mol for the propagation step. Solvent effects were found to be significant for the propagation step, changing the rate determining step from insertion to uptake for the most favorable case of insertion.

Keywords: catalysts; computer modeling; initiation; propagation; termination

Introduction

Single-site homogeneous catalysts have received increasing attention as alternatives to traditional Ziegler-Natta type heterogeneous catalysts. This is primarily due to their ability to achieve higher stereoselectivity, narrower molecular weight distribution, and higher activity. Among the more highly active homogenous catalysts are metallocenes and related organometallic compounds containing a Group IV transition metal. The general structure of these complexes contains a Group IV transition metal center (M) coordinated to two ligands (L) and two alkyl (R) groups: L_2MR_2.

These complexes by themselves are not very effective as polymerization catalysts, but require activation by a co-catalyst or a counterion. The co-catalysts are generally Lewis acids, such as tris(pentafluorophenyl)borane or methylalumoxane (MAO), whose function is to abstract one of

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the alkyl groups as R^- to produce the charge separated contact ion-pair, L_2MR-μR-A. This contact ion-pair can then dissociate to form the form the cationic complex, L_2MR^+, which is generally accepted [1-11] to be the activated metal catalyst, and the negatively charged counterion, AR^-.

Several theoretical studies, [12-19] investigating the insertion process, have been conducted, using the bare cation, L_2MR^+, as the model for the single site catalyst. However, recent findings indicate [7-10,20-21] that the anionic counterion plays an important role in the polymerization process. Calculations showed [20-21] that the energy required to separate the ions in the contact ion-pair was very high, which implied that the counterion would remain in the vicinity of the cation during the insertion process. Figure 1 below shows the mechanism for monomer (ethylene) insertion into the M-R bond of the catalyst, with the inclusion of the counterion.

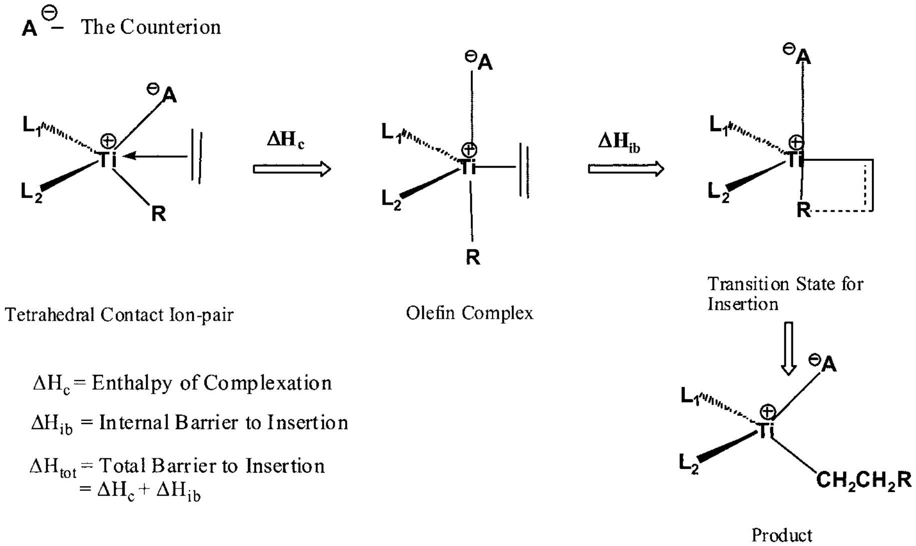

Figure 1. The mechanism for the complexation and insertion of the ethylene monomer into the metal-carbon bond of the cationic catalyst, L_2TiR^+, with the inclusion of the counterion.

Figure 1, however, shows only one of the ways in which the ethylene monomer can approach the contact ion-pair, L_2TiR-μR-A. Depending on the position of the ethylene monomer relative to the μ – alkyl bridge of the ion-pair, there are two modes of approach of the ethylene. It can attack the ion-pair cis to the μ-alkyl group (as in Figure 1), an approach which will be denoted as the "cis" approach. The alternate mode of attack of the monomer, trans to the μ-alkyl group, will be denoted as the "trans" attack.

