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Quantum-chemical study on the role of alkyl chloride Zr,Al-complexes in stereoselective alkene oligomerization

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Abstract: A theoretical study on the thermodynamic and activation parameters of two successive stages of alkene insertion into alkyl chloride bimetallic complexes $L_2ZrMeCl\text{-}AlMe_3$ (L = Cp, Ind, *ansa*-Me_2SiInd_2) and the modeling of the chain termination stage in $Cp_2ZrClAlk\text{-}AlMe_3$ were carried out. Dependence of the activity, chemo- and regioselectivity of the catalytic system on the structure of the active sites is discussed.

Keywords: metallocenes; olefin oligomerization; density functional theory; stereoselectivity

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1. Introduction

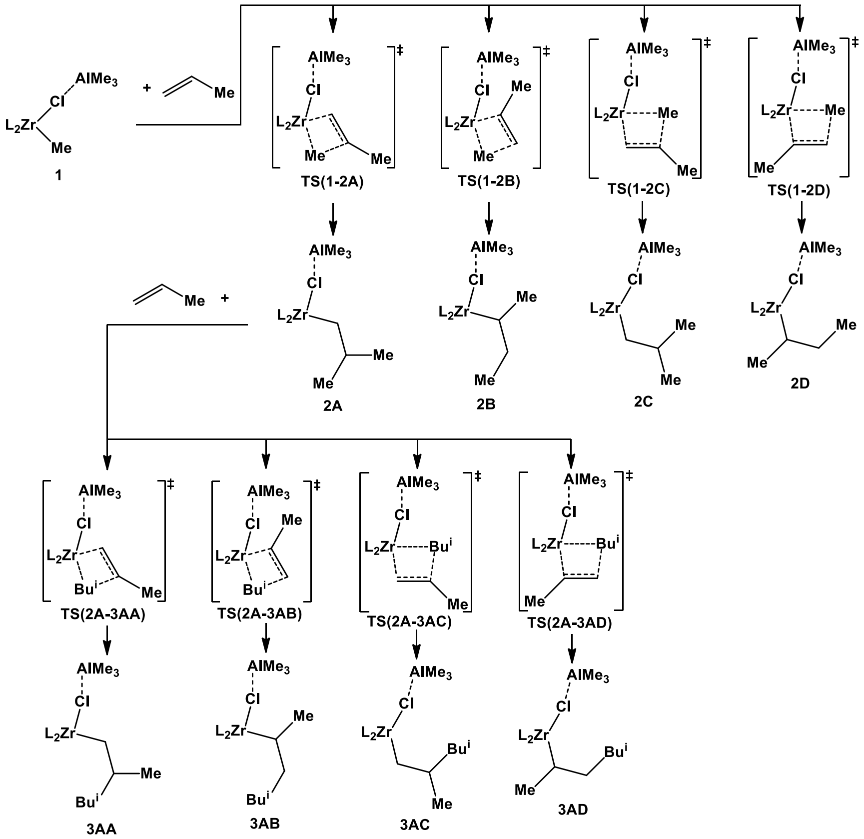
Catalytic reactions of alkene di-, oligo- and polymerization provide a variety of highly demanded products, which structure depends on the type of catalytic system [1-3]. Currently, a large number of catalytic systems have been proposed, including those based on transition metal complexes and organoaluminum compounds [3-9]. These systems are characterized by high activity and stereoselectivity. In this regard, the establishment of the reaction mechanisms remains an urgent problem. Our research focuses on bimetallic catalytic systems consists of Ti subgroup transition metals and organoaluminium compounds, which catalyze alkene hydro-, carbo- and cyclometalation [10,11]. These reactions can be considered as models of possible stages in the alkene di-, oligo- and polymerization processes. As a result of studying the alkene carbometalation by trialkylalanes in the presence of zirconocenes, the key intermediate $L_2ZrMeCl\text{-}AlMe_3$ was proposed [12, 13]. The intermediate regulates several catalytic cycles and the formation of the corresponding low molecular weight reaction products. In the presented work this intermediate was chosen as an example for studying the sequential stages of alkene insertion and chain termination to estimate the factors that determine the direction of the reaction, the catalytic system activity, and regioselectivity. For this purpose, we carried out a series of calculations on the thermodynamic and activation parameters of two successive stages of propene insertion into alkyl chloride bimetallic complexes $L_2ZrMeCl\text{-}AlMe_3$ (where $L_2 = Cp_2$, Ind_2, Me_2SiInd_2) and the process of β-H elimination in $Cp_2ZrClAlk\text{-}AlMe_3$.

