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Theoretical Study of the Copolymerization of Ethylene and Propylene by a Heterogeneous Ziegler−Natta Catalyst

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ABSTRACT: The copolymerization of ethylene and propylene by a heterogeneous Ti/$MgCl_2$ Ziegler−Natta catalyst is studied with density functional theory calculations. One particular model of an active site, the so-called "$TiCl_3$-based slope site", is looked at in detail. The influence of the previous monomer insertion is allowed for by examining sites where the growing polymer chain is modeled by a methyl, propyl, isobutyl, and 2-butyl group. Propylene is found to form a more stable π-complex with the active site than ethylene. Propylene is also found to have a lower barrier to insertion into the Ti−C bond than ethylene in most instances and to prefer to insert in a 1−2 orientation rather than a 2−1 orientation. The relative height of the insertion barriers of ethylene and propylene is in contradiction to experimentally observed copolymer compositions. Increasing steric bulk of the polymer chain disfavors propylene insertion relative to ethylene insertion and 1−2 propylene insertion relative to 2−1 insertion. Some of the insertion reactions examined are shown to be significantly stereoselective due to the interaction of propylene and the growing polymer chain. Despite these stereoselective reactions, the active site modeled here will not produce tactic polymer except under some special circumstances which are outlined.

1. Introduction

In recent publications,[1,2] we have applied quantum chemical methodologies to the study of ethylene polymerization by heterogeneous Ziegler−Natta catalysts. Polyethylene is not the only polymer that can be synthesized with Ziegler−Natta catalysts. A number of other α-olefins can be homopolymerized, and many copolymers can be formed by these catalysts.[3−5] Each homopolymer and copolymer will of course have its own distinct properties, and an enormous range of different plastics can be synthesized through suitable choices of monomers and reaction conditions. As a natural extension of previous work we have studied the homopolymerization of larger α-olefins and copolymerization reactions, placing particular emphasis on the copolymerization of ethylene with another linear α-olefin.

A wide range of copolymers can be synthesized using Ziegler−Natta catalysts. Possible monomers include ethylene, propylene, linear olefins such as 1-butene and 1-hexene, branched monomers such as 3-methyl-1-butene and 4,4-dimethyl-1-pentene, and cyclic monomers such as cyclohexene and cycloheptene. The composition of the copolymer formed in a given reaction largely can be related to the homopolymerization rates of the individual monomers. Ethylene homopolymerizations proceed significantly faster than those of other olefins, and as a result, the copolymer formed in the reaction of ethylene and another monomer will be made up mostly of ethylene. The reactivity of the monomers is not the only factor determining the composition of a copolymer. The reaction conditions, structure of the catalyst, identity of the cocatalyst, and particular combination of monomers have also been shown to be important.[3,5] Analyses of product copolymer produced by a given catalyst suggest that several different types of active site are present, each producing copolymer with an ethylene:α-olefin ratio differing from the others.[5]

The consideration of larger olefin monomers and copolymerization introduces somewhat more complexity than was present in the previous studies of ethylene homopolymerization. With the exception of ethylene and other symmetric monomers like cyclohexene, monomers have two possible modes of insertion: 1−2 (primary, head to tail) and 2−1 (secondary, head to head or tail to tail) insertion. In general, heterogeneous Ziegler−Natta catalysts cause 1−2 insertion of linear α-olefins.[3,6] The reactivity and regioselectivity of a given monomer will depend on the structure of the growing polymer chain near the active site and therefore on the result of the previous insertion reaction. Finally, α-olefins larger than ethylene can form tactic polymer through stereoselective insertions although this is less important in copolymerization reactions as the large proportion of ethylene in the polymer prevents tacticity from becoming an issue.

The present study will be restricted to the copolymerization of ethylene with propylene. The reactions corresponding to propylene homopolymerization are necessarily a subset of those of ethylene−propylene copolymerization. The results presented here thus should also provide some insight into the homopolymerization of propylene. Most of the conclusions from this study should be applicable to the reactions of other linear α-olefins since the polymerization properties of these higher olefins are generally fairly similar to those of propylene but different than those of ethylene. For example, the activity of a given catalyst to ethylene polymerization is usually about 20 times greater than its activity toward propylene polymerization while propylene polymerization is generally only about twice as fast as 1-butene polymerization.[3,5]

In our previous work a number of possible models for the active site were considered. For many of these sites, the monomer could approach from two different directions. All told, over a dozen reaction pathways were considered. If the monomer is propylene rather than ethylene, the complexity of the problem increases significantly as the many possible orientations of the

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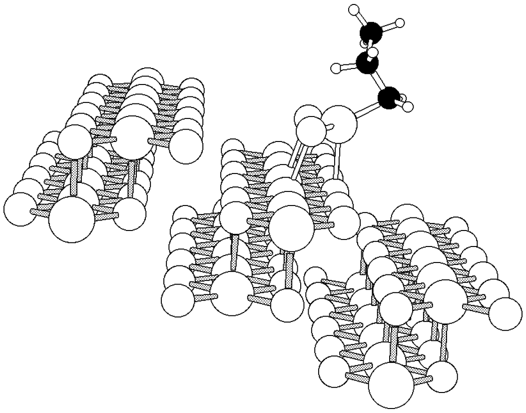


Figure 1. Assumed model of the active site with propyl group as the model of polymer chain.

approaching propylene molecule must be taken into account as well as the several different models of the growing polymer chain that will appear. If ethylene is added so that copolymerization may be considered, the situation becomes even more complex. At this point, two possible approaches can be taken. In one approach, several of the many possible insertion reactions can be eliminated on the basis of simple steric or chemical arguments and the remaining smaller set of reactions considered over a number of possible sites. Alternatively, all of the possible reactions could be examined for a single site. The focus of the present study was to try to uncover some general features of the propagation reactions of propylene homo- and copolymerization rather than to make comparisons between different site models. The second approach was therefore adopted. Of the various models proposed in the literature, that referred to in refs 1 and 2 as the “slope site” formed by a $TiCl_3$ molecule on the (100) surface of $MgCl_2$ was chosen. The site is pictured in Figure 1. A site that has Ti in the +3 oxidation state rather than +4 was adopted because previous studies have found that $TiCl_4$ binds only weakly to $MgCl_2$[1,17] while $TiCl_3$ binds more strongly. Our previous work has found no exceptionally strong case for preferring any of the three possible locations for placing a $TiCl_3$ molecule on $MgCl_2$ (two on the (110) surface and one, the slope site, on the (100) surface). The slope site was chosen at random from these three. Although the other two sites are different, previous studies have found sites containing Ti in the same oxidation state to have significant similarities.[1,2,17] The differences between active sites on the same location on the $MgCl_2$ surface but with Ti in differing oxidation states also appear to be fairly systematic as far as studies have found. The present work, while certainly not being able to cover all active site models in detail, should be able to give some insight into the copolymerization process at all of these sites.

A number of publications examining heterogeneous Ziegler−Natta catalysts by computational methods have appeared in the past few years.[1,2,7−34] In almost all cases, the monomer chosen in these investigations was ethylene. In a few, propylene was chosen[23,24,33,34] as the monomer of interest. In ref 23, the first and second 1−2 insertion of propene into the Ti−C bond of a particular model of the active site were investigated in some detail, and in ref 24 this analysis was further extended to include the 2−1 insertion. The work of Bhaduri, Kulkarni, and Mukhopadhyay should be of particular interest when compared with the present results as they compared the polymerization reactions of ethylene and propylene at a Ti(IV) active site with different Cl and alkoxy ligands bound to the Ti atom.[33,34] It should be noted, however, that the model of the active site in that study, where the active site is assumed to be cationic and the surface is neglected completely, is very different to that used here where we have taken a neutral species as our model for an active site.

