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Review

Ethylene polymerization catalyzed by a cyclophane-diimine-based Ni(II) complex, a quantum/molecular mechanic study

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ABSTRACT

In work, employing quantum/molecular mechanical calculations, we describe the main steps of ethene polymerization reactions catalyzed by a cationic Ni(II) complex, bearing a cyclophane α-diimine ligand. The combination of Density Functional Theory (DFT) and Molecular Mechanics (MM), within the ONIOM approach, was employed to evaluate the molecular structures and energies involved in ethene polymerization. All intermediate and transition state structures, obtained along these elementary step reactions, were treated as representative molecular arrangements of the polymerization process. The steric environment and the electronic influence imposed by the cyclophane ligand were evaluated for all intermediate and transition state structures, and correlated to that observed with the analogous bulky diimine ligand, *bis*[*N*-(2,6-diisopropylphenyl)imino]acenaphthene, present in the Brookhart's catalyst.

Contents

1. Introduction

Metallic complexes of late transition metals (Ni and Pd) bearing bulky α-diimine ligands are able to polymerize ethene, and α-olefins [1,2], leading to high molecular weight polymers with different microstructures [3,4]. This innovation expanded the number of applications of molecular Ziegler–Natta catalytic systems [5–7] for the development of new polyolefinic materials [8]. Particularly, cationic Pd(II) and Ni(II) complexes bearing bulky α-diimine ligands, such as *bis*[*N*-(2,6-diisopropylphenyl)imino]acenaphthene (see Fig. 1), containing non coordinating anions, are able to catalyze the homopolymerization of ethene, and generate a variety of polymers with different characteristics.

The singular structural aspects of these different polymers are attributed to an isomerization mechanism on the polymer chain known as "chain walking" [9]. This mechanism is based on successive β-eliminations and reinsertions reactions undergo by the growing chain. This process, indeed, the responsable the obtaintion

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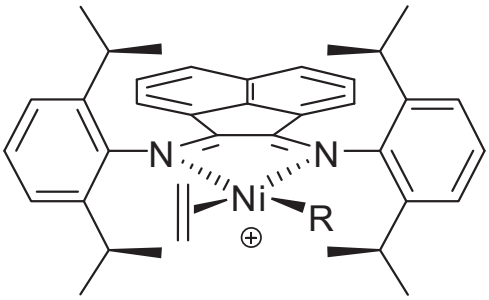

Fig. 1. Molecular structure of the Brookhart's catalyst, where R = H or an alkyl ligand.

of the diverse type of molecular microstrutuctures of the polymeric chain.

Chain walking occurs properly if the environment around the catalytic site, promoted by specific ligands, hinders termination polymerization reactions, such as β-hydride transfer from the growing chain to the monomer, and olefin change. Thus, under suitable polymerization reaction conditions, polyethylenes with different microstructures (from linear to hyperbranched) can be obtained [9]. Because of the unique characteristics of this catalytic system, several academic and industrial research groups are now involved in the development of new or improved molecular catalyst systems, that display, for example, higher thermal stability, or are able to produce other diverse polymeric materials [10–14].

Research groups headed by Ziegler [15] and Morokuma [16] initiated a series of theoretical studies on olefin polymerization, employing Brookhart catalytic systems. Most of these works compare generic substituted and non-substituted α-diimine ligands to evaluate the energies involved in the main steps of the polymerization process [17]. Recently, we published a theoretical study in which we treated all of the ground, intermediate and transition state structures of a series of elementary steps as representative structures of the polymerization process for a typical Brookhart bulky α-diimine catalyst system [18]. On this preview work, we carried out systematic evaluation of the structural arrangement of all structures (intermediates and transition states), giving particular interest in the olefin coordination angles on π-complexes, and agostic interactions during the growth of the polymer chain. Here it is important to remark that the π-complexes display large olefin coordination distortion angles, with significant participation of the d_z^2 orbital in the olefin-metal bond [18].

