Preliminary communication

Influence of rotation between agostic structures on ethene interaction with a zirconocene polymerization site

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Abstract

Density-functional theory has been used to study the first few steps of ethene polymerization with the single-site catalyst $Cp_2ZrCH_3^+$ (biscyclopentadienyl methyl zirconium cation). Insertion of the first monomer yields a γ-agostic product $Cp_2ZrC_3H_7^+$ which can transform into a more stable β-agostic conformation with an activation barrier of 11 kJ mol^{-1}. The interaction of the β-agostic structure with a second monomer leads to chain termination (front-side attack) or insertion (back-side attack) with barriers of about 35–40 kJ mol^{-1}. A more likely step appears to be insertion directly into the γ-agostic $Cp_2ZrC_3H_7^+$, to form the γ-agostic product $Cp_2ZrC_5H_{11}^+$ with a barrier of only 11 kJ mol^{-1}.

Keywords: Zirconocenes; Olefin polymerization; Agostic interactions; Density-functional theory

Over the last decade, there has been a considerable effort to develop single-site metallocene catalysts for polymerization of olefins [1,2]. A number of these catalysts have been well-characterized zirconocene cations formed by the alkylation of a dichloride with the subsequent formation of an ionic pair. The relative simplicity of the complexes have made them adequate for quantum-mechanical simulations [3–7], particularly after it has been shown that density-functional theory (DFT) is well suited for such systems [4–7]. Ziegler and coworkers have studied the insertion of ethene according to the reaction $Cp_2ZrCH_3^+ + C_2H_4 \rightarrow Cp_2Zr\text{-}C_3H_7^+$ (biscyclopentadienyl propyl zirconium cation) resulting in an agostic interaction between one of the hydrogen atoms on the γ-carbon atom and zirconium [5]. Further, they showed that a β-agostic structure represents a more stable complex. An attempt to study the transformation between the γ- and β-agostic states by a molecular-mechanics simulation appears less accurate due to the important changes in bonding during the rotation [6]. Recently, Lohrenz and coworkers extended the analysis to ethyl instead of methyl to represent the growing polymer chain [7]. In the present paper, we study the γ- to β-agostic rotational transformation of

$Cp_2ZrC_3H_7^+$ and how a second monomer may be inserted into the two agostic starting conformations with propyl to represent the polyolefin chain. Some of the mechanistic key points are illustrated in Fig. 1.

The density-functional calculations were carried out using the DMol program (Version 2.36) provided by Biosym [8]. Geometries were optimized at the level of the local-density approximation [9], with the correlation functional of Lee et al. [10]. Gradient corrections to the energy are based on the functionals proposed by Becke [11] (exchange) and Lee et al. [10] (correlation). A double-numeric basis set including polarization functions was used, with the 1s carbon and 1s to 3d zirconium orbitals assigned to a frozen core. Except for the linear-transit reaction coordinate, no geometrical restrictions were imposed during the calculations. Most of the stable configurations and transition states were optimized separately, lifting the constraint of the reaction coordinate [12].

In Fig. 2 the energy profile during rotation of the dihedral angle $\phi = \angle(Zr\text{-}C_3\text{-}C_4\text{-}C_5)$ is shown together with the $Zr\text{-}H_\gamma$ and $Zr\text{-}H_\beta$ distances. The carbon atoms are numbered 1 and 2 in the incoming ethene and 3 to 5 in the propyl group (or 3 in methyl), whereas β and γ denote the second and third carbon atom, respectively, from zirconium irrespective of the alkyl chain length. First of all it may be noted that a mini-

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chain length. First of all it may be noted that a minimum in the energy profile is obtained when the propyl chain is twisted $23.9°$ in order to minimize the nonbonding interactions between the hydrogen atoms, see Fig. 3a. Insertion of the monomer into $Cp_2ZrCH_3^+$ assuming a symmetry plane (i.e., $\phi = 0°$) results in a staggered conformation of the hydrogens. In a separate calculation of this insertion path with no symmetry restrictions, it was shown that the propyl chain assumes the $23.9°$ energy minimum directly. The $Zr-H_\gamma$ distance increases from 213 pm to 225 pm when ϕ is changed from $0°$ to $23.9°$. Thus, the agostic interaction suffers somewhat from this rotation. However, there is a stabilization energy relative to the forced planar $Zr-C_3-C_4-C_5$ conformation of 16 kJ mol^{-1}.