Unfortunately, due to the size of the counterions, theoretical studies of the mechanism outlined in Figure 1, where the counterion is incorporated, are difficult and involve considerable computational effort. Hence few examples of such studies are found in the literature.[20-31] Nifant'ev *et al.*[22] have studied ethylene insertion for the $Cp_2ZrEt^+A^-$ ($A^- = CH_3B(C_6F_5)_3^-$, $B(C_6F_5)_4^-$) systems. Lanza [23] investigated olefin insertion into the Ti-CH_3 and the Ti-C_3H_7 bond of the $H_2Si(C_5H_4)(^tBuN)TiCH_3$-$CH_3B(C_6F_5)_3$ ion-pair; Fusco [24] and Bernardi [25] studied the same process for $Cp_2(Ti/Zr)CH_3$-$Cl_2Al[O(Al(CH_3)_3AlHCH_3]_2$ and $Cl_2TiCH_3(\mu\text{-}Cl)_2AlH_2$ respectively. Chan *et al.*[26] have investigated the formation of ethylene separated ion-pair complexes for ion-pairs formed between different catalysts and the counterion $B(C_6F_5)_3CH_3^-$, as well as ethylene insertion [20] into the Zr-CH_3 bond in the Cp_2ZrCH_3-μ-CH_3-$B(C_6F_5)_3$ system.

In an earlier theoretical study, [31] we investigated the insertion of the ethylene monomer into the methyl chain of different catalyst systems of the type $L_1L_2TiCH_3^+$, in the presence of the counterion. The counterion used for the purpose of the investigation was $B(C_6F_5)_3CH_3^-$. For the sake of computational expediency, a QM/MM model was used for the counterion. This allowed us to study a large number of different systems. In the QM/MM model, the perfluorophenyl (C_6F_5) groups in $B(C_6F_5)_3CH_3^-$ were replaced with molecular mechanics (MM) atoms, and Cl atoms are used to cap the quantum mechanical (QM) system. Thus, $B(C_6F_5)_3CH_3^-$ was replaced with $BCl_3CH_3^-$ in the QM system. This model has been validated.[32-35]

In this present study, we investigate the approach of ethylene and its insertion into the Ti-methyl (initiation step) and Ti-propyl (propagation step) bonds for the $[CpNC(^tBu)_2TiR^+][B(C_6F_5)_3CH_3^-]$ ($R = CH_3$ and C_3H_7) ion-pair systems. The different approaches of the ethylene monomer, cis and trans to the μ-methyl group of the ion-pair, will be considered for each case. The purpose of the investigation will be to isolate the important factors that contribute to the barrier of insertion, and to compare and contrast the initiation and propagation steps for the same ion-pair system. The effect of the solvent on the insertion process will also be considered, with single point solvation calculations to determine the energy of solvation for the ion-pair, the olefin complexes and the transition states. Cyclohexane ($\varepsilon = 2.023$) will be used as the solvent.

Computational Details

The density functional theory calculations were carried out using the Amsterdam Density Functional (ADF) program version 2000.01, developed by Baerends *et al.* [36-39] and vectorized by Ravenek. [40] The electronic configurations of the atoms were described by a triple-ζ basis set on titanium ($n = 3$) for ns, np, nd and (n+1)s, augmented with a single (n+1)p polarization function. Double-ζ slater type orbitals (STO) basis were used for carbon (2s,2p), hydrogen (1s) and nitrogen (2s,2p), augmented with a single 3d polarisation function except for hydrogen where a 2p polarisation function was used. The gas phase energy difference was calculated by augmenting the local density approximation energy with Perdew and Wang's non-local correlation and exchange corrections (PWB91). [41] The solvation energies were obtained from a single point full QM calculation using the Conductor-like Screening Model (COSMO) [42,43] and optimized geometries from QM/MM calculations. A dielectric constant of 2.023 was used to represent cyclohexane as the solvent. The MM atoms were described using the SYBYL/TRIPOS 5.2 force field constants.[44] The code for QM/MM in ADF has been implemented by Woo *et al.* [45]

