A Density Functional and Molecular Mechanics Study Of β-Hydrogen Transfer in Homogeneous Ziegler−Natta Catalysis

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ABSTRACT: Models of catalytic complexes, of the type $Cp_2ZrC_2H_5^+$ and $Cp_2ZrC_4H_9^+$ ($Cp = \eta^5$-C_5H_5), for the β-hydrogen transfer processes in homogeneous Ziegler−Natta polymerizations have been studied using density functional methods. We investigated the geometries and the energetics of the processes corresponding to the β-hydrogen transfer either to the metal or to the monomer. A preference for the transfer to the monomer is shown by the noticeably smaller activation barrier. The analysis has been extended through molecular mechanics calculations to models of the catalytic complexes based on the ligands BenzInd and MeBenzInd (BenzInd = $(CH_3)_2Si$(benz[*e*]indenyl)$_2$ and MeBenzInd = $(CH_3)_2Si$(2-methylbenz[*e*]indenyl)$_2$). This analysis, in agreement with experimental results, indicates that the β-hydrogen transfer to the monomer is more difficult in the presence of the MeBenzInd ligand due to the nonbonded interactions of the 2-methyl substituents with the C_α of both the monomer and the growing chain.

Introduction

The application of quantum mechanics[1,2] and molecular mechanics techniques[2e,g,3,4] to possible model catalytic sites for the heterogeneous[1,3] and homogeneous[2,4] Ziegler−Natta polymerizations has allowed us to rationalize several experimental facts.

In particular, the main contribution of quantum mechanics calculations has been, in our opinion, to effectively assess the widely accepted Cossee mechanism[5] as a viable one for the chain growth reaction. They demonstrated that olefins may coordinate to the cationic active intermediates and that the insertion of the olefin into the metal−growing chain bond may occur with a modest energetic barrier. The consistent application to a series of ligands[2l,s] or metals[2r] clarified the role played by the ligand and/or the metal. Finally, also the chain termination reactions have been explored by quantum mechanics calculations, indicating that the β-hydrogen transfer to the metal is not an easy reaction[2l,r] and that other reactions, as the β-methyl elimination,[2m] or the σ metathesis,[2l] are possible ways for chain growth termination.

The main contribution of molecular mechanics calculations to the comprehension of the behavior of Ziegler−Natta catalysts has been, in our opinion, reported in seminal papers dealing with heterogeneous catalysts,[3] which introduced the concept, never considered before, that the mechanism of enantioselectivity involves a "chiral orientation of the growing chain".[3,4a−h,j,k] That is, to interactions of the methyl substituent of the coordinated propene with the growing chain, whose chiral orientation is determined by nonbonded interactions with chlorine atoms or with the π ligand of the metallocene, in the case of the heterogeneous and of the homogeneous catalysts, respectively.

Another interesting result of the nonbonded energy analyses, common to the considered metallocene models, is that the regiospecificity of polymerization (primary insertion of the propene is favored) is qualitatively accounted for by steric interactions in the model intermediates corresponding to the monomer coordination step,[4] without considering possible electronic factors.

Analogous conclusions have been drawn in recent combined ab-initio and molecular mechanics studies,[2e,g] in which the enantioselectivity in propene polymerization is ascribed to the chiral conformation of the growing chain, and the regiospecificity is explained on the sole basis of the molecular mechanics interactions active in the transition state of the insertion step.[2e] Finally, our previous molecular mechanics calculations[4k] have also been able to rationalize the probability distributions of stereochemical configurations of the regioirregular units determined by the NMR technique.[6]

Despite the efforts of many research groups, there still are some aspects which have not been investigated in detail; they essentially relate to the chain termination reaction.

^{1}H and ^{13}C NMR analyses show polypropene chains produced with zirconocene-based catalysts to be generally terminated by *n*-propyl and 2-propenyl end groups.[7] The 2-propenyl end groups could arise by transfer of a β-H atom from the polymer chain to the metal atom (see Scheme 1); the Zr−H unit generated by this process can then react with propene to form a Zr−*n*-propyl unit, from which a new polymer chain starts to grow. Another conceivable chain termination mechanism, also sketched in Scheme 1, is the transfer of a β-H atom from the Zr-bound polymer chain directly to the β-C atom of a coordinated olefin molecule; in this case, the 2-propenyl-terminated polymer chain and a new Zr−*n*-propyl unit are generated without intervention of a Zr−H intermediate.

For the case of some zirconocene-based catalyst, also 2-butenyl end groups[7c,d] are observed, which result from 2,1 propene insertion followed by β-H elimination (to the metal or directly to the monomer).

Other end groups, which arise from β-alkyl transfer to the Zr center,[8] from σ-bond metathesis with the olefin substrate,[9] or from alkyl exchange between Zr and Al centers,[10] are occasionally observed, in particular with sterically strongly hindered metallocene catalysts. These reactions do not appear to contribute significantly to chain termination in propene polymerization by MAO-activated Cp_2ZrCl_2 systems (MAO = methylaluminoxane, Cp = cyclopentadienyl).