2. Methods

The density functional theory (DFT) calculations were carried out using the Priroda-06 package [14,15]. The Perdew−Burke−Ernzerhof (PBE) gradient-corrected exchange-correlation functional [16] in conjunction with the 3ζ basis set [17] was employed. The electronic configurations of the molecular systems were described by the orbital basis sets of contracted Gaussian-type functions of size (5s1p)/[3s1p] for H, (11s6p2d)/[6s3p2d] for C, (15s11p2d)/[10s6p2d] for Al and Cl, and (20s16p11d)/[14s11p7d] for Zr, which were used in combination with the density fitting basis sets of uncontracted Gaussian-type functions of size (5s2p) for H, (10s3p3d1f) for C, (14s3p3d1f1g) for Al and Cl, and (22s5p5d4f4g) for Zr. The energy values reported here are all Gibbs energies at 298.15 K and 1.0 atmosphere pressure. Vibration frequency calculations, within the harmonic approximation, were performed to confirm whether each obtained geometry represented a transition state (one normal mode with an imaginary frequency) or a minimum (all normal modes have real frequencies) in the potential energy surface (PES). The character of the normal mode associated with the imaginary frequency was analyzed to ensure that the correct transition state was found.

3. Results and Discussion

First, the calculations of the thermodynamic and activation parameters of two sequential stages of propene insertion into bimetallic complexes $L_2ZrMeCl$ -$AlMe_3$ **1** (L_2= Cp_2, Ind_2, Me_2SiInd_2) were carried out (Scheme 1, Figure 1).



Scheme 1. Pathways of two spropene molecule insertion into complex **1**.

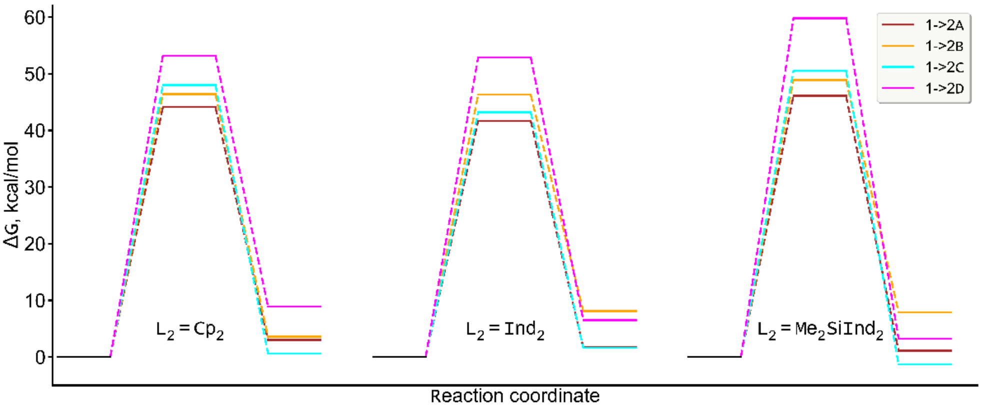


Figure 1. Energy diagram of the first propene molecule insertion.