First Insertion Study

The insertion of the ethylene monomer was first considered for the system $CpNC(^tBu)_2TiMe^+$ in the absence of the counterion. QM/MM atoms were used to model the tertiary butyl groups, with hydrogens used as capping atoms. Hence the QM portion of the cation was $CpNCH_2TiMe^+$. The values of the ethylene complexation energy, ΔH_c, and the internal insertion barrier, ΔH_{ib}, were found to be –20.0 kcal/mol and 3.1 kcal/mol respectively. The total barrier for insertion, found by summing up the two values, was calculated to be –16.9 kcal/mol, indicating that the process is highly exothermic in nature.

Therefore, using just the naked cation as a model for the catalyst, one would be led to conclude that the cationic $CpNC(^tBu)_2TiMe^+$system is an excellent polymerization catalyst. This view is modified substantially when the counterion, $B(C_6F_5)_3CH_3^-$, is included in the calculations. Figure

2 below shows the cis approach of the ethylene monomer towards the ion-pair, $[CpNC(^tBu)_2MeTi\text{-}\mu\text{-}MeB(C_6F_5)_3$. The reaction coordinate used for this approach is $\Delta R = R(Ti\text{-}\mu\text{-}CH_3) - R(Ti\text{-}X)$: the difference between the distance of the midpoint of the ethylene monomer and the carbon of the methyl bridge from the metal centre. The energy values denoted in the figures are solvent corrected, with the corresponding gas phase values denoted in parenthesis.

As shown in Figure 2, the ethylene forms a π complex at a distance of about 2.57 Å, at an energy cost of 7.7 kcal/mol in comparison to the separated species. The ethylene moiety in the π complex lies perpendicular to the plane formed by the metal centre, the methyl chain and the μ carbon of the counterion. The reason for the endothermic nature of this complexation is the displacement of the counterion from the metal centre, in order to accommodate the ethylene molecule.

The ethylene molecule, then proceeds to rotate itself into the insertion plane. There is a barrier to this rotation of about 2.8 kcal/mol, after which it forms the "in plane" olefin complex, which lies 10.3 kcal/mol above the separated reactant species. After formation of the olefin complex the ethylene then approaches the methyl chain, to enable insertion into the Ti-C bond. The system is slightly destabilized as a result, leading eventually to the transition state for insertion, lying 12.7 kcal/mol above the reactants. The counterion is only slightly displaced from the cation at this stage, by only about 2.5 Å.

After formation of the transition state, the ethylene inserts and proceeds to form the product with the propyl chain, which lies at –24.0 kcal/mol below the separated species. Hence the total barrier to insertion for the cis approach is 12.7 kcal/mol. This is significantly different from the findings in the naked cation case, where the insertion transition state was found to be lower in energy than the reactants.

The trans approach of the ethylene was also studied, and also found to lead to the formation of a π complex, followed by insertion into the metal carbon bond. Like in the cis case, the displacement of the counterion during insertion was quite small: 2.54 Å, which suggests that for the first insertion, the counterion is only slightly displaced from the metal centre. The total barrier to insertion for this case was 15.5 kcal/mol. This implies that, for the initiation step of the monomer, the ethylene would insert via the cis mode of approach in preference to the trans.