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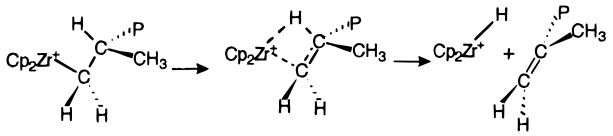
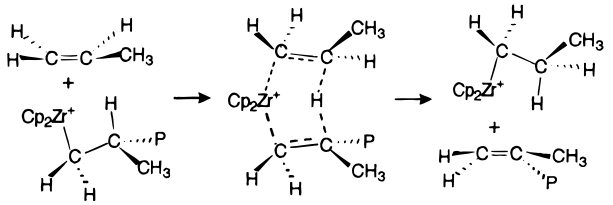
Scheme 1



β–hydrogen transfer to the metal



β–hydrogen transfer to the monomer

As regards the mechanism of the β-H elimination, it is generally accepted that both the transfer to the monomer and to the metal can occur. Evidence for a prevalent β-H transfer to a coordinated olefin, for the zirconocene polymerization catalysts, has been obtained from studies on ethene−propene copolymers[7b] and from studies on the dependence of the polypropene molecular weight from the monomer concentration.[7d,11,12] On the other hand, the feasibility of a direct transfer to the metal has been clearly established by Bercaw et al. from studies on scandocenes[13a] and by Jordan et al. from studies on zirconium and hafnium isobutyl complexes as models for propene polymerization.[13b]

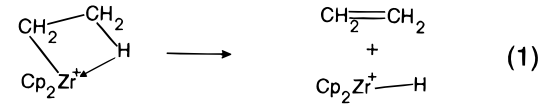
The relevance of the chain termination reactions is related to the role they play in determining the molecular masses of the obtained polymers. It is known that molecular weights accessible with metallocene-based catalysts are usually lower than with heterogeneous catalysts. Recent studies revealed that 2-methyl substituents at each ring ligand increase the molecular weights of the produced polymers considerably.[11,14]

In particular, it has been found that the molecular weight of polypropene samples obtained with the zirconocene complex $(CH_3)_2Si$(2-methylbenz[*e*]indenyl)$_2ZrCl_2$ (MeBenzInd in the following) largely exceeds that obtained with the zirconocene complex $(CH_3)_2Si$(benz[*e*]indenyl)$_2ZrCl_2$ (BenzInd in the following). From the analysis of the dependence of the degree of polymerization on the monomer concentration it has been concluded that for catalyst BenzInd, the relative rate constant for β-hydrogen transfer to the olefin ($k_{\text{transfer-monomer}}/k_{\text{propagation}}$) is nearly 10 times higher than for catalyst MeBenzInd, while the relative rate constants for β-hydrogen transfer to the metal ($k_{\text{transfer metal}}/k_{\text{propagation}}$) are similar for the two catalytic systems.[7c,11]

It is worth noting that the analysis of the end groups has also shown that only for the BenzInd catalyst does a substantial fraction of these β-hydrogen transfers to the olefin involve a secondary growing chain (in which the last insertion is 2,1, rather than the usual 1,2 insertion). As a consequence, the strong reduction of the relative rate constant for the β-hydrogen transfer to the olefin for the catalytic system with the 2-methyl substituent is, at least in part, due to its higher regiospecificity, which reduces the amount of 2,1 insertions.[7c] However, besides this indirect effect, also a direct influence of the 2-methyl substituent on slowing the kinetics of the β-hydrogen transfer to the monomer could be hypothesized.

The aim of this study consists of performing theoretical calculations based on density functional theory (DFT) and molecular mechanics (MM), on suitable models constituted by unassociated cationic species. The active role of the MAO, as well as the influence of the solvent, is neglected for pratical reasons and for the reason that the exact structure, as well as the exact role of the MAO cocatalyst in these systems, is still unknown.

In the first section we will compare, by DFT calculations, the two possible reaction paths which lead to the β-hydrogen transfer, with the aim of enlightening the main geometrical and energetic aspects of these processes, by studying the model systems $Cp_2ZrC_2H_5^+$ and $Cp_2ZrC_4H_9^+$ for the β-hydrogen transfer to the metal. The process sketched in eq 1 refers to the simple



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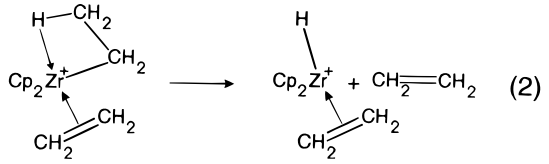

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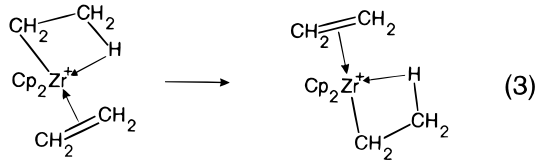

(3)

β-hydrogen transfer to the metal, while the process of eq 2 will be considered in order to investigate the effect of an olefin molecule on the β-hydrogen transfer to the metal process. In the last part of this section, by studying the system $Cp_2ZrC_4H_9^+$, we will study the β-hydrogen transfer to the monomer reaction sketched in eq 3.

In the second section, on the basis of the structures determined by DFT calculations, bulky substituents will be introduced by the MM technique in order to evaluate steric effects which can be present in the considered processes. In particular, a methyl group will be added to the ethylene, to convert it into a propene molecule; moreover, to better simulate the growing chain, a 2-methylbutyl group will be considered in place of an ethyl group. Finally, considering that the aromatic ligands usually used in propene polymerizations, in order to explicate their ability to produce stereospecific polymers, are *ansa*-zirconocenes noticeably bulkier than the simple Cp_2 ligand used in DFT calculations, we will replace the Cp rings with the ligands BenzInd and MeBenzInd, for which the chain termination reactions have been experimentally studied in detail, with the aim of finding possible direct interactions of the 2-methyl substituents in pseudotransition states of β-hydrogen transfer to the monomer.