2. Computational Details

The details of the calculations described in this paper are much the same as those described previously.[2] A brief outline will be given here, but previous work[2] should be consulted for further details.

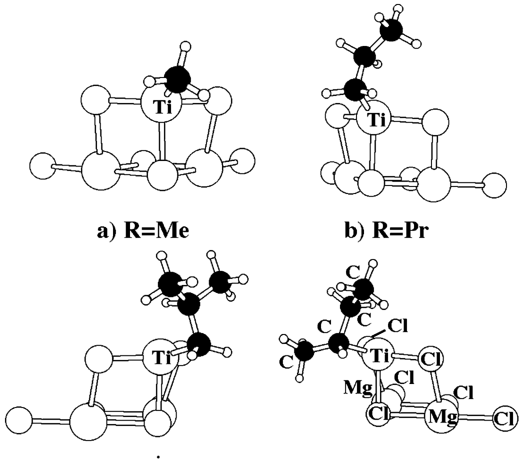
The catalyst active site, the closest piece of the surface to the active site, the polymer, and monomer were described using density functional theory (DFT). A combined quantum mechanical molecular mechanical (QM/MM) approach was used to describe most of the surface to which the active site is attached. The particular functional used in all DFT calculations was made up of an exchange correction given by Becke[35] and a correlation correction of Perdew[36] with the Vosko, Wilk, and Nusair parametrization of the electron gas.[37] This combination is also known as BP86. All calculations described in this paper were performed using the ADF 2002 program.[38−42]

The MM part of the QM/MM calculations is identical to that utilized in the previous work.[2] The surface model has the formula $Mg_{36}Cl_{72}$ (see Figure 1). The geometric parameters of the atoms in the surface were frozen at the bulk experimental values of $a = 3.640$ and $c = 17.673$ Å for $MgCl_2$.[43] In our initial work it was shown that freezing the $MgCl_2$ surface had only a small effect on the active site to surface binding energies.[1] The function of the MM atoms in this work is simply to provide steric bulk through nonbonding interactions. Therefore, only the parameters used to simulate van der Waals type interactions were included. To improve clarity, none of the MM atoms will be shown on all figures except Figure 1.

A valence triple-ζ Slater type orbital (STO) basis set was applied to the Ti of the active site while for the Mg, Cl, C, O, and H, atoms double-ζ basis sets were used. In addition, the Mg, Cl, O, and C basis sets are supplemented by one 3d polarization function, and the H basis set includes a 2p polarization function. The molecular density and the Coulomb and exchange potentials were fitted using an auxiliary s, p, d, f, and g set of STO functions[44] centered on each nucleus. The core definitions used to decide which orbitals to keep frozen were [Ne] for the active site Ti, the Cl, the Al, and the Mg atoms and [He] for C and O. The van der Waals parameters of the MM parts of the embedded cluster calculations were taken from the TRIPOS force field.[45] When TRIPOS did not include the required data, parameters were taken from the universal force field[46] (UFF).

The convergence criteria for geometry optimizations were 0.0001 au in the energy and 0.001 au $Å^{-1}$ or au rad^{-1} in the gradient. The integration accuracy parameter was chosen to be 5.0. Transition states were located by varying the C_1 to C_α bond distance until a force less than 0.001 au $Å^{-1}$ on this coordinate was obtained. The geometric parameters of all optimized structures can be found in the Supporting Information.

From the structure of the slope site given in Figure 1 it is apparent that the Ti atom in these sites may be



a) R=Me **b) R=Pr**

c) R=^{i}Bu **d) R=2-Bu**

Figure 2. Models of the growing polymer chain.

approached from two directions: either from directly perpendicular to the surface or parallel to the surface and from the opposite side to where the bridging Cl atoms sit. On many occasions in this study, structures or reactions will be differentiated depending upon which of these two sides the participating species lie. To keep clear just what is being discussed, the side of the active site that is approached in a perpendicular direction with respect to the surface will be referred to as the "front" side and the side of the active site that is approached in a direction that is parallel to the surface will be labeled the "back" side of the site. The orientation of a propylene monomer at insertion will be described by the usual 1−2 or 2−1 notation where a 1−2 insertion has the unsubstituted carbon atom bonded to the metal center while the opposite is the case for the 2−1 insertion. In some cases, an insertion reaction will be able to differentiate between the prochiral faces of the propylene monomer. When such a reaction has the *si* face of propylene facing toward the Ti−C bond it will be labeled *si*, and when the *re* face of propylene is facing the Ti−C bond it will be labeled *re*.

3. Resting States and π-Complexes

In heterogeneous Ziegler−Natta catalysis the resting state of the catalyst is usually regarded as the active site before any π-complexation by an olefin molecule has taken place (see Figure 2). A number of different possible R groups were considered as models of the growing polymer chain. With one exception, each model corresponds to the product resulting from one of the possible insertion reactions. These R groups include a propyl group (previous insertion reaction: an ethylene molecule, Figure 2b), an isobutyl group (1−2 insertion of propylene, Figure 2c), and a 2-butyl group (2−1 insertion of propylene, Figure 2d). The exception is the methyl group which was included as a model of a system with a polymer chain of minimal steric bulk (Figure 2a). Figure 2d explicitly labels all non-hydrogen atoms around the active site.

The first step in the polymerization reaction is the coordination of a monomer molecule to the Ti atom of the active site. The structures of the complexes formed between ethylene or propylene and each of the active site models were optimized. A number of possible structures were considered involving different directions of approach of the monomer, different conformations of the growing polymer chain, and, in the case of propylene coordination, different orientations of the monomer. The calculated π-complexation energies are listed in Table 1, and the structures of the π-complexes are illustrated in Figures 3 and 4.

The notation (Me-up) and (Me-down) applied to the π-complexes where the polymer chain is modeled by a 2-butyl group and the monomer approaches from the front side needs to be explained. In all of the π-complexes the R group attached to the Ti atom is arranged to create space for the monomer and to retain the agostic interaction between Ti and the β-hydrogen. This does not fully define the conformation of the 2-butyl or propyl alkyl chains if the monomer approaches from the front side. Both alkyl groups have a γ-carbon which can be pointing toward or away from the surface. For the most part, in this study the γ-carbon is assumed to be in the position leading to the least steric crowding, i.e., pointing toward the surface. In the case of the 2-butyl group the β-methyl group can also point toward the surface (down) or away from the surface (up). Both possibilities are considered here and are illustrated in Figures 3g,h and 4g,h.

In earlier work considering ethylene polymerization, in addition to a lowest energy π-complex structure was found, several other structures where the monomer was rotated about an axis from the Ti atom the midpoint of the C−C double bond were also considered. The highest energy structures as a function of rotation about this bond were found to only be 2−3 kcal/mol higher in energy.[1] Propylene is a larger monomer, and several sterically larger models of the growing polymer chain are considered here. Further, a 180° rotation about the previously mentioned axis or the axis along the C−C double bond of the monomer leads do a different structure, unlike ethylene. Therefore, in the process of finding the lowest energy π-complexes illustrated in Figure 4, a few possible orientations of the monomer were considered. The binding energies of the least stable complexes found are also listed in Table 1 in order to give an idea of the range of energies found.