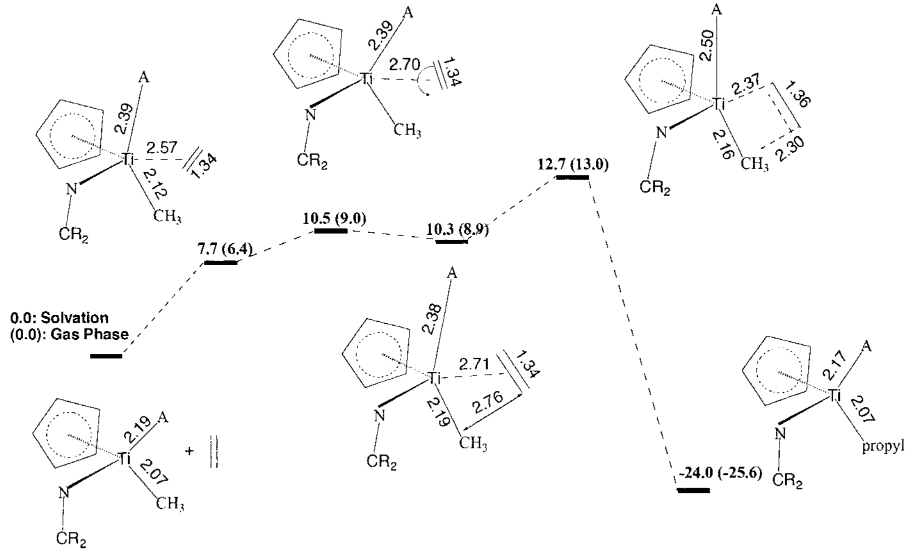

Figure 2. The energy profile for the cis approach of the ethylene monomer towards the contact ion-pair $[\mathrm{Cp}\{\mathrm{NC}({}^t\mathrm{Bu})_2\}\mathrm{TiMe}^+][\mathrm{CH_3B(C_6F_5)_3}^-]$.

Second Insertion Study

The results of the first insertion study indicated that the counterion had to be included to get a clear understanding of the insertion process. Therefore, for the second insertion investigation (the propagation step), we have ignored the naked cation case and focussed our attention on the approach and insertion of the ethylene monomer toward the contact ion-pair, $[\mathrm{Cp}\{\mathrm{NC}({}^t\mathrm{Bu})_2\}\mathrm{TiPr}^+][\mathrm{CH_3B(C_6F_5)_3}^-]$: the product from the initiation step, as discussed in the previous section.

The propyl chain in the contact ion-pair, $[\mathrm{Cp}\{\mathrm{NC}({}^t\mathrm{Bu})_2\}\mathrm{TiPr}^+][\mathrm{CH_3B(C_6F_5)_3}^-]$, can orient itself in different conformations. It is necessary to study these different conformations in order to determine the most stable resting state. This was done by a linear transit wherein the dihedral angle, θ, formed between the C_β-C_α-Ti and the C_α-Ti-μC planes was altered (see Figure 3 below) from −180 to 180 degrees, in order to rotate the chain so as to determine the most stable resting states. The accompanying energy profile in Figure 3 shows that the most stable resting states of the ion-pair correspond to the staggered conformations of the chain, with θ at -55° (**A**), 55° (**C**) and 178° (**B**) respectively. In contrast, the eclipsed conformation, with θ equaling 0° (**D**) was found to be an energy maxima, lying 7.6 kcal/mol above the most stable conformation, **A**.