Methods

(A) Density Functional. The density functional calculations were carried out by using the HFS-LCAO package ADF, developed by Baerends et al.;[15] the

geometry optimization procedure applied for the calculations was based on the method developed by Versluis and Ziegler.[16] The electronic configurations of the systems were described by an uncontracted triple-ζ STO basis set[17] on Zr for 4s, 4p, 4d, 5s, and 5p. Double-ζ STO basis sets[17] were used for C (2s,2p) and H (1s) of the Cp rings. These basis sets were augmented with single 3d and 2p polarization functions for the C and H atoms not belonging to the Cp rings, respectively. The $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ configuration on Zr and the $1s^2$ on C were treated by the frozen-core approximation;[15b] a set of auxiliary s, p, d, f, and g STO functions,[18] centered on all nuclei, was used to fit the molecular density. Geometry optimizations were carried out at the local density approximation (LDA) level, while the reported energy differences were evaluated on the LDA geometries by including Becke's nonlocal exchange corrections and Perdew's nonlocal correlation correction.

(B) Molecular Mechanics. The MM calculations have been performed on structures deriving from the DFT calculations, by substituting the Cp_2 ligand with the BenzInd or MeBenzInd ligand and by replacing some of the hydrogen atoms of the olefin and of the ethyl group with suitable alkyl substituents, in order to model structures closer to those present in the propene polymerization. In particular, one of the hydrogens of the olefin has been replaced by a methyl group, to represent the one of the propene molecule, and the two β-hydrogens of the ethyl group not involved in the agostic interaction have been replaced by a methyl group and an ethyl group, to simulate the methyl group of the last inserted monomer and the remainder of the growing chain, respectively.

A prochiral olefin such as propene may give rise to nonsuperposable coordinations, which can be labeled with the notations *re* and *si*.[19] The coordination of the BenzInd and MeBenzInd ligands is also chiral and can be labeled with the notation (*R*,*R*) or (*S*,*S*) according to the rules of Cahn−Ingold−Prelog[20] extended to chiral metallocenes as outlined by Schlögl.[21] The symbols (*R*,*R*) and (*S*,*S*) indicate the absolute configuration of the bridgehead carbon atom of the two ligands. Without loss of generality, all the reported calculations refer to the (*R*,*R*) coordination of the π ligands.

Considering that we choose the BenzInd and MeBenzInd ligands to be (*R*,*R*) coordinated to the metal, by analogy with the models of various catalytic systems leading to isospecific polymers previously studied, we can reasonably assume that in the growing step reaction the monomer is *re* coordinated to the metal, and thus the chirality of the tertiary carbon atoms of the last inserted unit is *S*. Moreover, as the starting point for the energy minimizations, conformations corresponding to minimum energy situations for strictly analogous systems, extensively studied in the past,[4a−h,j,k] have been used.

The geometry of coordination of the ligands has been optimized by including the force field developed by Bosnich for bent metallocenes.[22] Anyway, for the sake of simplicity, we fixed all the bond distances, with the exception of the distance to the Zr center of the Cp rings, and all the angles C−C−C and C−C−H of the aromatic skeleton of the ligands. The relative geometry of the alkyl group, of the olefin, and of the metal has been kept fixed at the values determined by the DFT calculations; anyway, in the geometry optimization this moiety has been allowed to freely move, has a rigid body, in order to minimize the energy of interaction with the ligands. The geometry of all the alkyl groups replacing the hydrogens on the olefin and on the ethyl group has been optimized, using the parameters proposed by Flory for the bending and torsional contributions.[23] The calculation method for the nonbonded energy has been previously described in detail and is not reported here. We only recall that the parameters adopted are those proposed by Karplus.[24]

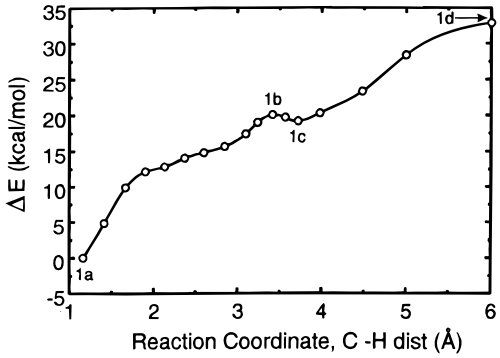

Figure 1. Energy profile for the β-hydrogen transfer to the metal, represented in eq 1. The structures corresponding to the minima and to the transition state, labeled with **1a**−**1d**, are sketched in Figure 2.

Although the energy optimizations are more complete than in previous works,[4a−h,j,k] we still believe that the numerical results of our calculations cannot be trusted as such. This is especially true for conformations far from the energy minima, because of the inaptitude of the energy functions in such regions and because of the simplifying assumption of constancy (rather than near-constancy) of several internal coordinates. However, we also believe that the trends suggested by our results are realistic, in the sense that conformations having low energy according to our calculations are not likely to be substantially different from the energy minima of the catalytic system. Furthermore, although the numerical values of the energy differences depend on the exact geometry and on the energy parameters adopted in the calculations, no reasonable adjustment of these parameters seems to be able to modify our conclusions.