A continued rotation to $\phi = 70°$ results in a transition state (Fig. 3b) at an energy barrier of only 11 kJ mol^{-1}. Finally, the β-agostic state in Fig. 3c, stabilized by an additional 26 kJ mol^{-1} is obtained at a dihedral angle of $129.4°$. Due to the increased stabilization and the moderate rotational barrier, insertion into the β-agostic structure was attempted. To be reasonably sure that the starting geometry does not influence the final result, we investigated the approach of the monomer from both sides of the structure. Front-side attack (i.e. from the β-agostic side of $Cp_2ZrC_3H_7^+$) was studied with $Zr-C_1$ as linear-transit reaction coordinate [13], while for the

Fig. 2. Effect of the γ- to β-agostic rotation in $Cp_2ZrC_3H_7^+$, as defined by the $Zr-C_3-C_4-C_5$ dihedral angle, on the total relative energy (top) and the accompanying $Zr-H_\gamma$ and $Zr-H_\beta$ distances (bottom).
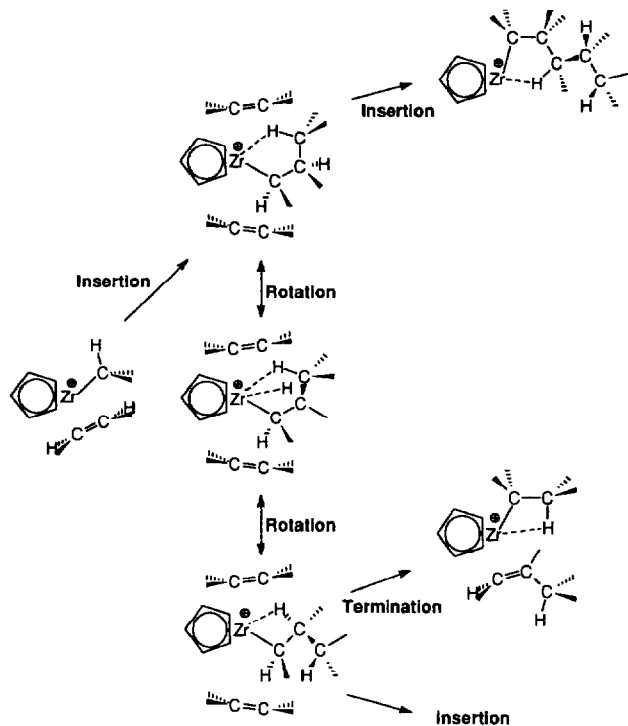