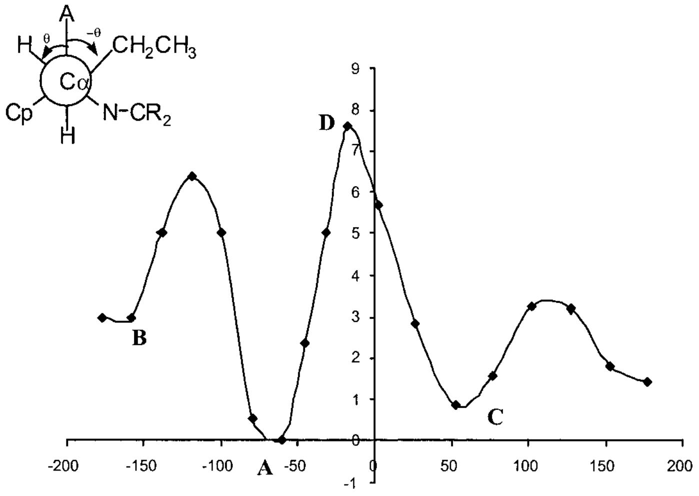

Figure 3. The relative stabilities of the different chain conformations, formed by rotation of the propyl chain in the contact ion-pair $[Cp\{NC(^tBu)_2\}TiPr^+][CH_3B(C_6F_5)_3^-]$.

For the insertion studies, the four different conformations, **A**, **B**, **C**, **D** shown in Figure 3 were considered. Beginning with the ion-pair in these four states, the approach of the ethylene monomer cis and trans to the μ-methyl bridge was studied. This gave rise, therefore, to eight possibilities, which will be discussed. The relative energies of the olefin complexes and insertion barriers were calculated with respect to the totally separated species: ethylene monomer and **A**, the most stable conformation of the ion-pair in its resting state.

Figure 4 below shows the cis approach of the ethylene monomer towards the contact ion-pair in the conformation **C**. This was found to be the most favourable insertion pathway for the propagation step. A π complex is formed similiar to the case for the first insertion. Insertion follows as the ethylene moiety approaches the α carbon.

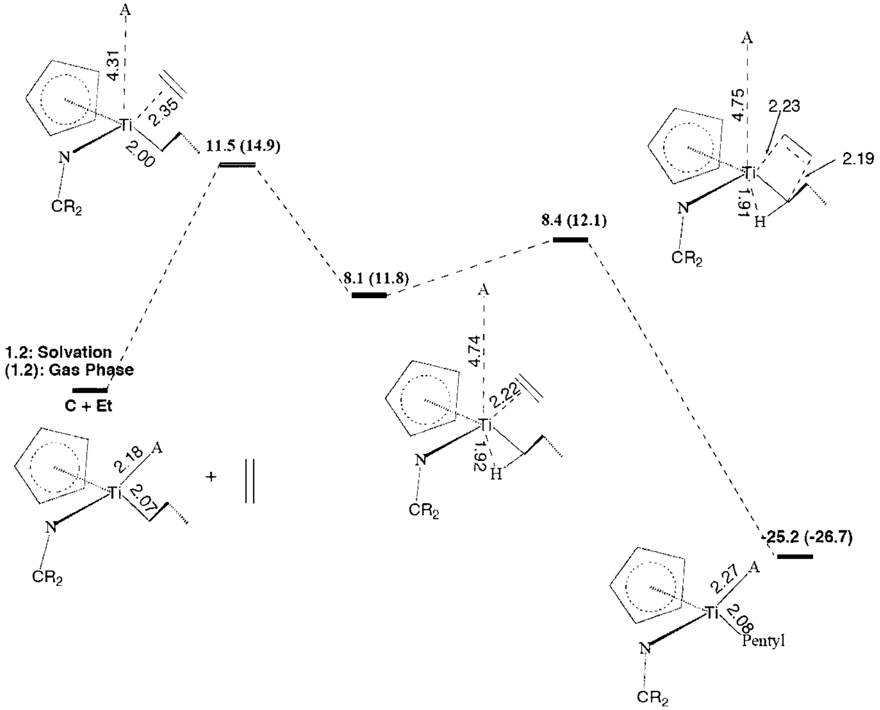

Figure 4. The energy profile for the cis approach of the ethylene monomer towards the contact ion-pair $[Cp\{NC(^tBu)_2\}TiPr^+][CH_3B(C_6F_5)_3^-]$, with the propyl chain lying out of the insertion plane, for the case **C**.