Results

Density Functional. β-Hydrogen Transfer to the Metal. Figure 1 reports the optimized energy as a function of the distance C_β−H, under the constraint of C_s symmetry, for the β-hydrogen transfer to the metal reaction for the system $Cp_2ZrC_2H_5^+$.

This process can be thought to start with the β-agostic alkyl model system **1a** and then go through the transition state **1b** to the ethylene adduct **1c**, which can dissociate to give the ethylene free hydride **1d**. The main geometrical parameters characterizing the structures **1a**−**1d** are reported in Figure 2.

Structure **1a** shows a strong agostic interaction of the β-hydrogen with the metal, this is clearly indicated by the short distance Zr−H, which is equal to 2.09 Å and by the long distance of the C_β−H bond involved in the agostic interaction, which is equal to 1.16 Å, to be compared with the bond distance of 1.10 Å of the other two C_β−H bonds not involved in the agostic interaction. The Zr−Cn_{Cp} distance (Cn_{Cp} = center of the cyclopentadienyl ring) is equal to 2.15 Å, not far from, considering that LDA geometries tend to underestimate bond lengths, the experimental value of 2.21 Å observed in

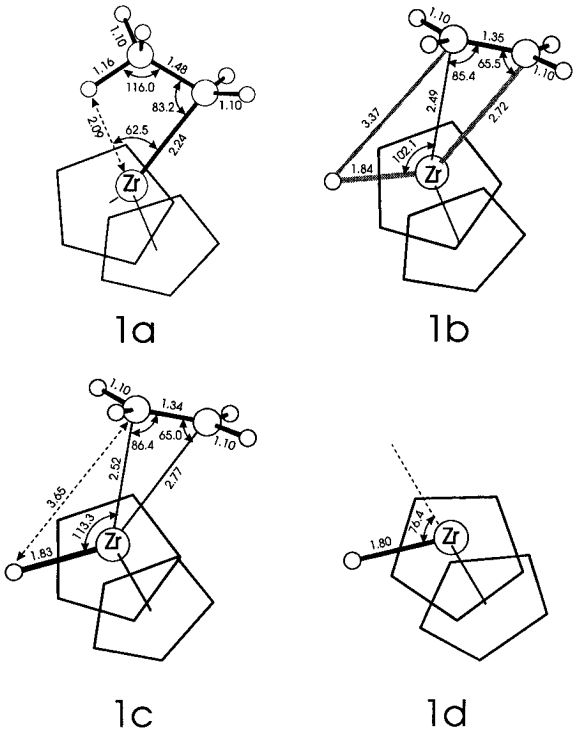

Figure 2. DF-optimized geometries (in Å and deg), of the minima and transition state of the β-hydrogen transfer to the metal. Structures **1a**−**1d** correspond to the situations labeled **1a**−**1d** in Figure 1. For clarity, only the C−C bonds are sketched for the π ligands, while the bonds which are in the course of formation or breaking are sketched in gray.

the "cationic-like" X-ray structure[25] of $(C_5H_4Me)_2Zr(CH_2CH_3)(PMe_3)^+$, while the angle $Cn_{Cp}-Zr-Cn_{Cp}$ is equal to 137.8°, in good agreement with the experimental value of 132.3° observed in the above mentioned complex. Moreover, also the values calculated for the bond distances $Zr-C_\alpha$ and $C_\alpha-C_\beta$ and the agostic distance Zr−H obtained by DFT calculations, which respectively are equal to 2.24, 1.48, and 2.09 Å, agree well with those present in $(C_5H_4Me)_2Zr(CH_2CH_3)(PMe_3)^+$ (2.29, 1.47, and 2.16 Å, respectively). Finally, the angle $Zr-C_\alpha-C_\beta$ found by us is equal to 83.2°, still in good agreement with the value of 84.7° experimentally observed in the same complex.

Structures **1b** and **1c** are very similar to each other, indicating that the transition state **1b** is very close to the product **1c**: the $C_\alpha-C_\beta$ and Zr−H bond lengths are equal to 1.35 and 1.34 Å and to 1.84 and 1.83 Å, in **1b** and **1c**, respectively, while the distance C_β−H elongates from 3.37 to 3.65 Å on passing from **1b** to **1c**.

Structure **1d**, the free zirconocene hydride, shows a little decrease of the bond distances Zr−H (1.80 Å) and $Zr-Cn_{Cp}$ (2.13 Å), probably due to the increased electron deficiency at the metal atom after the detachment of the olefin. The hydrogen is not located in the plane defined by the Zr atom and by the centroid of the Cp rings; the bent sandwich angle is equal to 76.4°.

