Notes

Proposed Polymerization Termination Mechanism for 3-R-Indenyl *ansa*-Zirconocenes (R = *n*-Alkyl) Based on DFT Calculations and Experimental Observations

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Metallocene compounds have been widely used as catalysts for the polymerization process. In turn, polymerization reactions and their mechanisms have been the subject of extensive experimental[1] and theoretical[2−4] studies looking for a better control of molecular weights and in general of polymer architecture. In this context, chain termination reactions play a critical role in the molecular weight of the obtained polymers. A few different kinds of chain termination processes have been reported. Among them, β-hydride elimination or β-hydrogen transfer to the metal (i), β-hydrogen transfer to the monomer (ii), alkene C−H bond activation by metal−alkyl complexes (iii), and hydrogenolysis (iv) are the most extensively studied. In the β-hydride elimination (i) the reactant is an alkyl−metallocene complex with a β-agostic interaction, and the products are a vinyl-terminated polymer chain and a metallocene hydride complex. The β-hydrogen transfer to the monomer (ii) is a bimolecular reaction where the reactants are the alkyl−metallocene complex with a β-agostic interaction and the new monomer to be inserted. In this mechanism the vinyl chain migrates out, and in the case of an ethylene insertion, an ethyl β-agostic complex is formed. In the alkene C−H bond activation by metal−alkyl complexes (iii) the reactants are the same as in case (ii) although the products of the reaction are in this case an alkane-terminated polymer chain and a vinyl−metallocene. Finally, hydrogenolysis reaction (iv) occurs in presence of hydrogen gas and leads to the formation of an alkane and a hydride complex. The energetics of these reactions depends on the type of catalysts (metal atom and substituents), the solvent, the monomer, etc. Additionally, other mechanisms for chain termination may also be considered.

In this study, we have performed calculations based on the density functional theory (DFT) to investigate the experimental differences observed in the molecular weights of the polymers obtained using different zirconocene catalysts. Geometric structures and Gibbs free energy profiles were obtained using the B3LYP[5,6] hybrid DFT functional and LANL2DZ[7] basis set for all atoms. All calculations were performed using the Gaussian03 package.[8] Thermodynamic data were calculated for

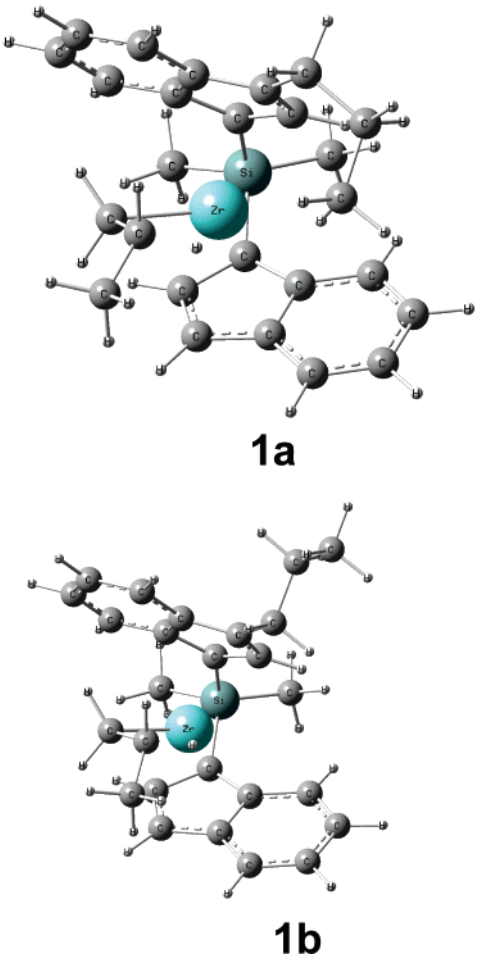
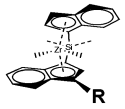


Figure 1. *n*-Propyl substituent conformations.

Chart 1. Catalysts Considered in the Present Work



R= methyl, ethyl, n-propyl, n-butyl

Table 1. $\Delta G^{\#}$ Values Obtained as Differences in *G* Energy between Transition State and Reactant for Each Process (Values Are in kcal/mol)

R	propagation[a]	H transfer to monomer[a]	H transfer to metal
H	15.7	17.9	28.6
methyl	14.4	18.6	30.1
ethyl	14.1	18.9	30.0
propyl	14.3	18.8	30.3
butyl	14.4	18.9	29.9

[a] The reactant is assumed to be the sum of the cationic species and the ethylene monomer for the Gibbs energy estimation.

