Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Molecular Catalysis A: Chemical 231 (2005) 27–34

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

www.elsevier.com/locate/molcata

Investigation of 1-hexene isomerization and oligomerization catalyzed with β-diketiminato Ni(II) bromide complexes/methylaluminoxane system

Junkai Zhang, Haiyang Gao, Zhuofeng Ke, Feng Bao, Fangming Zhu, Qing Wu*

Institute of Polymer Science, School of Chemistry and Chemical Engineering, Sun Yat-Sen (Zhongshan) University, Guangzhou 510275, China

Received 11 October 2004; received in revised form 8 December 2004; accepted 20 December 2004

Abstract

β-Diketiminato Ni(II) bromide complexes were synthesized and used to catalyze isomerization and oligomerization of 1-hexene in the presence of methylaluminoxane (MAO). GC–MS and GC analysis confirmed that the products are mainly hexene isomers and dimer isomers. 3-Hexene isomers, trimers and higher oligomers were not detected. The results were ascribed to the configuration of the β-diketiminato Ni(II) catalyst. The migration of the Ni atom from a secondary or tertiary carbon to another one along the alkyl chain of the Ni-alkyl intermediates is blocked by the coordination wedge of the β-diketiminato ligands. However, the migration of the Ni atom from a primary carbon to the adjacent secondary or tertiary carbon is thermodynamically favored.

Keywords: β-Diketiminato Ni(II) complexes; 1-Hexene; Isomerization; Oligomerization; Methylaluminoxane

1. Introduction

In 1995 [1], Brookhart and co-workers first reported the bulky α-diimine Ni(II) and Pd(II) catalysts. These late transition metal (LTM) catalysts are very active and efficient in ethylene polymerization [2], and the obtained ethylene polymers are of a novel branching rich microstructure. In the past decade, the researches on the α-olefin polymerization by using these LTM catalysts were focused on the topics including temperature, pressure, ligand structure [1,3], and mechanism [4]. The bulky axial aryl groups of the α-diimine catalysts retard the chain transfer, and thus lead to the formation of high molecular weight polymers. The concept of the axial steric bulk makes the application of the LTM in α-olefin polymerization become promising. The resting state of the cationic α-diimine catalyst species is an olefin/M-alkyl complex, which adopts a square planar structure [3a] (**1** in Fig. 1).

Researches [5] on β-diketiminato metal complexes went afresh hot in the middle of 1990s. The chemistry of unsaturated three-coordinate β-diketiminato LTM complexes was studied effectively by Holland's group [6] and Warren's group [7]. The neutral three-coordinate β-diketiminato LTM alkyl complexes (Fe, Co) adopt a tetrahedral structure. Due to the reduction of Ni(II) atom by alkylation agents, the direct synthesis of the β-diketiminato Ni-alkyl complexes by using methyllithium or Gringnard reagents was reported unproductive [6f]. Warren and co-workers reported series of four-coordinate β-diketiminato Ni-alkyl lutidine complexes that adopt square planar structure [7d] (**2** in Fig. 1). Recently, the lutidine-free Ni(II) β-agostic alkyl complexes were successfully isolated and characterized [7f] (**3** in Fig. 1). The alkyl intermediates of the β-diketiminato system favor the pseudo four-coordinate β-agostic alkyl **3** over the four-coordinate ethylene/M-alkyl complex **1**.

Recently, Gibson gave a review [8] on β-diketiminato transition metal complexes that were used as the α-olefin polymerization catalyst. However, the reports on α-olefin

---

* Corresponding author. Tel.: +86 20 84113250; fax: +86 20 84112245.
E-mail address: ceswuq@zsu.edu.cn (Q. Wu).

1381-1169/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2004.12.024

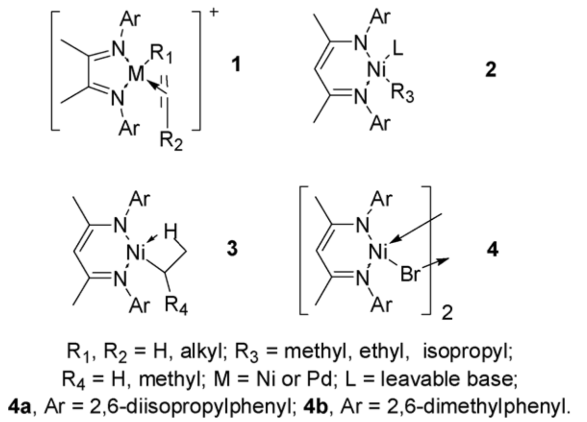


Fig. 1. Structures of the α-diimine catalyst species and β-diketiminato complexes.

polymerization by using the β-diketiminato LTM complexes as catalyst precursor are rare in the past decade [7d,9].