As regards the energetics of the process, it should be noted that it is highly endothermic; there is a steep increase of the energy, as the C_β−H distance increases, the transition state for the transfer to the metal is at 19.9 kcal/mol, and the olefin−hydride complex represents a minimum at 19.2 kcal/mol. The inverse process, i.e. the insertion of the olefin into a Zr−H bond, presents a very small barrier, only 0.7 kcal/mol, indicating that the olefin−hydride complex should be considered a

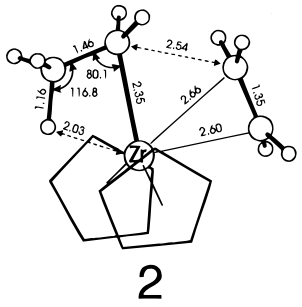

Figure 3. DF-optimized geometry (in Å and deg), of the minimum corresponding to the reactant of the β-hydrogen transfer to the metal reaction, in the presence of a coordinated olefin molecule, sketched in eq 2 (referred as **2** in the text). For clarity, only the C−C bonds are sketched for the π ligands.

transient species. The barrier for the transfer to the metal can be compared with the experimental results obtained by Burger, who found an activation energy in the range 19.4−24.9 kcal/mol for the β-hydrogen transfer to the metal, for various alkyl groups in neutral scandocene complexes,[26] and with the general finding that the β-hydrogen transfer to the metal is not an easy process for Zr complexes.[27]

The same process has been studied by Ziegler, on the same system, using DFT,[2l] and by Morokuma, on model systems of the type $SiH_2Cp_2MeC_3H_7^+$ with Me = Ti, Zr, and Hf, by classical *ab-initio* methods.[2r] Our results are obviously strictly coherent with those of Ziegler; anyway, it has to be pointed out that we have been able to locate a minimum corresponding to the olefin−hydride adduct along the reaction path, due to a denser gridding.

On the other hand, our results are slightly different from those of Morokuma. The DFT−LDA geometries present strong agostic interactions which are much less evident at the Hartree−Fock level, and the olefin coordination distance is noticeably shorter at the DFT−LDA level, with respect to that obtained at the Hartree−Fock level.

Before concluding this section, we report on the possible effect of a coordinated olefin molecule on the β-hydrogen transfer to the metal. Structure **2**, obtained under the constraint of C_s symmetry, represents the starting point for this reaction. This structure presents the β-hydrogen agostic bond on the opposite side with respect to the monomer, while the starting point for the β-hydrogen transfer to the monomer, which will be discussed in the following section, presents the agostic bond on the same side of the monomer. The main geometric features (see Figure 3) indicate that also **2** presents a strong agostic interaction of the alkyl group with the metal. With respect to **1a** there is an elongation of 0.09 Å of the s bond Zr−C, while the C−C bond distances of the alkyl group and of the olefin are practically unchanged with respect to the values present in **1a** and **1c**, respectively. Finally, the energy of coordination of the olefin is equal to 10.6 kcal/mol. On the other hand, any attempt to localize a structure presenting two olefin molecules coordinated to the system Cp_2ZrH^+ has failed. This result suggests that in the equatorial belt of the model complex there is not enough space for the coordination of these three species without pushing the H atom bonded to the metal into contact with one of the olefins. Possibly due to the small barrier to the insertion of the olefin into a Zr−H bond, all our attempts to localize a structure with two olefin

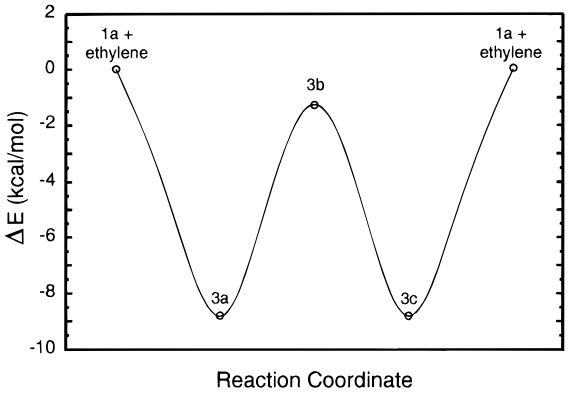

Figure 4. Energy profile for the *β*-hydrogen transfer to the monomer, represented in eq 3. The structures corresponding to the minima and to the transition state, labeled with **3a** and **3b**, are sketched in Figure 5.

molecules coordinated to the system Cp_2ZrH^+ converged into **2**, suggesting that the presence of a second olefin molecule should not facilitate the *β*-hydrogen transfer to the metal.

***β*-Hydrogen Transfer to the Monomer.** Figure 4 reports the optimized energy profile, for the *β*-hydrogen transfer to the monomer reaction, for the system $Cp_2ZrC_4H_9^+$.

This process can be thought of as starting with the coordination of an ethylene molecule to the model system constituted by **1a** to give the *β*-agostic alkyl model system **3a**, in which the alkyl group and the olefin simulate the growing chain and the monomer molecule, respectively. Then, **3a** goes through the transition state **3b** to the ethylene adduct **3c** (which in the framework of our simplified models is equivalent to **3a**), in which the olefin and the alkyl group simulate the alkene terminal of the polymer chain and an alkyl group from which a new polymer chain could start to grow, respectively. Finally, **3c** can dissociate to give the alkene free *β*-agostic alkyl model system **1a**. The main geometrical parameters characterizing the structures **3a** and **3b** are reported in Figure 5.

Structure **3a**, obtained under the constraint of C_s symmetry, shows a stronger *β*-agostic interaction of the ethyl group with the metal with respect to **1a**, this is clearly indicated by the shorter Zr−H distance, which is equal to 2.04 Å, and by the longer C_β−H distance, which is equal to 1.18 Å. Another peculiar feature is the very short distance of one of the carbon atoms of the olefin with the hydrogen involved in the agostic interaction, which is equal to 1.94 Å, indicating that some interaction between the alkyl group and the olefin is already occurring at the coordination level. This is also indicated by a shrinkage of the C−C bond of the alkyl group, which is now equal to 1.45 Å, and by an increasing of 0.10 Å of the bond distance Zr−C_α of the alkyl group, with respect to the analogous values observed in **1a**. On the other hand, the structural parameters of **3a** are very similar to those present in **2**, from which **3a** differentiates by the fact that the *β*-hydrogen agostic bond now faces the olefin in a way suitable for the transfer.