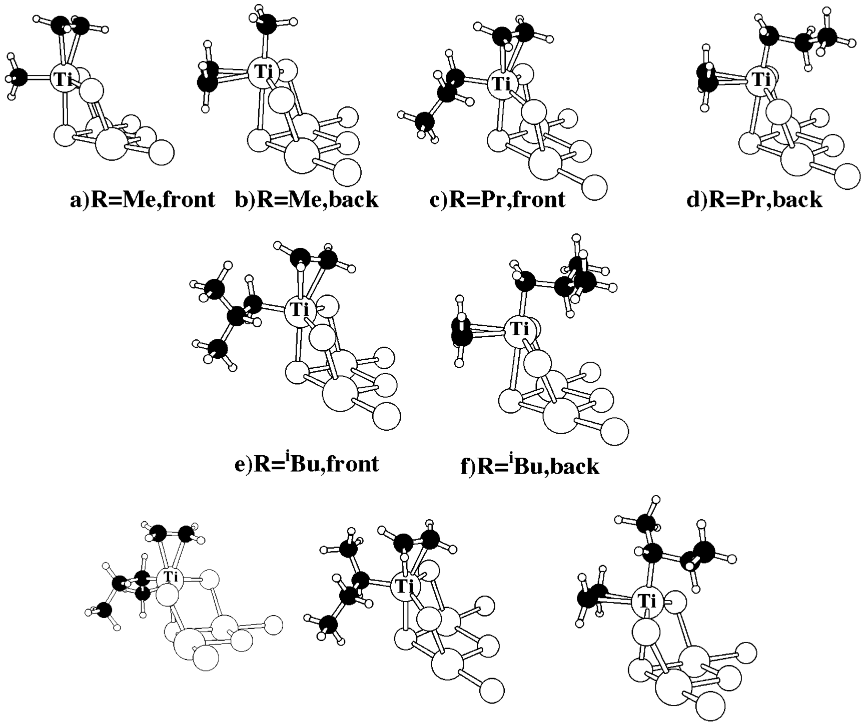
In all cases the propylene has a higher complexation energy than ethylene with the equivalent active site model. The difference varies between 2 and 4 kcal/mol depending on the face of the site to which the monomer is complexed and the structure of the R group. The explanation for the perhaps counterintuitive result that the more sterically bulky propylene molecule binds more strongly to the active site is fairly straightforward. An olefin forms a complex with an early transition metal through donation of π-electron density into the vacant d-orbitals of the metal. The binding is enhanced in the present case because the Ti atom is in the +3 oxidation and has a free d-electron which can be back-donated into the π^* orbital of the olefin. Propylene binds more strongly than ethylene because the presence of the extra carbon atom causes the double bond to be more electron rich, allowing for greater donation into the Ti d-orbitals and stronger bonding. A similar trend has been found for late transition metal[47] and metallocene catalysts.[48]

The complexation energies are relatively independent of the identity of the alkyl group attached to Ti. The only exception is the site where the alkyl group is methyl which binds both ethylene and propylene about 2.5 kcal/mol more strongly than the others. When R = Me, ethylene and propylene have binding energies of 18.7 and 20.9 kcal/mol, respectively, while the sites with other alkyl groups have π-complexation energies in the

Table 1. Complexation Energies[a] and Monomer C to Ti Distances[b] of Ethylene and Propylene with $TiCl_3$-Based Slope Sites[c]

R group	face of site	ethylene E^{π}	ethylene R_{C_1Ti}	ethylene R_{C_2Ti}	propylene E^{π}_{min}	propylene R_{C_1Ti}	propylene R_{C_2Ti}	propylene E^{π}_{max}
Me	front	−18.7	2.47	2.41	−20.9	2.43	2.52	−20.3
Me	back	−13.6	2.34	2.35	−16.4	2.30	2.43	−16.3
Pr	front	−15.9	2.46	2.42	−18.6	2.42	2.50	−17.8
Pr	back	−13.1	2.39	2.39	−15.6	2.36	2.49	−15.3
^{i}Bu	front	−14.3	2.47	2.43	−18.3	2.43	2.51	−14.7
^{i}Bu	back	−13.1	2.39	2.39	−15.5	2.36	2.49	−15.3
2-Bu (Me-up)	front	−14.6	2.46	2.42	−18.6	2.42	2.49	−15.3
2-Bu (Me-down)	front	−14.9	2.48	2.42	−18.7	2.44	2.50	−16.0
2-Bu	back	−12.8	2.38	2.39	−15.2	2.36	2.47	−14.2

[a] Energies in kcal/mol. [b] Bond lengths in Å. [c] Included in the propylene results are the complexation energies corresponding to the most and least favorable orientations of the monomer.


a)R=Me,front b)R=Me,back c)R=Pr,front d)R=Pr,back

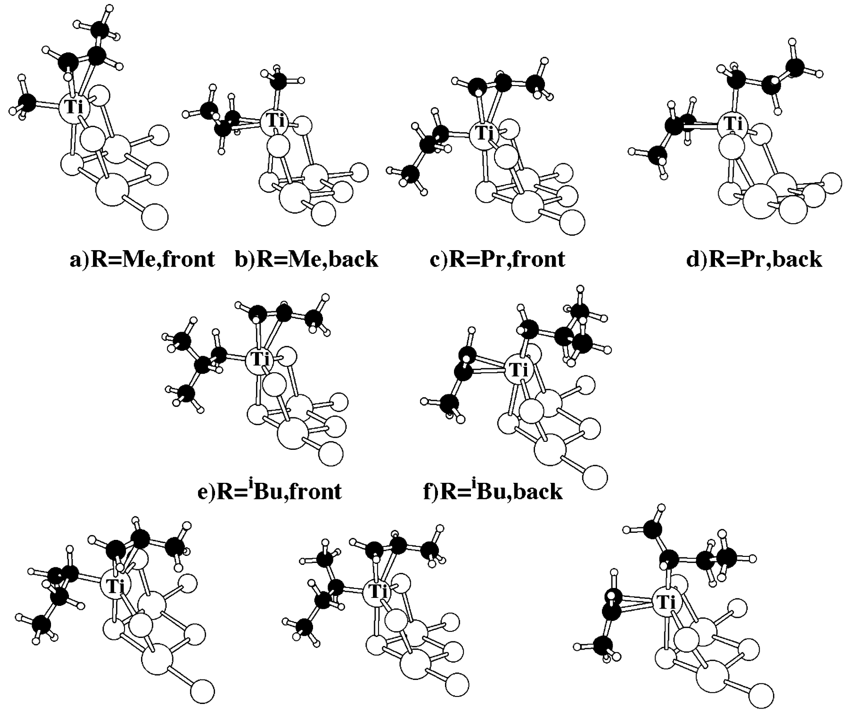
e)R=^{i}Bu,front f)R=^{i}Bu,back

g)R=2-Bu(Me down), front h)R=2-Bu(Me up), front i)R=2-Bu,back

Figure 3. Complexes of ethylene with the active site showing different directions of approach of the ethylene molecule and different alkyl chains attached to the Ti atom.