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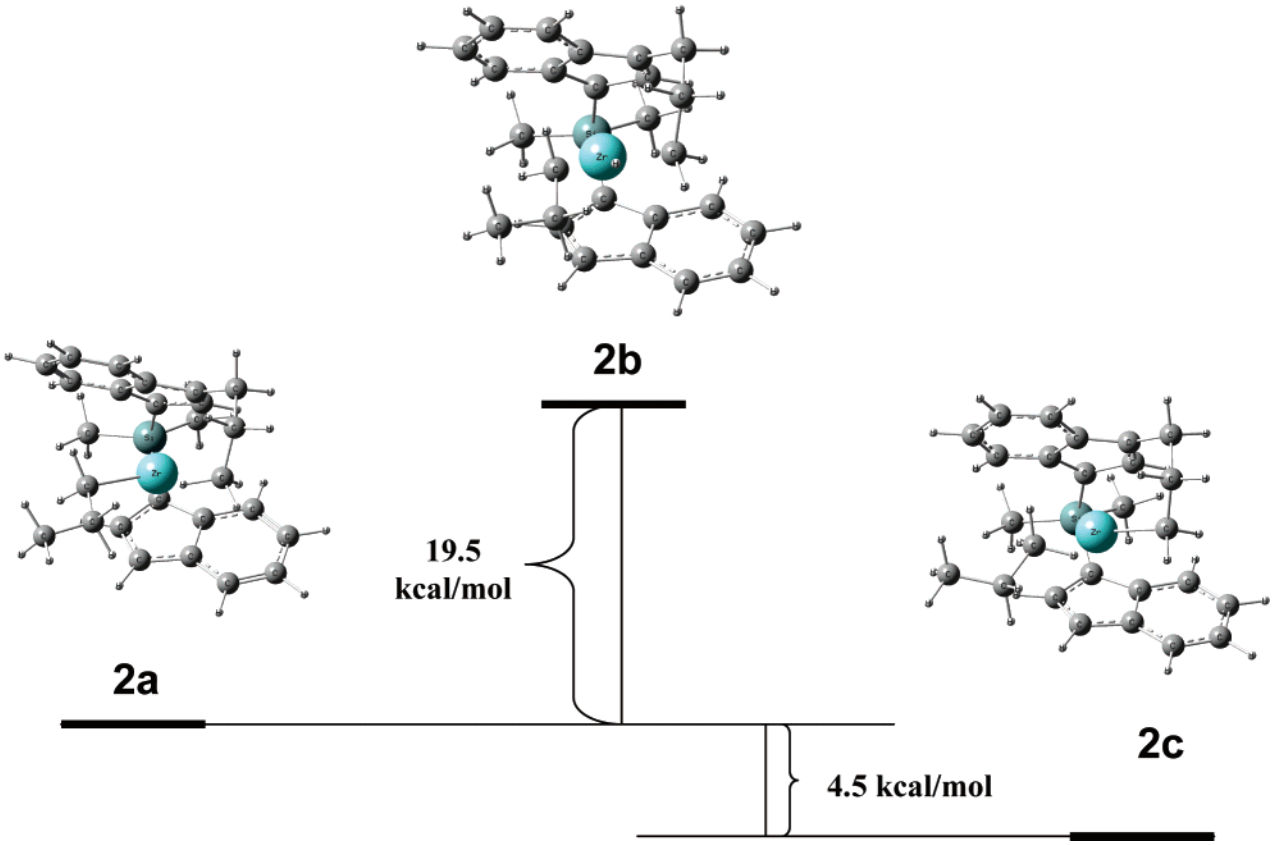

Figure 2. Reaction profile.

1 bar ethylene pressure and 298 K using standard statistical thermodynamic methods implemented in the Gaussian package.[9]

It has been experimentally observed in our laboratory[10] that silyl-bridged bis-indenyl catalysts containing linear alkyl substituents in the 3-position of the indenyl ligand (see Chart 1) yield polyethylenes with different molecular weights depending on the alkyl chain length. In this sense, catalysts containing linear alkyl substituents with three or more C atoms give rise to a dramatic decrease in the polymer molecular weight. Meanwhile, the methyl- and ethyl-substituted indenyl catalysts give molecular weights of the same order. Finally, the unsubstituted catalyst yields a polymer with slightly lower molecular weight.