Structure **3b** is obtained under the constraint of C_{2v} symmetry. The higher symmetry is adopted in order to save computer time and corresponds to the assumption that in the transition state the hydrogen atom which is going to be transferred is at equal distances from the partially bonded carbon atoms of the olefin and of the growing chain. The most peculiar features can

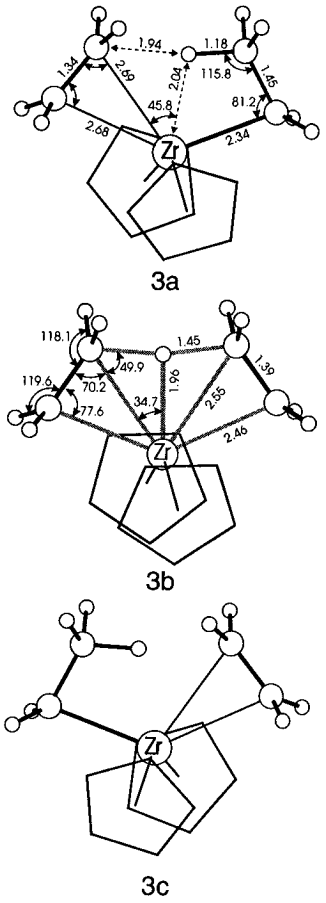

Figure 5. DF-optimized geometries (in Å and deg), of the reactants and of the transition state of the *β*-hydrogen transfer to the monomer. Structures **3a** and **3b** correspond to the situations labeled **3a** and **3b** in Figure 5. For clarity, only the C−C bonds are sketched for the *π* ligands, while the bonds which are in the course of formation or breaking are sketched in gray.

be considered the distances of the hydrogen atom which is going to be transferred from the carbon atoms and from the metal. The distance from these carbon atoms is equal to 1.45 Å, a value which is close to the average of the two analogous distances present in **3a**, while the distance from the metal atom is decreased from 2.04 to 1.96 Å, almost a bond distance, indicating a participation of the metal atom in the transfer process. The C−C bond distance is equal to 1.39 Å, revealing the essentially double bond character of the same. Also the distances of the carbon atoms from the metal indicate the essentially double character of the C−C bonds. In fact, these distances are 2.46 and 2.55 Å, distances noticeably longer than the usual for a *σ* Zr−C bond. Finally, it has to be noted that the distance between the two carbon atoms which are exchanging the hydrogen atom and the C−Zr−C angle defined by these two carbon atoms and by the metal atoms decrease only 0.22 Å and 3.6° on going from **3a** to **3b**, indicating that the transfer does not require a noticeable displacement of the heavy atoms, a fact that is important in the dynamics of the reaction.

As regards the energetics of the reaction, the coordination of the olefin to **1a** is still an exothermic process, but the coordination energy, 8.7 kcal/mol, is obviously smaller with respect to the coordination energy of the ethylene to the hydride structure **1d** (see Figure 1), due to the presence of the electron donating ethyl group bonded to the metal. Moreover, **2** and **3a** are almost isoenergetic, in fact, **2** is favored by only 1.9 kcal/mol. The energy of the transition state **3b** is 7.5 kcal/mol

higher than that of the reagent **3a**, suggesting that the β-hydrogen transfer to the monomer is a viable process for chain growth termination. Anyway, it has to be considered that this process, especially in the case of propene polymerization, could suffer steric restrictions due to nonbonded interactions present in the transition state. This point will be discussed in the following section.

The activation energy for the β-hydrogen transfer to the monomer (7.5 kcal/mol) can be safely compared with the activation energy for the chain growth step obtained by Ziegler (0.7 kcal/mol for the insertion of ethylene in the system $Cp_2ZrCH_3^+$),[21] due to the fact that we have used the same methodology and the same basis set. The barrier for the β-hydrogen transfer to the monomer is considerably higher, consistently with the experimental results indicating that the polymer propagation is the most favorable process for these systems.

A different chain growth termination process which has been examined by Ziegler involves a vinylic C−H bond activation. The product of the reaction, as well as for the β-hydrogen transfer, either to the monomer or to the metal, is an alkene-terminated polymer chain and an alkyl-initiated polymer chain. The electronic barrier of this process is 7.4 kcal/mol, indicating that both the C−H activation and the β-hydrogen transfer to the monomer have to be considered as processes viable for chain growth termination.

Another chain growth termination process whose energetics can be described by Ziegler's paper involves the β-methyl transfer to the metal. The barrier to the elimination is approximately 10 kcal/mol (see Figure 5 in ref 2l), and the process is endothermic by approximately 9 kcal/mol, again, a value greater than that here obtained for the β-hydrogen transfer to the monomer.