ranges 14−16 and 18−19 kcal/mol respectively for ethylene and propylene (see Table 1). To see why this is the case, the energies of the resting states with R = Me and Pr were recalculated with the structure distorted to match the corresponding π-complexes when an ethylene monomer is bound to the backside of the site. In this way the energy cost of distorting the site to accept the monomer can be separated from the other contributions. It was found that the energy required to distort the site with a Me group attached was 9.7 kcal/mol while 11.2 kcal/mol was required to distort the site with a propyl group. Thus, 1.5 kcal/mol of the approximately 2.5 kcal/mol greater stability of the complexes when R = Me is due to the lesser energy cost of distorting the site to accommodate a monomer. The site with an attached methyl group is easier to distort because of the lack of an agostic interaction with a β-hydrogen. With the addition of a β-agostic interaction the alkyl group takes up more space around the Ti atom and therefore will interact more strongly with the Cl ligands also attached to the Ti. The remaining 1.0 kcal/mol of greater stability of the π-complexes in the presence of the methyl alkyl chain can be attributed to a similar cause. That is, a complexed monomer will experience less steric repulsion from the smaller methyl group than the larger alkyl chains.

As well as being relatively independent of the identity of the alkyl chain (beyond the presence or absence of a β-agostic interaction), the binding energy of a propylene monomer at the active site appears to be relatively insensitive to its orientation. The highest energies found for each combination of propylene with a face of the site and polymer chain model listed in Table 1 are not much higher than the lowest. In all cases, the higher energy structure have the methyl group of the propylene pointed toward the polymer chain. The lower energy structures illustrated in Figure 4 have the methyl group directed away. When the monomer approaches from the backside, the polymer chain is folded right out of the way, and all possible orientations of the propylene are essentially equal in energy. The greatest change in energy with respect to orientation of the propylene is found for the cases where the monomer approaches from the front side, and one methyl group of the growing



a)R=Me,front **b)R=Me,back** **c)R=Pr,front** **d)R=Pr,back**

e)R=^{i}Bu,front **f)R=^{i}Bu,back**

g)R=2-Bu(Me down), front **h)R=2-Bu(Me up), front** **i)R=2-Bu,back**

Figure 4. Complexes of propylene with the active site showing different directions of approach of the propylene molecule and different alkyl chains attached to the Ti atom.

polymer chain is pointed toward the monomer (isobutyl and 2-butyl (Me up)). To see whether a larger difference in energy could be obtained a more extreme case, the π-complex with an alkyl chain R of 2-butyl (Me up) with the γ-carbon also pointing upward was also calculated. This conformation of the alkyl chain actually destabilized the π-complex even when the propylene methyl group was directed away from it (complexation energy of 16.0 kcal/mol compared with 18.5 kcal/mol in most other cases) and gave an even less stable complex when the propylene methyl pointed toward the alkyl chain (complexation energy of 12.5 kcal/mol).

It should be kept in mind that the "higher" energies do not correspond to transition states but are other local minima. It is therefore not possible to evaluate how easily a monomer could rotate while bound to the Ti atom from these results.

As was found previously for ethylene,[1] the propylene monomers bind more strongly to the "front" side of the active site than to the "back" side irrespective of the form of the alkyl group or the identity of the monomer. To discern why this should be so, the energy of the active site with a propyl group as the alkyl group was calculated at the same geometries as the front and back π-complexes of ethylene but with the ethylene molecule removed. This was done in order to evaluate the energy required to rearrange the propyl group when ethylene approaches from each direction. The energies of the two structures differ by 3.2 kcal/mol, with the site rearranged to mimic the front complex lower in energy. This energy difference is very similar to the difference in the front and back complexation energies of ethylene at this site (2.8 kcal/mol). The preferential binding on the front sides of the sites is therefore due to the lower energetic cost of rearranging the site to accept a monomer. That is, considerably more rearrangement of the alkyl chain is required for the back conformation than the front conformation, Figures 3 and 4 starting from the free uncomplexed active sites in Figure 2.

The π-complexation energies obtained here are difficult to compare with previous studies of Ziegler–Natta catalysis involving propylene because of the very different models of the active site assumed in each case. For what it is worth, Boero et al. found that propylene binds much less strongly than ethylene to a site with Ti in the +4 oxidation state on the (110) face of $MgCl_2$.[23] Bhaduri, Mukhopadhyay, and Kulkarni obtained π-complexation energies that were somewhat larger than those given here. This is understandable given that they chose a cationic model of the active site. Their calculations did show, however, that propylene binds more strongly than ethylene to their active site model also.[33]

4. Insertion Barriers

The geometry and energies of the chain propagation transition states of ethylene and propylene with the chosen model of the active site were studied. All possible reactions were considered including ethylene following ethylene (Figure 5c,d), 1–2 insertion of propylene following ethylene (Figure 6c–e), 2–1 insertion of propylene following ethylene (Figure 7c,d), insertion of ethylene following 1–2 insertion of propylene (Figure 5e,f), insertion of ethylene following 2–1 insertion of propylene (Figure 5g–i), 1–2 insertion of propylene following 1–2 insertion of propylene (Figure 6f–h), 1–2 insertion of propylene following 2–1 insertion of propylene (Figure 6i–n), 2–1 insertion of propylene following 1–2 insertion of propylene (Figure 7e,f), 2–1 insertion of propylene following 2–1 insertion of propylene (Figure 7g–i), and the insertion of ethylene and propylene into the Ti–C bond when the R group is a methyl group (Figures 5a,b, 6a,b, and 7a,b). The reaction taking place from both the front and backside π-complexes were considered. In many of the reactions, there is no way

Table 2. Reaction Energies and Geometrical Parameters of the Polymerization Reaction of Ethylene with $TiCl_3$-Based Slope Sites

R group	face of site	$R_{C\alpha C_1}$[a]	E[b]
Me			
	front	2.04	−2.9
	back	2.31	−5.6
Pr−prev monomer ethylene			
	front	2.08	−2.9
	back	2.25	−4.0
^{i}Bu−prev monomer 1−2 propylene			
	front	2.08	−2.1
	back	2.24	−3.4
2-Bu−prev monomer 2−1 propylene			
Me-up	front	2.07	−3.7
Me-down	front	2.02	1.2
	back	2.18	−1.5

[a] $R_{C\alpha C_1}$ in angstrom. [b] E in kcal/mol.

Table 3. Reaction Energies and Geometrical Parameters of the Polymerization Reaction of Propylene with $TiCl_3$-Based Slope Sites

R group	face of site	orient	$R_{C\alpha C_1}$[a]	E[b]
Me				
	front	1−2	2.03	−4.5
	back	1−2	2.35	−7.7
	front	2−1	2.02	−1.0
	back	2−1	2.30	−6.7
Pr−prev monomer ethylene				
	front	1−2 (*si*)	2.07	−2.6
	front	1−2 (*re*)	2.07	−3.8
	back	1−2	2.21	−5.6
	front	2−1	2.05	−2.6
	back	2−1	2.21	−4.7
^{i}Bu−prev monomer 1−2 propylene				
	front	1−2 (*si*)	2.03	−0.2
	front	1−2 (*re*)	2.07	−2.9
	back	1−2	2.20	−4.5
	front	2−1	2.00	−1.9
	back	2−1	2.22	−4.0
2-Bu−prev monomer 2−1 propylene				
Me-up	front	1−2 (*si*)	2.05	−1.0
Me-up	front	1−2 (*re*)	2.05	−2.5
Me-down	front	1−2 (*re*)	2.03	0.5
Me-down	front	1−2 (*si*)	2.00	−1.0
	back	1−2 (*si*)	2.17	0.2
	back	1−2 (*re*)	2.15	−2.3
Me-up	front	2−1	2.05	−3.4
Me-down	front	2−1	2.01	0.4
	back	2−1	2.23	−2.7

[a] $R_{C\alpha C_1}$ in angstrom. [b] E in kcal/mol.