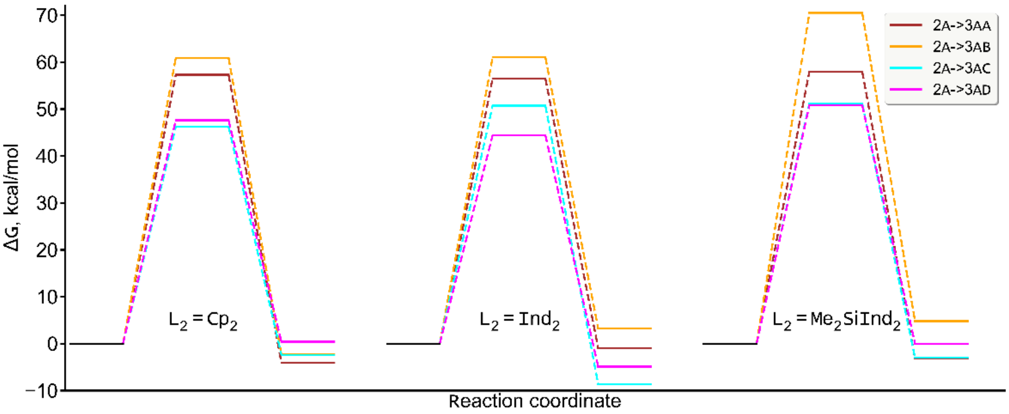
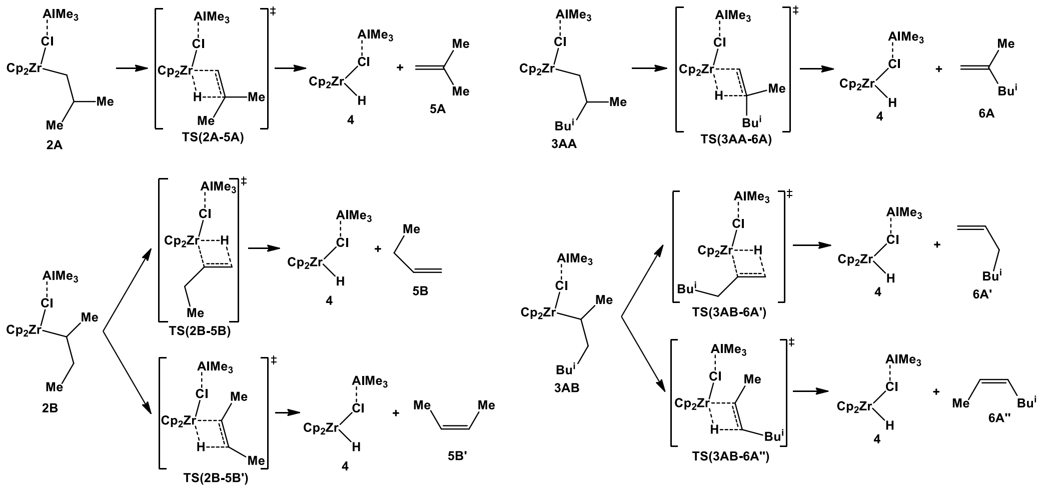


Figure 2. Energy diagram of the second propene molecule insertion (chain growth).

As follows from Figure 1, the reaction of complex **1** with propene is characterized by a positive change in the Gibbs free energy for most cases. Its values vary from -1.3 kcal/mol (L=Me$_2$SiInd) to 1.6 kcal/mol (L=Ind). Analysis of the activation parameters indicates that the alkene insertion should run via the front side of the complex, and the 1,2-addition of the olefin is preferable, which is in agreement with experimental data [12, 13]. Thus, at this stage, an isobutyl fragment should be predominantly formed along with pathway **A**. When comparing the energy parameters of pathway **A** for studied zirconium complexes, it turned out that the most reactive in the carbometalation reaction is the indenyl complex Ind$_2$ZrClMe-AlMe$_3$ (41.7 kcal/mol), therefore, it was chosen for further chain growth modeling (Figure 2).

It was found that the insertion of the second propene molecule is a thermodynamically more favorable process in comparison with the first stage for all studied complexes (Figure 2). A comparative analysis of the energy parameters of the four reaction pathways showed that pathways **C** and **D** could be predominantly realized for all complexes, i.e. the coordination of the alkene occurs from the outside, which is obviously due to the steric factor. Thus, the bis(cyclopentadienyl)zirconium complex **2A** can lead to regioerrors, since the difference between the barriers $\Delta G^{\neq}$ (**2A→3AC**) and $\Delta G^{\neq}$ (**2A→3AD**) does not exceed 0.7 kcal/mol. The bulky indenyl ligands, as well as the *ansa*-bisindenyl ligand, should demonstrate relatively higher regioselectivity due to the large difference between the barriers. For example, for L=Ind the formation of the **3AD** product goes through the barrier of 44.4 kcal/mol, while for **3AC** $\Delta G^{\neq} = 50.7$ kcal/mol. Moreover, for the indenyl complex, the conformation of the growing alkyl fragment becomes a more significant factor based on the thermodynamic stability of the second stage products. For example, the structures **3AA** and **3AC** differ only in the conformation of the alkyl chain. Indeed, the difference in the $\Delta G°$ values of the reactions in the case of L=Ind reaches 7.7 kcal/mol, while the difference in $\Delta G°$ values for L=Cp does not exceed 1.7 kcal/mol. Thus, the course of the reaction depends not only on the η^5-ligand type but also on the structure and conformation of the growing alkyl fragment.