Molecular Mechanics. Nonbonded Energy Contribution to the Energies for the β-Hydrogen Transfer Processes. The electronic energy profiles above described have to be considered, especially for the β-hydrogen transfer to the monomer, only a contribution to the real energy profiles. A first MM analysis has been performed on structures **1a**−**1c**, **3a**, and **3b**, by replacing the two hydrogen atoms of the C_β of the alkyl group not involved in agostic interactions with a methyl group and an ethyl group, to simulate the methyl group of the last inserted unit and the growing chain, respectively, and by replacing one of the hydrogens of the olefin with a methyl group, to transform the ethylene molecule into a propene molecule coordinated in a way suitable for primary insertion. This analysis indicates that, independently of the chirality of coordination of the propene (*re* or *si*), nonbonded interactions are not of great relevance in **1a**−**1c** (3.0, 4.2, and 4.6 kcal/mol, respectively), while a considerable steric energy is present in **3a** and **3b** (10.6 and 15.2 kcal/mol, respectively). These interactions are essentially between the methyl group of the propene and the alkyl groups bonded to the C_β of the growing chain. Thus, according to the performed calculations, a noticeable contribution due to nonbonded interactions should be added to the electronic energy profiles reported in the previous section for the β-hydrogen transfer to the monomer. This contribution reduces the difference between the energy barriers of the two β-hydrogen elimination processes.

Effect of the 2-Methyl Substituents in *ansa*-Metallocenes: BenzInd and MeBenzInd Ligands.

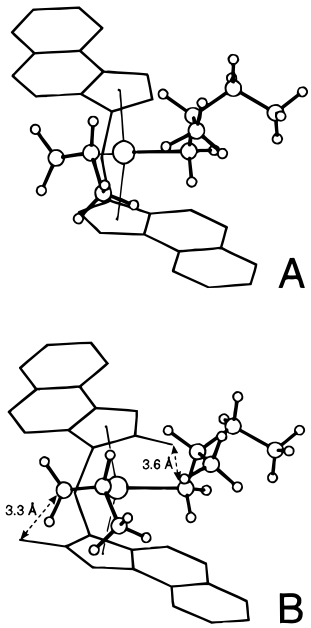

Figure 6. MM models for the pre-insertion intermediates of the chain growth reaction with the BenzInd (A) and MeBenzInd (B) ligands. The propene molecule is *re* coordinated, and the growing chain is modeled by a 2-methylbutyl group, to simulate the last portion of a polypropene chain. For clarity, only the C−C bonds are sketched for the π ligands.

The contribution of the nonbonded interactions to the activation energies of the insertion and transfer (to the metal and to the monomer) reactions, due to the 2-methyl substitution in ansa-metallocenes has been evaluated for the case of the BenzInd and MeBenzInd ligands.

A preliminary MM analysis has been performed on models of coordination intermediates for the primary insertion of the *re*-coordinated propene (favored with the (*R*,*R*) coordinated ligands). The minimum energy conformations of the *re* coordination intermediates are sketched in Figure 6A,B for the BenzInd and MeBenzInd ligands, respectively. These models present substantially similar coordinations and conformations of the monomer and of the growing chain. In particular, both present the methyl group of the propene and the second atom (and its substituents) of the growing chain on opposite sides with respect to the plane defined by the Zr−C bonds, and as a consequence, in the framework of our model are considered suitable for the insertion reaction (pre-insertion intermediates). This analysis indicates that a slight increase of the steric energy (3.3 kcal/mol) is present on passing from the BenzInd to the MeBenzInd ligand. This increase of the energy suggests that the insertion reaction is somewhat hindered by the presence of 2-methyl substituents on the ligand. This result is in qualitative agreement with the experimental results of Brintzinger,[7c,11] which found a decreased polymerization activity when 2-methyl substituents are present.

The MM analysis performed on the precursor and on the transition state of the β-hydrogen transfer to the metal (derived from structures **1a** and **1b**, respectively) in the presence of the MeBenzInd and of the BenzInd ligands reveals an analogous contribution of the nonbonded interactions (3.3 and 3.4 kcal/mol, for the precursor and the transition state, respectively) due to the presence of the methyl group in MeBenzInd.

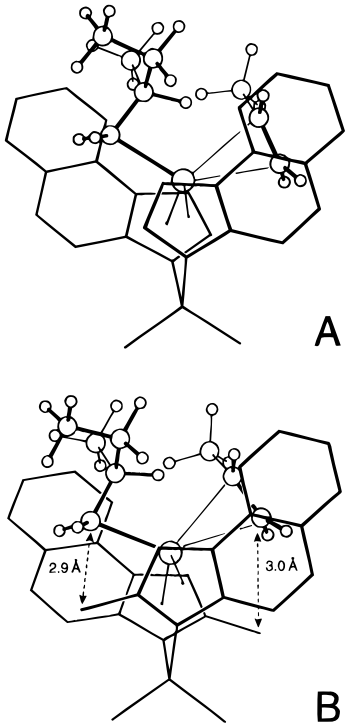

Figure 7. MM models for the reactants of the β-hydrogen transfer to the monomer reaction with the BenzInd (A) and MeBenzInd (B) ligands. In this case the monomer is a propene molecule *re* coordinated, and the growing chain is modeled by a 2-methylbutyl group, to simulate the last portion of a polypropene chain. For clarity, only the C−C bonds are sketched for the π ligands. Thinner lines indicate bonds connecting atoms which in the sketches are below the metal atom.