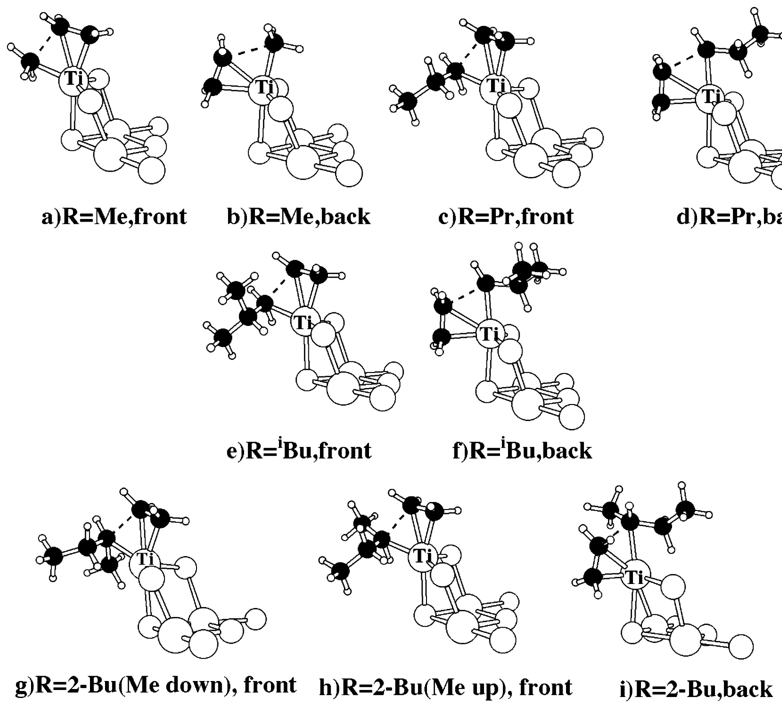
in which the *si* and *re* faces of the prochiral carbon of the propylene monomer can be differentiated. However, in four cases stereocontrol may occur, namely when the 1−2 insertion is from the front and the alkyl group is propyl, isobutyl, or 2-butyl (Figure 6c,d,f,g,j,k) and 1−2 insertion from the back when the alkyl group is 2-butyl (Figure 6m,n). In these four cases insertion with both the *si* and *re* faces of propylene were considered. The calculated insertion barriers relative to the separated active site and monomer and C_α−C_1 transition state distances of reactions where the monomer is ethylene are listed in Table 2. The values for the reactions involving propylene are listed in Table 3. The transition state geometries are illustrated in Figures 5−7.The insertion barriers are calculated with respect to the separated monomer and site. As was the case with the homopolymerization of ethylene,[1] the barriers are, for the most part, lower in energy than the separated components, leading to the negative energy values in Tables 2 and 3. The lowest barriers are therefore the most negative values. It should be noted that in terms of free energy all of the insertion barriers will be positive with respect to the separated components since the monomer will lose all of its translational and rotational entropy in binding to the site. At 350 K, the entropy change corresponds to about 15 kcal/mol of free energy.

The transition state geometries all have a four-membered ring structure in accordance with the generally accepted mechanism postulated by Cossee and Arlman[49−51] and show a β-agostic interaction with Ti. When the monomer approaches from the front side, an α-agostic interaction is also possible (see Figures 5−7).

In all cases, the barrier to insertion in the presence of a given R group is lower when the monomer approaches from the backside than when it approaches from the front side. This is in contrast to the π-complexes where approach of the monomer from the front is predicted to lead to a more stable complex than when the monomer approaches from the backside. Further, the value of the C_1−C_α distance at the transition state is greater when the monomer approaches from the backside, suggesting that transition state is earlier in this case.

The preferences for π-complexation on the front side and insertion on the backside are related. It was noted in the previous section that the energy required to rearrange the alkyl chain to make space for an approaching monomer is less if the monomer approaches the front side. Less energy is required because when the monomer approached from the back, the α-carbon of the alkyl chain is forced to be trans to the surface Cl directly bonded to the Ti (see Figure 3b for example) while the same carbon atom can avoid being directly trans to any Cl when the monomer approaches the front side (Figure 3a for example). Placing the Ti−C bond directly opposite to a Cl atom appears to weaken it. This hypothesis is supported by two test calculations where the geometry of the bare active site with R = Pr was optimized with the α-carbon constrained to remain either on the front or backside of the Ti. It was found that the Ti−C_α bond was longer when C_α was on the front side (trans with the surface Cl) than when it was on the backside (trans with no Cl). A weaker Ti−C_α bond when C_α is on the front side trans to the surface Cl increases the energetic cost of forming a π-complex with the monomer on the backside in comparison the front complex. At the same time, a weaker Ti−C_α bond causes the barrier to insertion of a monomer to be lower, thus favoring insertion from the backside over the front side.

In terms of the composition of the polymer produced, the present calculations predict that an active site with the titanium atom in the +3 oxidation state will produce a copolymer that is somewhat enriched in propylene. After an insertion of an ethylene (R group: propyl) the lowest calculated barrier was for the 1−2 insertion of propylene at the backside of the site (−5.6 kcal/mol) followed by 2−1 insertion of propylene (−4.7 kcal/mol) followed by insertion of ethylene (−4.0 kcal/mol) both also at the backside of the site. After a 1−2 insertion of propylene (R group: isobutyl) the lowest calculated barrier was for a further 1−2 insertion from the backside (−4.5 kcal/mol) followed by a 2−1 insertion from the same side (−4.0 kcal/mol) closely followed by insertion of ethylene, also from the backside (−3.4 kcal/mol). After a 2−1 insertion of propylene (R group:



a)R=Me,front b)R=Me,back c)R=Pr,front d)R=Pr,back

e)R=^{i}Bu,front f)R=^{i}Bu,back

g)R=2-Bu(Me down), front h)R=2-Bu(Me up), front i)R=2-Bu,back

Figure 5. Transition states of insertion of ethylene into the Ti−C bond of the active site with the monomer approaching from two possible directions and the various different alkyl groups attached to Ti.

2-butyl) the lowest barrier is to the insertion of ethylene on the front side (−3.7 kcal/mol) followed by 2−1 insertion of propylene on the same side (−3.4 kcal/mol). The preference of propylene insertion over ethylene obviously decreases as the steric bulk of the R group increases, as might be expected. This conclusion is supported by the insertion barriers of the site when R is a methyl group. Here, where R has minimal steric bulk, the preference for propylene over ethylene is most pronounced with a lowest barrier to propylene insertion of −7.7 kcal/mol as compared to the equivalent barrier to ethylene insertion of −5.6 kcal/mol.