It is interesting to note, from Figure 4 above, that the counterion is much displaced from the metal centre during the insertion (from 2.18 Å to 4.75 Å), leading to significant charge separation. Hence solvent effects become significant, and play a role in influencing the rate determining step. In the gas phase, it is the insertion step that is rate determining, as seen in Figure 4. However, after solvent effects have been taken into account, the uptake of the monomer prior to formation of the π complex becomes the rate determining step. The barrier to insertion is, therefore, the uptake barrier: 11.5 kcal/mol. This is 1.2 kcal/mol lower than the barrier obtained during the initiation step (12.7 kcal/mol), which implies that the insertion of the monomer becomes easier with increase in the chain length, as has been observed experimentally by Liu *et al.*[46]

Two of the eight cases of ethylene approach do not lead to insertion but to termination. These are (i) the cis approach towards conformation **D** and (ii) trans approach towards **B**. In these two cases, the approach led to the chain transfer from the alkyl chain to the monomer. As an illustration, the trans approach towards **B** is shown in Figure 5 below. After the formation of the π complex, the insertion of the ethylene monomer would involve the rotation of the β carbon of the propyl chain out of the insertion plane, to facilitate the approach of the ethylene towards the α carbon. The barrier to this rotation was found to be high (~22 kcal/mol). Instead, the ethylene preferred to extract the β hydrogen from the chain, leading to termination (see Figure 5). The barrier to the chain termination was found to be 20.1 kcal/mol, which is higher than the insertion barrier by 8.6 kcal/mol.

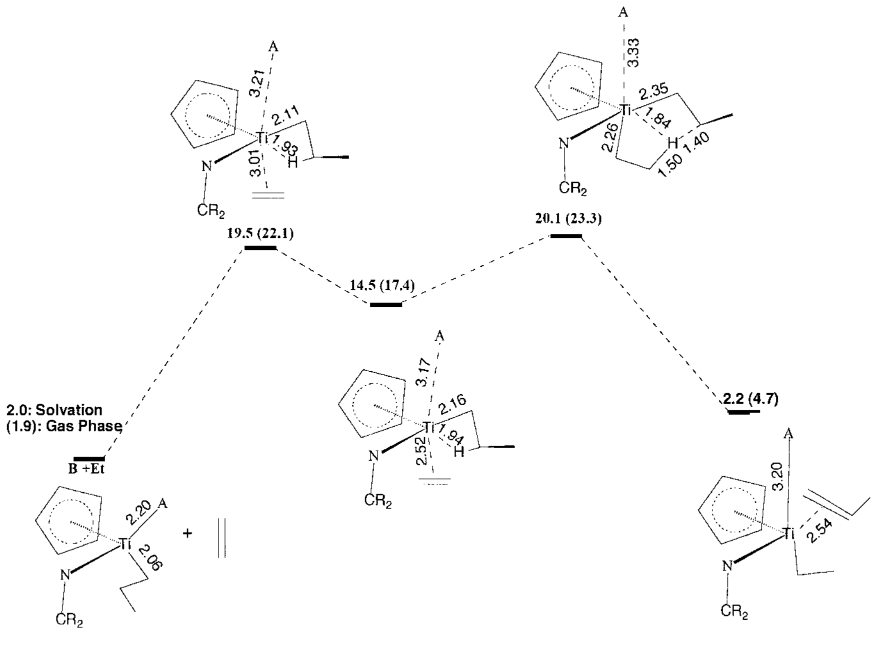

Figure 5. The energy profile for the trans approach of the ethylene monomer towards the contact ionpair $[Cp\{NC(^tBu)_2\}TiPr^+][CH_3B(C_6F_5)_3^-]$, for the case **B**.