Fig. 1. Suggested reaction schemes for interaction of ethene with $Cp_2ZrCH_3^+$. For clarity, only one of the Cp rings is shown in each structure. In reality, zirconium is tetrahedrally coordinated to two Cp rings, the agostic hydrogen atom, and the first carbon atom of the polymer chain.
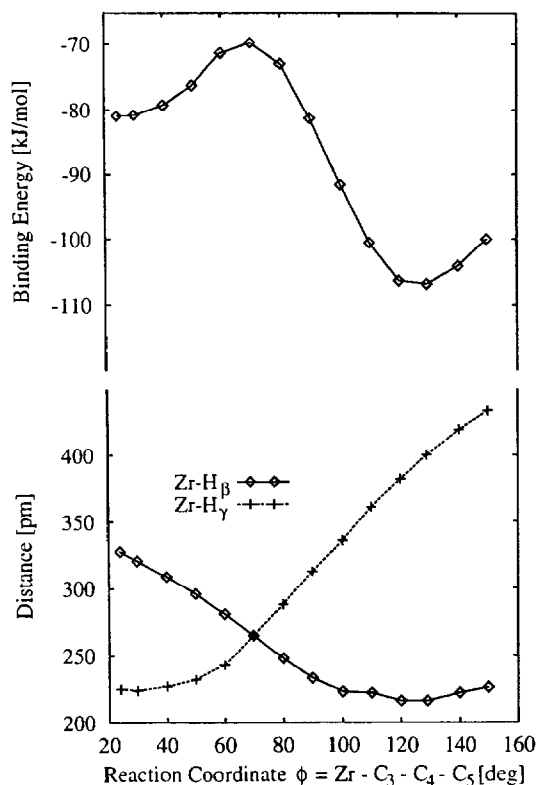
back-side approach (i.e., from the same side as the first monomer was added) we used C_2-C_3. The result of front-side attack is chain termination with chain transfer to the monomer according to the reaction $Cp_2ZrC_3H_7^+ + C_2H_4 \rightarrow Cp_2ZrC_2H_5^+ + C_3H_6$. The energy barrier against this process is 42.6 kJ mol^{-1} [14]. In Fig. 3d the configuration is given for the ethyl/propene π-complex after termination. The back-side approach results in insertion and formation of a δ-agostic pentyl structure, in accordance with previous calculations on the β-agostic ethyl compound [7]. Our calculations yield an energy barrier of 35.5 kJ mol^{-1}, which is comparable with 28.9 kJ mol^{-1} as found in Ref. [7]. An alternative termination mechanism, the β-hydrogen elimination, has been shown to be thermodynamically highly unlikely [5]. We have reached the same conclusion for the reaction β-agostic $Cp_2ZrC_3H_7^+ \rightarrow Cp_2ZrH^+ + C_3H_6$, which is endothermic by 113.4 kJ mol^{-1}.

The moderate γ to β rotational barrier indicates considerable rotational flexibility and even the possibility of thermodynamic equilibrium. It should be noted however, that the reverse rotation results in a larger barrier of 37 kJ mol^{-1}. Alternative reactions may take place, starting at arbitrary values of the dihedral angle ϕ, but the most obvious is to attempt insertion into the γ-agostic structure. Indeed, side on monomer and a

C_2–C_3 linear transit results in the expected insertion. The product $Cp_2ZrC_5H_{11}{}^+$ (Fig. 3e) again shows the γ-agostic stabilization, although the dihedral angle ϕ
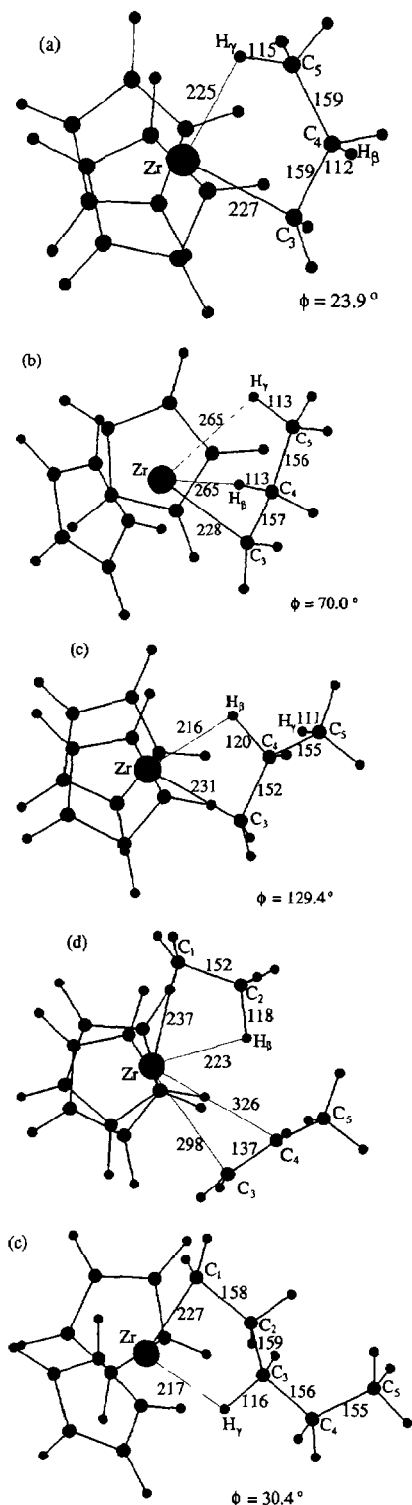