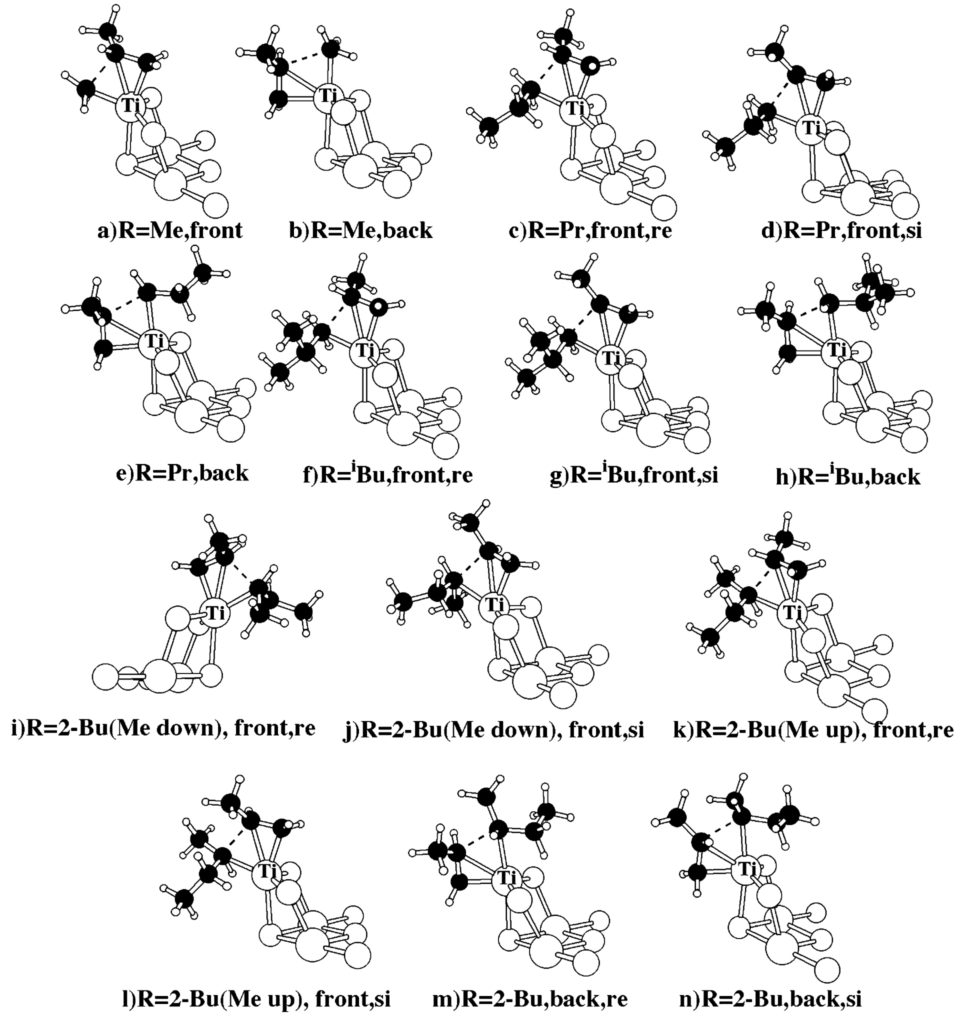
Propylene inserts more easily into the Ti−C bond than ethylene because of the comparative properties of their respective double bonds. The presence of a methyl group at one end of the propylene double bond causes the carbon at that end to be more electron rich than the other. The increased electron density at C_2 promotes the insertion reaction giving, in the absence of large steric effects, lower barriers to insertion for propylene in comparison with the more electron-deficient double bond of ethylene.

Note that a difference in barrier height of 1 kcal/mol corresponds to a difference in reaction rate of about a factor of 4 at 350 K. Thus, it would appear that the active site modeled here would produced polymer that contains ethylene and propylene in a ratio of about 1:5 and that ethylene is most likely to be incorporated into the polymer following a 2−1 propylene insertion. There is no distinct preference of “like to follow like”, i.e., of an ethylene insertion to follow an ethylene insertion and a propylene insertion to follow a propylene insertion over other possible reaction, indicating that this catalyst would not produce block copolymers.

In terms of regioselectivity of the propylene insertion reaction, the calculations predict that in most cases 1−2 insertion will proceed more easily than 2−1 insertion, though not by much. The lowest insertion barriers to 1−2 insertion are 1.0, 0.9, and 0.5 kcal/mol lower than the lowest barrier to 2−1 insertion at the site with R = methyl, propyl, and isobutyl, respectively. In the case of R = 2-butyl the lowest barrier to 2−1 insertion (−3.4 kcal/mol) is 0.9 kcal/mol lower than the lowest barrier to 1−2 insertion (−2.5 kcal/mol). Clearly, the preference for 1−2 over 2−1 insertion decreases as the bulk of the R group increases. A more sterically hindered transition state would obviously favor the orientation of propylene where the larger end of the monomer was pointing away from the alkyl group or 2−1 insertion. The explanation for why 1−2 insertion is favored over 2−1 insertion when a sterically small R group is present is related to the earlier discussion outlining why the propylene insertion barriers were generally lower than those of ethylene. This result was attributed to additional electron density on C_2. The double bond of propylene is therefore asymmetric in terms of charge. The orientation of the propylene double bond with respect to the Ti−C bond that gives the greatest stabilization of the transition state (in the absence of significant steric repulsion from R) is that which leads to 1−2 insertion.

The polymer chain attached to the active site is rather flexible and could attain a number of different conformations. For the most part, only one conformation of the alkyl group in combination with a given monomer, orientation of the monomer, and face of approach is shown in the figures. A few other conformations also were examined. These structures generally differed from those shown in the placement of the γ-carbon. Moving this carbon has little effect on the polymerization reaction as it changed the insertion barrier by about 1 kcal/mol (or less). The optimized structures of the transition states with differing conformations of the γ carbon can be found in the Supporting Information.

Although the influence of conformational changes leading to relocation of the γ carbon were found here to have relatively minor influence on the polymerization reaction, it should not be assumed that carbon atoms even further from the Ti atom in longer polymer chains



a)R=Me,front b)R=Me,back c)R=Pr,front,re d)R=Pr,front,si

e)R=Pr,back f)R=^{i}Bu,front,re g)R=^{i}Bu,front,si h)R=^{i}Bu,back

i)R=2-Bu(Me down), front,re j)R=2-Bu(Me down), front,si k)R=2-Bu(Me up), front,re