DFT calculations have been performed in order to shed light on the interpretation of the above-described phenomena. Both the chain growth step and the most common termination reactions (β-elimination and β-transfer to monomer) applied to the *n*-Pr^+ cationic species have been investigated. Table 1 shows the results obtained for different alkyl-substituted catalysts ranging from the unsubstituted to the *n*-butyl compounds. No significant differences among the different alkyl-substituted systems can be observed. It is however clear that the unsubstituted compound would give lower molecular weight polymers because the energy barrier difference between propagation and termination reactions is the lowest of all compounds. This decrease is in fact experimentally observed.

The energies tabulated correspond to the trans conformations of the alkyl chains. These conformations are those adequate to accommodate an incoming olefin in the active site, which is the initial state for insertion and H transfer to monomer reactions.

Therefore, the purpose of the present paper is to describe an alternative termination mechanism as revealed by some theoretical calculations. This mechanism is indeed able to explain the differences experimentally found in the polymerization behavior.

Lewin et al.[11] have proposed an unimolecular C−H bond metathesis reaction for Sc, Y, and Lu metallocenes which goes through a so-called tuck-in complex. This complex is formed by the interaction of a methyl group, corresponding to an indenyl ligand substituent, with the metal center. We suggest a similar process occurring as a termination mechanism with the *n*-propyl-substituted indenyl zirconocene.

Various conformations of the linear alkyl chain substituent containing at least two C atoms can be located. In particular, it is possible to find one structure where the terminal methyl group of the alkyl substituent is oriented toward the metal center, as shown in Figure 1a. The geometries displayed in Figure 1 correspond to the *n*-propyl substituent. This conformation presents a weak agostic interaction between one H atom of the methyl terminal group and the metal center. The calculated energy is 2.4 kcal/mol lower than the value corresponding to the less strained conformer shown in Figure 1b. For the ethyl case the energy difference between both conformers is however 3.1 kcal/mol in favor of the less strained structure. In this case the methyl group cannot form agostic interactions with the Zr atom.

The propyl conformer can undergo chain rotation approaching, thus, the methyl H atoms to the metal center and breaking the β-agostic interaction. This new conformer, shown in Figure 2a, is 5.0 kcal/mol less stable than structure **1a**.

The terminal methyl H atom activated by the agostic interaction can migrate to the methylene unit of the growing polymer chain attached to the metal atom. A transition state structure (Figure 2b) between the reactant (**2a**) and the product (**2c**) has been located by using the QST2 methodology[12] incorporated in the Gaussian03 code. The transition state

geometry presents the reactive H atom halfway between the terminal methyl of the alkyl substituent and the last methyl unit of the growing polymer chain. The vibrational analysis of the optimized transition state presents one negative eigenvalue of the Hessian matrix. The corresponding normal mode shows the H vibrating between both methyl units, indicating the correctness of the transition state found. The energy barrier of the process is 19.5 kcal/mol. This value is comparable to that obtained for the β-transfer to monomer termination reaction (18.8 kcal/mol), which suggests that this new polymerization termination mechanism is competitive with the classical end polymerization processes. The corresponding product presents a metallacycle structure and the polymer chain ejected from the catalyst, as can be seen in Figure 2c. The metallacycle is formed by the metal atom, the indenyl ligand, and the propyl chain linked to both the indenyl ligand and the metal center.

The proposed mechanism can only take place in those catalysts having three or more C atoms in the 3-indenyl linear alkyl substituent. Thus, these results can give a plausible explanation about the sharp decrease in polymer molecular weight experimentally observed when using this type of zirconocene catalyst.

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Supporting Information Available: PDB format files (1a.pdb, 1b.pdb, 2a.pdb, 2b.pdb, 2c.pdb) for each structure shown in the figures and described in the text; output files obtained from frequency calculations with the Gaussian 03 package (1a.out, 1b.out, 2a.out, 2b.out, 2c.out). This material is available free of charge via the Internet at http://pubs.acs.org.

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