Fig. 3. Cationic structures and selected bond lengths (pm) in: (a) $Cp_2ZrC_3H_7{}^+$, γ-agostic; (b) $Cp_2ZrC_3H_7{}^+$, γ,β-agostic transition state; (c) $Cp_2ZrC_3H_7{}^+$, β-agostic; (d) $Cp_2ZrC_2H_5{}^+$–(C_3H_6), terminated π-complex; (e) $Cp_2ZrC_5H_{11}{}^+$, γ-agostic product. The atom size increases in the order H, C, Zr.
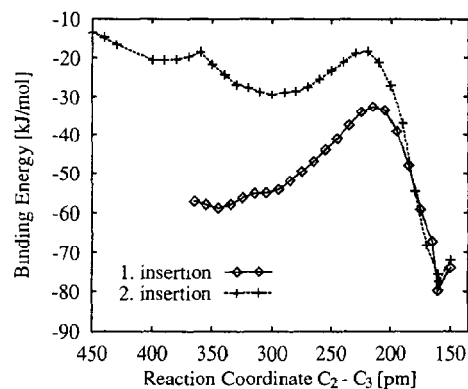

Fig. 4. Reaction profiles for front-side insertion of ethene to $Cp_2ZrCH_3{}^+$ (solid line) and γ-agostic $Cp_2ZrC_3H_7{}^+$ (dashed line).

(Zr–C_1–C_2–C_3 in Fig. 3e) has increased from 23.9° to 30.4° and the Zr–H_γ distance changed from 227 pm to 217 pm. This observation is not unexpected since the added carbon atom which is bonded to the γ-carbon induces a more reactive hydrogen. The results point to the importance of starting such mechanistic studies with a sufficiently long polymer chain.

In Fig. 4 the energy profiles for the first and second insertion are compared in more detail. It is satisfying that the energy of insertion is similar in the two cases, about 80 kJ mol^{-1}. The reaction profiles are, however, very different, and the activation energy is drastically reduced from 26 to 11 kJ mol^{-1}. The apparent reason for the ease of insertion with a longer alkyl chain is the destabilization of the π-complex from -59 to -29 kJ mol^{-1}. Evidently, the hydrogen–hydrogen repulsions as well as the γ-agostic interaction facilitate the monomer insertion.

To conclude, we find that the torsional movement between the γ- and β-agostic H–Zr states is likely to be a key step in the mechanism for olefin polymerization by metallocene catalysts. It seems like a front-side insertion to a rotationally optimized γ-agostic structure is the main insertion path, whereas attack on the β-agostic structure leads to termination by chain transfer to monomer (front-side) or to insertion (back-side), both with substantially higher energy barriers.

Acknowledgments

References and notes

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[9] We have performed a linear-transit calculation for the reaction $Cp_2ZrCH_3^+ + C_2H_4 \rightarrow \gamma$-agostic $Cp_2ZrC_3H_7^+$ with geometries optimized when gradient corrections to the energy are included. The only effect when compared with the LDA calculation, is an overall downward shift of the energy curve by about 8 kJ mol^{-1}.

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[12] For the reaction $Cp_2ZrCH_3^+ + C_2H_4 \rightarrow \gamma$-agostic $Cp_2ZrC_3H_7^+$, the π-complex, the transition state and the product were all optimized without geometry constraints. For the reaction γ-agostic $Cp_2ZrC_3H_7^+ + C_2H_4 \rightarrow \gamma$-agostic $Cp_2ZrC_5H_{11}^+$, only the product was optimized without geometry constraints. For the rotation γ-agostic $Cp_2ZrC_3H_7^+ \rightarrow \beta$-agostic $Cp_2ZrC_3H_7^+$, all three stationary points were optimized without geometry constraints.

[13] A similar linear-transit calculation with C_2–C_3 as reaction coordinate gave essentially the same result.

[14] The transition state was optimized after performing a linear-transit calculation with C_2–H_β as reaction coordinate.