l)R=2-Bu(Me up), front,si m)R=2-Bu,back,re n)R=2-Bu,back,si

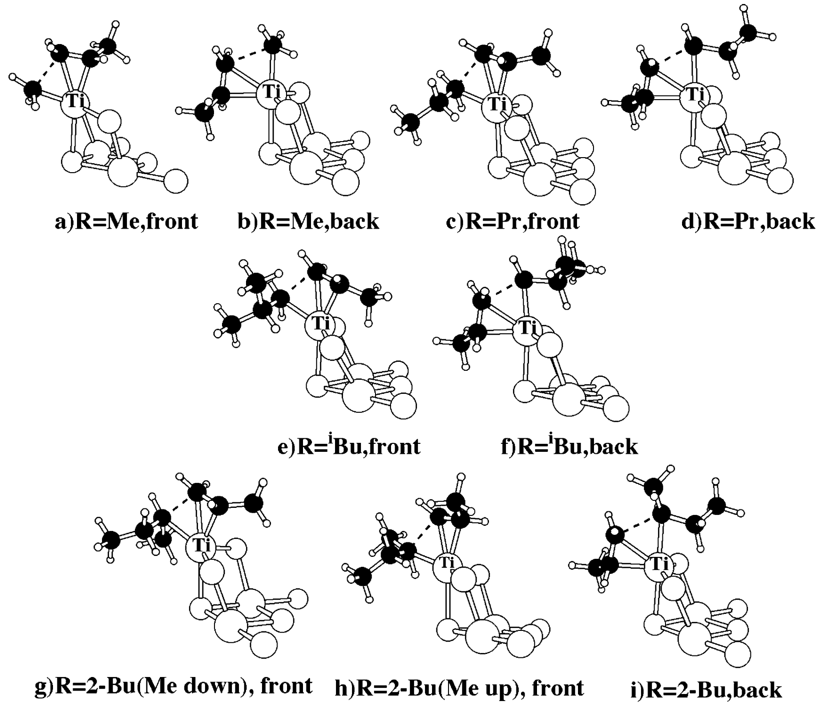
Figure 6. Transition states of insertion of propylene in a 1−2 fashion into the Ti−C bond of the active site with the monomer approaching from two possible directions and the various different alkyl groups attached to Ti.

will have even less influence. Among all the many possible conformations of longer chains several are likely to exist where carbon atoms a number of bonds from Ti are near to the active site. In these conformations these more remote carbons could have a significant influence on the progress of the reaction by blocking the approach of the monomer or causing a particular transition state geometry to become less favorable. The influence of such longer polymer chains on the performance of the active site is an interesting subject but is beyond the scope of the present work.

The effect of changing the placement of the β-methyl group of the 2-Bu alkyl group (Figure 2d) when the monomer approaches the front side was also studied (Figure 5g,h, Figure 6i−l, and Figure 7g,h). Perhaps surprisingly, the apparently more sterically crowded structures ("methyl up") have lower barriers to insertion than the less sterically crowded ("methyl down") structures. This is easily understood, however, if it is noticed that the methyl down structures are unable to stabilize the transition state through an agostic interaction with an α hydrogen. Removing this agostic interaction costs more energy than the added steric repulsion introduced by pushing the monomer and polymer chain closer together. Such steric repulsion is not especially great anyway as the methyl group is rotated away from the monomer as the C−C bond is formed as illustrated by a comparison of Figures 4h and 6k,l.

As was noted earlier, some of the transition states examined should be able to discriminate between the prochiral faces of propylene. An examination of these reactions should shed some light on the stereoselectivity of the propylene polymerization reaction. In the cases where stereoselectivity could be possible the transition states when the propylene molecule approaches with both the *si* and the *re* face toward C_α were found (see the *si* and *re* entries in 3 and Figure 6). The relative orientations of the monomer and R group were chosen such that the *si* insertions placed the methyl group of the monomer closer to R and further away in the *re* insertions. As would be expected, the *re* insertions barriers are all lower. The difference between the *si* and *re* barriers are fairly significant, and in particular, the reaction which could produce polypropylene of some kind of tacticity, 1−2 insertion when R is an isobutyl group, favors the *re* insertion by 2.7 kcal/mol over the *si* when stereoselectivity is possible.

Although the particular reactions we have just discussed are stereoselective, it is very likely that the present active site model cannot produce tactic polymer. The slope site is unchanged by reflection through a plane perpendicular to the surface that cuts the Ti atom. All of the transition states in Figure 6 therefore can be converted from *re* to *si* and vice versa by reflection through this plane. It would seem then that this site cannot produce anything other than atactic polymer.



a)R=Me,front b)R=Me,back c)R=Pr,front d)R=Pr,back

e)R=^{i}Bu,front f)R=^{i}Bu,back

g)R=2-Bu(Me down), front h)R=2-Bu(Me up), front i)R=2-Bu,back

Figure 7. Transition states of insertion of propylene in a 2−1 fashion into the Ti−C bond of the active site with the monomer approaching from two possible directions and the various different alkyl groups attached to Ti.

This analysis relies on the assumption that the polymer chain is fairly mobile. If this is the case, then any given insertion of a propylene monomer could be *re* or *si* with equal probability. On the other hand, if the polymer chain interacts with its environment such that a certain conformation is more favorable, then stereoselection may occur. For example, suppose that the site is as pictured in Figure 6f and that, because of constraints on its motion, the polymer chain will always be in that conformation with the chain to the left (out of the page in Figure 6f). In that situation, *si* insertion would be favored and a tactic polymer chain should be produced. If the polymer chain motion is hindered in this way, then the mirror image of the situation just described (*re* insertion favored) is equally likely to occur. We are not in any position to comment on the mobility of a polymer chain, especially once it becomes quite long. Note that Boero et al. found that a growing chain of polyethylene will drop onto the support surface leaving one side of the site open for approach of a monomer[22] so such a situation may not be unrealistic. It should also be noted that several of the possible reactions, especially those where the monomer approaches from the back size, cannot discriminate between the *r* and *si* face of propylene.

As a final comment on this point, we should point out that, whatever the mobility of the growing polymer chain might be, the present results are still of interest as they suggest that, in situations where stereoselection can occur, the polymer chain can have an important influence on the stereoselectivity of the site. That is, direct tacticity control can be important in propylene synthesis with a heterogeneous Ziegler−Natta catalyst.

Boero et al. looked at polypropylene synthesis and found that 1−2 insertion had a much lower barrier than 2−1 insertion, assuming an isobutyl group as the model of the growing polymer chain.[23,24] They also found that the stereospecificity of the reaction was controlled by the site rather than the polymer chain or indirect tacticity control. Their model of the active site is chiral even in the absence of a growing polymer chain while in the present model chirality can only be introduced by the polymer chain, and indirect tacticity control is not possible. Bhaduri et al. found that the insertion of propylene proceeds with a lower barrier than the ethylene reaction. Interestingly, they noted that changing the ligands bound to Ti from Cl to bulky O−^{t}Bu favored ethylene insertion over propylene insertion.

5. Concluding Remarks

In this work the copolymerization of α-olefins by heterogeneous Ziegler−Natta catalysis was studied for the first time with quantum mechanical calculations. The results obtained provided insight into several aspects of the reaction including the structure and stability of the π-complexes, the structure of the transition state, and the influence of the growing polymer chain on chemo-, regio-, and stereoselectivity.

For the most part, the calculations seem to be in concert with what is known experimentally or what would be expected from simple chemical intuition. In most cases where results are more surprising, such as the greater π-complexation energies of propylene in comparison with ethylene, explanations are provided here. The one obvious exception is the finding that the barriers to insertion of a propylene monomer are lower than those of ethylene. If this was the case under experimental conditions, then the polymer produced would be made up of mostly propylene monomers. Polymers of this type are not produced, and ethylene−propylene copolymerizations give compounds that are significantly enriched in ethylene.

Although the model examined in the present study is unable to reproduce the experimentally observed relative ordering of the insertion barriers of ethylene and propylene, as the first study of its type it does provide considerable insight into the copolymerization reaction at the microscopic level. Given this starting point, further progress should be possible, hopefully leading to an improved model that can better reproduce experimental results.

