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Theoretical studies on the role of bridging group of Cp ligands for the Ziegler–Natta catalysis

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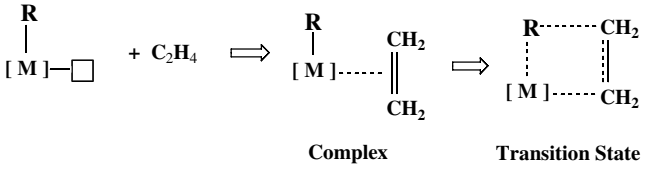
Abstract

The homogeneous Ziegler–Natta reaction mechanisms of olefin with metallocenes by incorporation of nine bridging atoms or groups at the cyclopentadienyl (Cp) ring as ligands were studied by ab initio MO and density functional methods. The formation energy of the complex between ethylene and the metallocene by incorporation of bridging of oxygen atom is the most stable, and the difference from that of non-bridged system is about 5 kcal/mol. The energy barriers at the transition states from the reactants for all systems treated here indicate negative values, except for the MP3/6-31G(d) calculation values for the AlH and GaH bridged systems. The largest difference of the energy barriers at the transition states from the complexes is only 1–2 kcal/mol at the B3LYP calculation level. It was established that the distance between Ti atom and the bridging atom and/or the electronic density of the bridging group are closely related to the potential energy.

Keywords: Ab initio MO; Density functional method; Ziegler–Natta catalysis

1. Introduction

In the past two decades metallocenes have become one of the most important catalyst systems for the Ziegler–Natta polymerizations of olefins. The potential to alter the steric and electronic properties of these systems by different substitution at the cyclopentadienyl (Cp) ring or by incorporation of different bridging atoms has been experimentally realized in a host of examples, often giving rise to different polymer properties. A popular current thought is that the active species in the polymerization is a cationic complex such as Cp_2MR^+ and that the reaction proceeds, through a four-centered transition state is in the Cossee mechanism [1] for Ziegler–Natta catalysis.



The metallocenes of Group 4, $Cp_2\ MX_2$, belong to a class of bent-sandwiches and have been utilized as precursors to homogeneous catalysts for polymerization of olefin. Attempts to relate structural characteristics to reactivity continue as the understanding of the catalytic process increases. Ansa-metallocenes are "sandwich" molecules where the two rings are connected by a chelate bridge. The introduction of the chelate bridge leads to a more fixed ligand geometry about the metal center. The relation between the geometrical character of bridged ansa-metallocene and the reactivity has been studied [2–8] experimentally.

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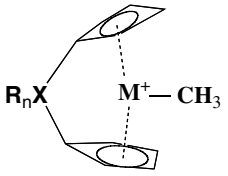

Corey and co-workers [2] synthesized ansa-metallocenes bridging with dimethylcarbon and detected X-ray crystal structures. Alt and Köppl [5] studied the reactivity (molecular weights) for many bridged or non-bridged metallocenes. They proposed (4,4′,5,5′-tetramethyl)bis(fluorenylidene)(1,2-ethylidene)zirconium dichloride as the most active metallocene complex there. Recently, Braunschweig and co-workers [8] reported that metallocene bridging with boron atoms represents very active catalysis.

On the other hand, many theoretical studies [9–18] of Ziegler–Natta catalysis polymerization with bridged metallocenes have been reported. Most of these papers treated with SiH_2-bridged metallocenes catalysis. However, it is unknown the variation of reactivity of ansa-metallocenes by including of the different bridged groups.

In the present paper, the reaction mechanisms of nine bridged metallocenes ($[XH_n(Cp_2)TiCH_3]^+$: XH_n = BH, AlH, GaH, CH_2, SiH_2, GeH_2, O, S, and Se) and ethylene have been reported. The relationships between the potential energies and some geometrical parameters and/or electronic states are also discussed.

2. Method of calculations

All equilibrium- and transition-state geometries were determined by the use of analytically calculated energy gradients with the B3LYP/LanL2DZ calculation level.[14–22] The stationary points were identified as the equilibrium or saddle point by examining the calculated normal vibrational frequencies. The force constant matrix and thereby the vibrational frequencies were calculated by analytical second-derivative procedures. Additional calculations were preformed to obtain improved energy comparisons – the calculations at the B3LYP/Lanl2DZ-optimized structures by the B3LYP and the MP3 methods [23–27] with the 6-31G(d) level basis sets [28–37]. Ab initio molecular orbital calculations were carried out using the GAUSSIAN98 program [38].

3. Results and discussion

3.1. Complex formation energy and activation energy barrier

The complexes and transition states of the ethylene insertion process with ansa-metallocenes of nine bridging groups (CH_2, SiH_2, GeH_2, BH, AlH, GaH, O, S, and Se) between two Cp ligands and with non-bridged system were calculated by the B3LYP and MP3 calculation levels. The relative energies from the reactants were listed in Table 1. By the B3LYP calculations, the difference of the energies with both basis sets of the LanL2DZ and the 6-31G(d) is small, and the largest difference is 2.0 kcal/mol for the complex formation energy of the bridged system including X = B. On the other hand, the difference of the energies with the both basis sets by using of the MP3 method is quite large, and the largest difference is 7.9 kcal/mol for the complex formation energy of the bridged system including X = B. For both basis sets, the relative energies by the MP2 (and/or MP4) method are remarkably more stable than those calculated with the B3LYP and/or MP3 methods, although these are not shown here. Although the complex formation energies by the MP3/LANL2DZ calculations are also more stable than those by the B3LYP/LanL2ZD calculations, the energies obtained by the MP3/6-31G(d) level are almost similar to those by the B3LYP/6-31G(d) method. For the transition states, the difference between activation energies for each system by the MP3/LANL2DZ method and by the B3LYP/LANL2DZ (or 6-31G(d)) is small, but the difference by the B3LYP/6-31G(d) and by the MP3/6-31G(d) methods is quite large.

The energies of the complex formation calculated by all methods used here are lower than that of the reactant. The non-bridged system has the smallest complex formation

Table 1
Stabilization energies for the complex and the activation energies for the transition state (kcal/mol)

	Complex				Transition state			
	B3LYP		MP3		B3LYP		MP3	
	LanL2DZ	6-31G(d)	LanL2DZ	6-31G(d)	LanL2DZ	6-31G(d)	LanL2DZ	6-31G(d)
Non	−11.4	−10.9	−17.0	−11.0	−5.0	−5.3	−4.3	1.7
BH	−15.4	−13.4	−23.0	−15.1	−10.3	−9.9	−10.4	−3.8
AlH	−11.5	−10.9	−18.6	−11.2	−6.0	−6.1	−5.5	1.4
GaH	−11.6	−11.5	−18.7	−11.9	−6.1	−7.1	−5.6	0.7
CH_2	−14.8	−14.1	−22.0	−14.9	−9.7	−9.9	−10.6	−4.0
SiH_2	−12.8	−11.3	−20.1	−12.6	−7.4	−7.4	−7.6	−0.5
GeH_2	−12.2	−12.4	−19.7	−12.6	−6.8	−7.6	−6.8	−0.5
O	−17.0	−15.7	−23.2	−16.3	−12.1	−11.2	−13.3	−6.9
S	−14.9	−13.6	−22.5	−15.0	−9.6	−9.9	−10.8	−3.7
Se	−14.0	−13.5	−21.6	−14.2	−8.7	−7.2	−9.6	−2.8