Second, the modeling of the chain termination stage for the complexes Cp$_2$ZrClAlk-AlMe$_3$ (Scheme 2) was carried out taking into account the possibility of β-H elimination and the formation of the products with a double bond.



Scheme 2. Chain termination after the insertion of the first (left) and second (right) propene molecules.

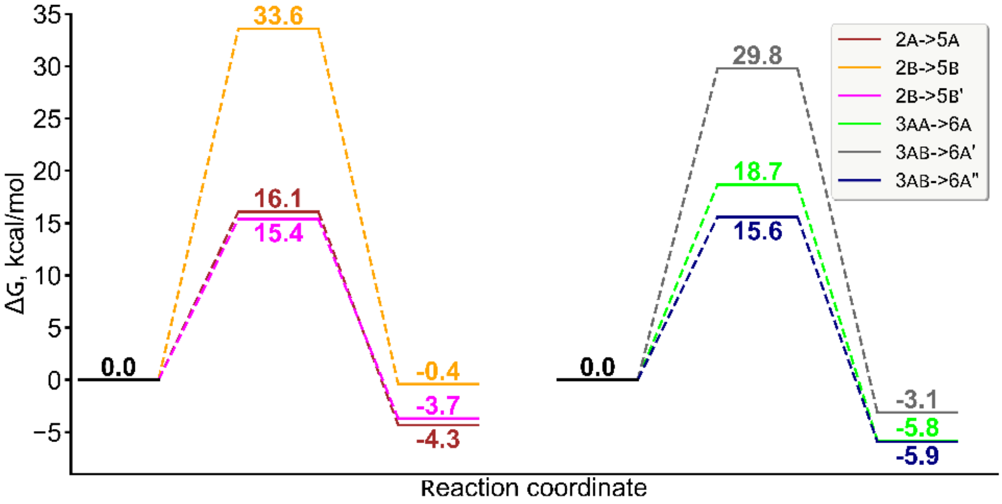


Figure 3. Energy diagram of chain termination after the insertion of the first (left) and second (right) olefin molecules.

Possible pathways of β-H elimination were studied for complexes **2A** and **2B** (Scheme 2, Figure 3). As follows from calculated thermodynamic data and the activation barrier (Figure 3), the formation of vinylidene product **5A** is more favorable. The product **2B**, isomeric to **2A**, preferably could be transformed to but-2-ene **5B**', while but-1-ene **5B** should not be formed due to the higher barrier (the pathway of its formation implies the C-H activation in the methyl substituent). The modeling of possible pathways of β-H elimination was carried out similarly for the complexes **3AA** and **3AB**. It was shown that the pathways of chain termination with the formation of products **6A** and **6A**" are the most energetically favorable.

2. Conclusions

A set of theoretical studies was carried out to determine the thermodynamic and activation parameters of two successive stages of propene insertion into methyl chloride bimetallic complex $L_2ZrMeCl$-$AlMe_3$ **1** (L=Cp, Ind, *ansa*-Me_2SiInd_2), which is proposed as the key intermediate of the alkene carbometalation reaction.

It was found that, for all complexes, the most energetically favorable pathway for the insertion of an olefin molecule into the initial complex **1** is the alkene 1,2-coordination to a metal alkyl via the front side of the complex. Comparative analysis of the energy parameters of the reactions with the first propene molecule for complexes with various ligands showed that the most reactive in the carbometalation reaction should be the indenyl complex $Ind_2ZrClMe$-$AlMe_3$.

The chain growth, i.e. the insertion of the second akene molecule into $L_2ZrAlkCl$-$AlMe_3$ **2** is thermodynamically more favorable, regardless of the type of ligand. However, the reaction with the indenyl and *ansa*-indenyl complexes is characterized by lower activation barriers. Due to the steric reason of the alkyl fragment in complex **2**, the direction of the propene molecule coordination changes, i.e. the insertion is predominantly realized from the outside of the complex.

It was found that the regioselectivity of the catalytic systems significantly depends on the structure of the η^5-ligand in the key intermediate. Thus, complexes with bis-indenyl ligands should provide better regioselectivity.

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Conflicts of Interest: The authors declare no conflict of interest.

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