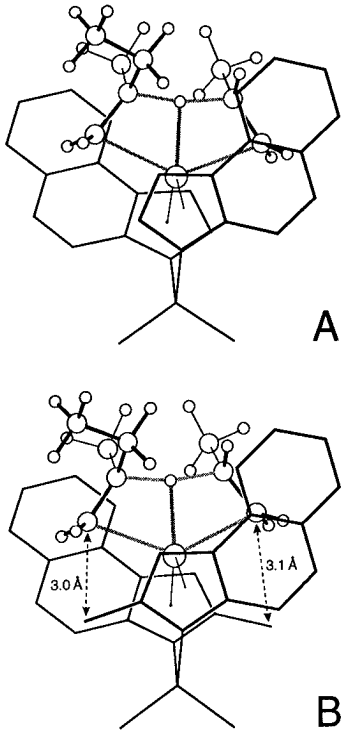

Figure 8. MM models for structures close to the transition state of the β-hydrogen transfer to the monomer reaction with the BenzInd (A) and MeBenzInd (B) ligands. In this case the monomer is a propene molecule *re* coordinated, and the growing chain is modeled by a 2-methylbutyl group, to simulate the last portion of a polypropene chain. For clarity, only the C−C bonds are sketched for the π ligands, while the bonds which are in the course of formation or breaking are sketched in gray. Thinner lines indicate bonds connecting atoms which in the sketches are below the metal atom.

Noticeably greater is, instead, the energy contribution calculated in the same way for the precursor and for the transition state of the β-hydrogen transfer to the monomer (derived from structures **3a** and **3b**, respectively), which in this case is equal to 6.0 and 4.7 kcal/mol for the precursor and the transition state, respectively.

The models corresponding to the starting structures and to the transition states for the β-hydrogen transfer to the monomer, in the presence of the BenzInd and MeBenzInd ligands, are reported in Figures 7A,B, and 8A,B, respectively. It is apparent that short distances are observed between the C_α of the growing chain and of the monomer, with the methyl groups of the aromatic ligand (2.9 and 3.0 Å, respectively), for the starting structure in the case of the MeBenzInd ligand (Figure 7B), while these interactions are obviously absent for the starting structure in the case of the BenzInd ligand (Figure 7A). Moreover, these interactions are only slightly reduced in the transition state; in fact the distances between the C_α of the growing chain and of the monomer, with the methyl groups of the ligand, are equal to 3.0 and 3.1 Å, respectively (Figure 8B), indicating that the effect of the methyl groups of the aromatic ligand, although less pronounced, is still present.

It is worth noting that the MM energy increases due to the presence of a 2-methyl substituent are larger for the β-hydrogen transfer to the monomer (6.0 and 4.7 kcal/mol for the precursor and the transition state, respectively) than for the insertion reaction (3.3 kcal/mol for the pre-insertion intermediate). Hence, the 2-methyl substituents on the ligands hinder the transfer to monomer more than the insertion reaction.

Analogous results are obtained by considering the models (precursors and pseudotransition states) including a secondary (rather than a primary) growing chain. In fact, the MM energy increases, on passing from the BenzInd to the MeBenzInd ligand, are much larger for the β-hydrogen transfer to the monomer (11.0 and 12.6 kcal/mol for the precursor and the transition state, respectively) than for the insertion reaction (6.5 kcal/mol for the pre-insertion intermediate). These results suggest that, for a secondary growing chain, in the presence of the 2-methyl substituents on the ligand the transfer to monomer is even more hindered.

This analysis confirms the hypothesis of Brintzinger,[7c,11] that the inhibition of the β-hydrogen transfer to the monomer, in the presence of the 2-methyl substituents, is essentially due to larger steric interactions in the more crowded equatorial belt of the metallocene.

Conclusions

The geometries and the energetics of the processes corresponding to the β-hydrogen transfer either to the metal or to the monomer have been investigated using density functional methods. Our analysis indicates that the β-hydrogen transfer to the metal is not an easy reaction, and an activation barrier of 19.9 kcal/mol is calculated for this process. Moreover, the whole process, without including the detachment of the olefin, is endothermic by 19.2 kcal/mol.

The other β-hydrogen transfer processes examined, the transfer to the monomer, is instead a viable process. The calculated electronic activation barrier is equal to 7.5 kcal/mol, and the geometry of the transition state

suggests a noticeable contribution of the metal to facilitate the transfer process. This indication is supported by the short distance (1.96 Å) of the hydrogen which is going to be transferred from the metal atom.

The MM analysis indicates that only slight steric interactions are present in models corresponding to the β-hydrogen transfer to the metal when some hydrogen atoms of the simplified systems are replaced with the alkyl groups which are present in the termination reaction of a polypropene chain. On the other hand, a similar analysis on the models corresponding to the β-hydrogen transfer to the monomer, indicates that a noticeable steric contribution to the activation energy due to interaction between the alkyl substituent of the monomer, and atoms of the growing chain, is present.

The MM analysis, performed on models of catalytic complexes based on the BenzInd and MeBenzInd ligands, indicates that the presence of 2-methyl substituents on the ligand increases in analogy to amounts of the steric energy for the models corresponding to the chain growth reaction and to the β-hydrogen transfer to the metal. A more pronounced effect of the 2-methyl substituents is observed for the β-hydrogen transfer to the monomer, in the case of either a primary or a secondary growing chain, both for the precursor and for the transition state. In particular, our results suggest that this behavior should be due to steric interactions of the methyl groups of the aromatic ligand with the C_α both of the growing chain and of the monomer.

These results are in agreement with the experimental findings that the β-hydrogen transfer to the monomer is inhibited by the presence of 2-methyl substituents on *ansa*-metallocene ligands.

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