Such alternative models could simply be arrived at by placing the active site at one of the binding points on the (110) surface of $MgCl_2$. Previous studies examining several site models to not seem to imply that these alternative locations will be strongly different from the slope site.[1,2,17] Sites based on $TiCl_4$, which would be more sterically hindered, were found to be significantly different than those based on $TiCl_3$[1,2,17] and may well be better candidates as models of copolymerization active sites. In this case there still remains the issue of the stability of the active site itself, however. Another possible change would be to introduce more steric bulk around active site, for example through the complexation of an electron donor to the Ti atom. Such a modification should favor ethylene insertion over propylene insertion and 1−2 insertion of propylene over 2−1 insertion. Furthermore, it is likely to render the model active site chiral and therefore capable of catalyzing stereoselective insertion of propylene even in the absence of direction from the growing polymer chain (indirect tacticity control). Electron donors have been found to be crucially important in the creation of catalysts capable of making isotactic polypropylene.[3,4]

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Supporting Information Available: Cartesian coordinates of all optimized structures in text form. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Seth, M.; Margl, P. M.; Ziegler, T. *Macromolecules* **2002**, *35*, 7815.
(2) Seth, M.; Ziegler, T. *Macromolecules* **2003**, *36*, 6613.
(3) Boor, John, J. *Ziegler−Natta Catalysts and Polymerizations*; Academic Press: New York, 1979.
(4) Barbé, P. C.; Cecchin, G.; Noristi, L. *Adv. Polym. Sci.* **1987**, *81*, 1.
(5) Krentzel, B. A.; Kissin, Y. V.; Kleiner, V. J.; Stotskaya, L. L. *Polymers and Copolymers of Higher α-Olefins*, Hanser/Gardener, Cincinnati, OH, 1997.
(6) Kissen, Y. V. *Isospecific Polymerization of Olefins*; Springer-Verlag: New York, 1985.
(7) Giunchi, G.; Clementi, E.; Ruiz-Vizcaya, M. E.; Novaro, O. *Chem. Phys. Lett.* **1977**, *49*, 8.
(8) Novaro, O.; Blaisten-Barojas, E.; Clementi, E.; Giunchi, G.; Ruiz-Vizcaya, M. E. *J. Chem. Phys.* **1978**, *58*, 2337.
(9) Fujimoto, H.; Yamasaki, T.; Mizutani, H.; Koga, N. *J. Am. Chem. Soc.* **1985**, *107*, 6157.
(10) Sakai, S. *J. Phys. Chem.* **1994**, *98*, 12053.
(11) Sakai, S. *Int. J. Quantum Chem.* **1997**, *65*, 739.
(12) Colbourn, E. A.; Cox, P. A.; Carruthers, B.; Jones, P. J. V. *J. Mol. Catal.* **1994**, *4*, 805.
(13) Jensen, V. R.; Borve, K. J.; Ystenes, M. *J. Am. Chem. Soc.* **1995**, *117*, 9.
(14) Lin, J. S.; Catlow, C. R. A. *J. Mol. Catal.* **1993**, *3*, 1217.
(15) Lin, J. S.; Catlow, C. R. A. *J. Catal.* **1995**, *157*, 145.
(16) Cavallo, L.; Guerra, G.; Corradini, P. *J. Am. Chem. Soc.* **1998**, *120*, 2428.
(17) Monaco, G.; Toto, M.; Guerra, G.; Corradini, P.; Cavello, L. *Macromolecules* **2000**, *33*, 8953.
(18) Gale, J. D.; Catlow, C. R. A.; Gillan, M. J. *Top. Catal.* **1999**, *9*, 235.
(19) Puhakka, E.; Pakkanen, T. T.; Pakkanen, T. A. *Surf. Sci.* **1995**, *334*, 289.
(20) Puhakka, E.; Pakkanen, T. T.; Pakkanen, T. A. *J. Mol. Catal. A* **1997**, *120*, 143.
(21) Shiga, A.; Kawamura-Kuribayashi, H.; Sasaki, T. *J. Mol. Catal. A* **1995**, *98*, 15.
(22) Boero, M.; Parrinello, M.; Terakura, K. *J. Am. Chem. Soc.* **1998**, *120*, 2746.
(23) Boero, M.; Parrinello, M.; Hüffer, S.; Weiss, H. *J. Am. Chem. Soc.* **2000**, *122*, 501.
(24) Boero, M.; Parrinello, M.; Weiss, H.; Hüffer, S. *J. Phys. Chem. A* **2001**, *105*, 5096.
(25) Boero, M.; Parrinello, M.; Terakura, K.; Weiss, H. *Mol. Phys.* **2002**, *100*, 2935.
(26) Costuas, K.; Parrinello, M. *J. Phys. Chem. B* **2002**, *106*, 4477.
(27) Weiss, H.; Boero, M.; Parinello, M. *Macromol. Symp.* **2001**, *173*, 137.
(28) Toto, M.; Morini, G.; Guerra, G.; Corradini, P.; Cavallo, L. *Macromolecules* **2000**, *33*, 1134.
(29) Martinsky, C.; Minot, C. *Surf. Sci.* **2000**, *467*, 152.
(30) Martinsky, C.; Minot, C.; Ricart, J. *Surf. Sci.* **2001**, *490*, 237.
(31) Skalli, M. K.; Markovits, A.; Belmajdoub, A. *Catal. Lett.* **2001**, *76*, 7.
(32) Markovits, A.; Minot, C. *Int. J. Quantum Chem.* **2002**, *89*, 389.
(33) Bhaduri, S.; Mukhopadhyay, S.; Kulkarni, S. *J. Organomet. Chem.* **2003**, *671*, 101.
(34) Mukhopadhyay, S.; Kulkarni, S.; Bhaduri, S. *J. Mol. Struct. (THEOCHEM)* **2004**, *673*, 65.
(35) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
(36) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.
(37) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.
(38) Te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; Van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931.
(39) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41.
(40) Versluis, L.; Ziegler, T. *J. Chem. Phys.* **1988**, *88*, 322.
(41) Te Velde, G.; Baerends, E. J. *Phys. Rev. B* **1991**, *44*, 7888.
(42) Fonseca Guerra, C.; Snijders, J. G.; Te Velde, G.; Baerends, E. J. *Theor. Chim. Acta* **1998**, *99*, 391.
(43) Dorrepaal, J. *Appl. Crystallogr.* **1984**, *17*, 483.
(44) Krijn, J.; Baerends, E. J. *Fit Functions in the HFS Method*, Tech. rep., Department of Theoretical Chemistry, Free University, Amsterdam, The Netherlands, 1984.
(45) Clark, M.; Cramer, R D, I.; Van Opdenbosch, N. *J. Comput. Chem.* **1989**, *10*, 982.
(46) Rappé, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard, W A, I.; Skiff, W. M. *J. Am. Chem. Soc.* **1992**, *114*, 10024.
(47) Michalak, A.; Ziegler, T. *Organometallics* **1999**, *18*, 3998.
(48) Froese, R. D. J.; Musaev, D. G.; Morokuma, K. *J. Mol. Struct. (THEOCHEM)* **1999**, *461*, 121.
(49) Cossee, P. *J. Catal.* **1964**, *3*, 80.
(50) Arlman, E. *J. Catal.* **1964**, *3*, 89.
(51) Arlman, E.; Cossee, P. *J. Catal.* **1964**, *3*, 99.

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