Collected in Figure 6 are the results for the eight cases of monomer approach, cis and trans to the conformers **A**, **B**, **C** and **D**, leading either to insertion or termination. The gas phase values are also included in the parenthesis for comparison. Cis and trans approaches for the out-of-plane conformations, **A** and **C,** both lead to insertion, and have lower barriers than for the in-plane cases, **B** and **D** (see Figure 6). This suggests that the alkyl chain in the ion-pair would prefer to sit out of the insertion plane during monomer approach. The most likely mode of insertion would be through the cis attack for the **C** case (discussed in Figure 4 above). It is also clear from the values obtained that the ion-pair would strongly prefer insertion to termination, since the two approaches leading to termination have barriers much higher than the insertion barrier for the most favourable insertion case - cis approach, **C**.

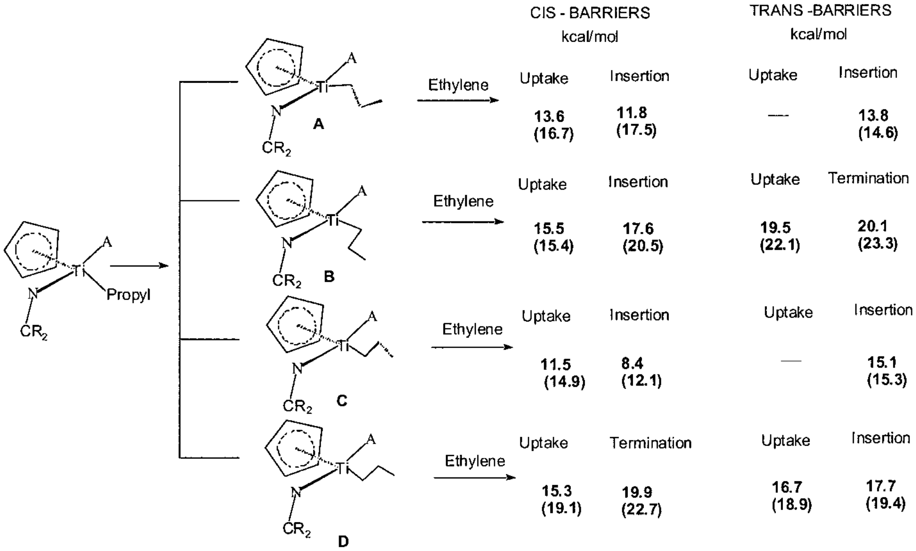

Figure 6. Overall picture of the Second Insertion Step – the barriers obtained from the cis and trans approaches of the ethylene monomer towards the contact ion-pair $[Cp\{NC(^tBu)_2\}TiPr^+][CH_3B(C_6F_5)_3^-]$, with the propyl chain in different conformations.

Conclusions

A density functional study was conducted on the approach and insertion of the ethylene monomer into the Ti-C_α bond for the ion-pair $CpNC(^tBu)_2RTi$-μ-Me-$B(C_6F_5)_3$(R = methyl, propyl). The chief conclusions from the study are summarized below.

(a) The counterion plays a very significant role in the insertion process for both the first (R = methyl) and second (R = propyl) insertions of the ethylene monomer. The incorporation of the counterion makes the insertion process highly endothermic, in contrast to the corresponding naked cationic case, where the insertion was found to be exothermic. Moreover, for the second insertion, the presence of the counterion influences the alkyl chain conformation of the ion-pair, making the out-of-plane chain conformations more favourable for insertion than the in-plane ones.

(b) The barrier to second insertion for the most favorable approach (11.5 kcal/mol) is found to be 1.2 kcal/mol lower than the barrier for the first insertion (12.7 kcal/mol). This reduction in the height of the barrier, upon going from first to second insertion, corroborates experimental findings. [46]

(c) Solvent effects become important with the increase in the chain length. The displacement of the counterion increases during most approaches of the ethylene monomer during the second insertion, thereby increasing the charge separation between cation and anion. Therefore, incorporation of the solvent effects reduces the barriers to uptake and insertion to a significant extent. In fact, for the cis approach of ethylene towards **A**, inclusion of solvent effects reverses the rate determining step, making the uptake barrier higher than the insertion.

Acknowledgement

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