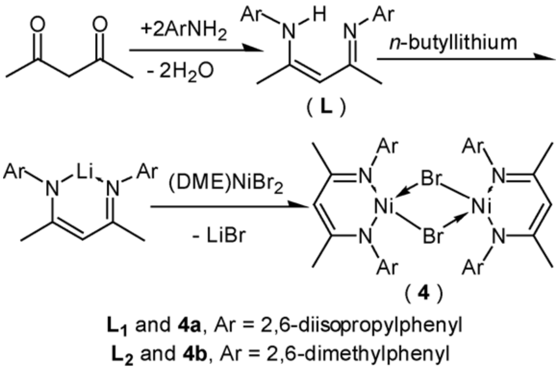
Non-skeleton isomerization of α-olefins, which was catalyzed by the transitional metal catalysts, had been reported everywhere [10]. The isomerization of the substrates was also reported coming along with the α-olefin oligomerization and polymerization, which were catalyzed by the cationic LTM active center [11]. To our knowledge, the isomerization and oligomerization of 1-hexene catalyzed by the neutral LTM active center were still not reported.

We report here the isomerization and oligomerization of 1-hexene catalyzed by using the Ni{(N(C_6H_3-R_2-2,6)C(Me))$_2$CH}Br/MAO (**4** in Fig. 1). One goal is to reveal the behaviors of the β-diketiminato Ni-R (R = hexyl) intermediates. That would help understanding the behaviors of β-diketiminato Ni-P (P = polymeric alkyl) intermediates in the ethylene polymerization process. The other is to make clear the insertion behaviors of α-olefin to the β-diketiminato Ni-P intermediates in the α-olefin copolymerization process. The β-diketiminato Ni(II)/MAO system catalyzed ethylene polymerization and corresponding characterization will be published elsewhere in the near future.

2. Results and discussion

2.1. β-Diketiminato nickel complexes (4)

Ni{(N(C_6H_3-R_2-2,6)C(Me))$_2$CH}Br (**4a**, R = isopropyl; **4b**, R = methyl) was prepared according to the literature method [6c], following a two step procedure as shown in Scheme 1. Lithium β-diketiminato salts were used as prepared in toluene solution and (1,2-dimethoxy-ethane)$NiBr_2$ ((DME)$NiBr_2$) was used as the Ni(II) source. ^{1}H NMR chemical shifts of these β-diketiminato Ni(II) complexes were paramagnetically induced by the unpaired spin of the Ni atom [12] (see Fig. 2). ^{1}H NMR spectrum indicates that there is an equilibrium that shifts between monomer and dimer [6c], depending on the concentration, temperature and the solvent used. The uncertain assignments of the $CH(CH_3)_2$ (e) and the *m*-Ar (f) in **4a** [6c] were clarified by comparing the corresponding chemical shift of **4a** with **4b**. Compared with **4a**, small bulk complex **4b** is relative stable and likely to adopt dimer form in solution. Complexes **4a** and **4b** are noteworthy thermal-stable, but sensitive to air and moisture.



Scheme 1. The preparation of β-diketiminato ligand (**L**) and β-diketiminato Ni(II) complexes (**4**).

2.2. The isomerization and dimerization of 1-hexene

Table 1 lists the isomerization and oligomerization data of 1-hexen obtained by using **4a** and **4b** in the presence of MAO. GC–MS analysis confirmed the trace of C7 heptene isomers. This indicates that Ni(II) bromide complex is methylated by MAO and Ni–CH_3 intermediate is produced as the initial active species. The products are mainly C6 olefin isomers and C12 olefin dimers. These even number olefins suggest the involvement of the Ni(II)-hydride (Ni–H) intermediate in the isomerization and oligomerization process. The Ni–H intermediate might be produced after the insertion of 1-hexene into the Ni–CH_3 bond and following the release of C7 heptene via β-H elimination.

GC–MS analysis confirmed that the C6 products are mainly liner inner hexenes (*trans*- and *cis*-2-hexene, see Fig. 3). Scheme 2 shows the proposed mechanism of the 1-hexene isomerization. Fig. 4 illustrates the nomenclature used in this work for the Ni-alkyl intermediates. The 2-Ni-hexyl intermediates might derive from two procedures. One is 2,1 insertion of 1-hexene to the Ni–H active species. The other is the migration conversion (chain walking) of 1-Ni-hexyl intermediate originated from the 1,2 insertion of 1-hexene to the Ni–H intermediate. The wedge shape configuration of the β-diketiminato Ni(II) active species might favor the 1,2 mode insertion of 1-hexene over the 2,1 mode (see Fig. 5). The β-diketiminato Ni(II) catalysts show strong tendency of isomerizing the α-olefin substrate comparing with the pyridine bisimine Fe(II) system, of which only the small bulk catalysts exhibit this trend [11a,11b]. This isomerization phenomenon was also observed going along with the 1-hexene polymerization process that was catalyzed by the α-diimine Pd(II) catalyst. After 3 h reaction at 0 °C, 71% of the all hexenes in the