Recently, Guan and co-workers [8,13,19–21] proposed a new Brookhart type catalyst for olefin polymerization, which bears a cyclophane α-diimine ligand (see Fig. 2). This cyclophane ligand is very rigid, and when coordinated to the metal center, strongly shields all sides of the catalytic metal center, with the exception of two *cis* coordination sites. Furthermore, because of their structural features, cyclophane ligands can improve the thermal stability of the catalytic complex. However, despite their promise, the use and mechanistic implications of cyclophane transition-metal complexes in olefin polymerization remains mostly unexplored [22] Therefore, we report a chemical computational study of the elementary steps of an ethene polymerization reaction performed with an *m*-terphenyl-based cyclophane Ni(II) catalyst, and compared with the counterpart, bearing the conventional bulky α-diimine ligand, *bis*[*N*-(2,6-diisopropylphenyl)imino]acenaphthene [18].

2. Methods

All calculations reported in the present study were performed using the Gaussian03 program [23], and molecular structures were drawn using the ORTEP 3 program [24]. Theoretical calculations

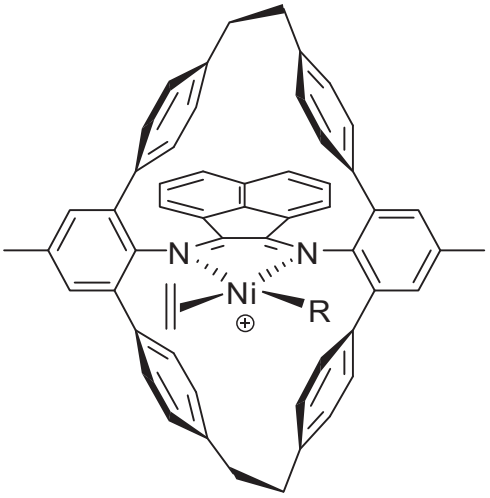

Fig. 2. Molecular structure of the Brookhart–Guan's catalyst, where R = H or an alkyl ligand.

were always compared to similar experimental and theoretical studies, in order to validate our results. All calculations reported here were carried out in the gas phase, taking in account just the cation fragments of the species of interest. The ligand, *m*-terphenyl-based cyclophane, will be hereafter referred to as diimine.

Full geometry optimization and frequency calculations were performed using a combined quantum-mechanic (QM) and molecular-mechanic (MM) approach, according to ONIOM methodology [25,26]. The set of atoms treated with QM and MM are assigned in Fig. 3. Local minima were identified by the absence of negative eigenvalues (NIMAG = 0) in the Hessian matrix following vibrational frequency analysis, while transition state structures had only one negative eigenvalue (NIMAG = 1).

Using this ONIOM approach, we can also obtain the gradient and Hessian of the energies, allowing for optimization and frequency calculations to be performed on the optimized structures. The QM regions were treated at the gradient-corrected Density Functional Theory (DFT) level [27] using the three-parameter fit of the exchange-correlation potential suggested by Becke, B3, in conjunction with the correlation function suggested by Lee, Yang and Parr, LYP [28,29]. The inner shell electrons of the Ni atom (1s, 2s and 2p) were treated by the effective core potential of Hay and Wadt, LANL2DZ [30], and the valence electrons (3s, 3p, 4s and 3d) were included explicitly in the calculations, using the associated

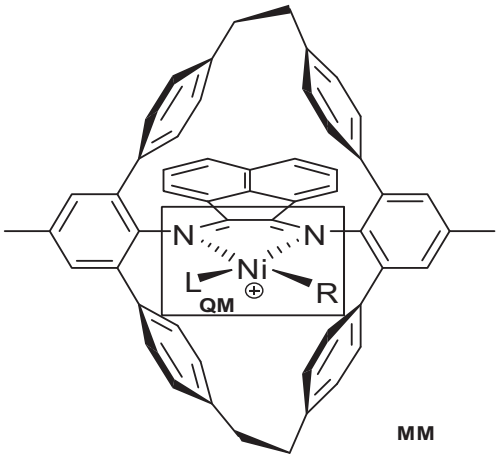

Fig. 3. QM/MM partitions adopted for the molecular systems studied, where R = H or an alkyl ligand; L = η^2-olefin ligand or vacant site.