

Ethylene polymerization and oligomerization catalyzed by bulky β -diketiminato Ni(II) and β -diimine Ni(II) complexes/methylaluminoxane systems

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

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

Received 13 November 2005; received in revised form 11 December 2005; accepted 21 December 2005

Available online 3 February 2006

Abstract

β -Diketiminato complexes $\text{Ni}\{(\text{N}(\text{Ar})\text{C}(\text{Me})_2\text{CH})\text{Br}$ (**9**), $\text{Ni}\{(\text{N}(\text{Ar})\text{C}(\text{Me})_2\text{CH})\text{PPh}_3\text{Br}$ (**10**) and β -diimine complexes $\text{Ni}\{(\text{N}(\text{Ar})\text{C}(\text{Me})_2\text{CH}_2)\text{Br}_2$ (**5**) ($\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$ (**a**), $2,6\text{-Me}_2\text{C}_6\text{H}_3$ (**b**)) were used as catalyst precursors for ethylene polymerization in the presence of methylaluminoxane (MAO). High molecular weight ethylene polymers as well as short chain oligomers (C4–C8) were simultaneously produced from the catalysis reactions. Ethylene polymers obtained by using these β -N–N Ni(II)/MAO catalyst systems are mainly methyl branched. Small amounts of even number branches were also observed in the ^{13}C NMR spectra of the obtained ethylene polymers, which are believed generating from the incorporation of simultaneously produced α -olefins. Except methyl branch and the branches derived from the incorporation of α -olefin oligomers, the formation of other branch types via the chain walking process is not favored in β -diketiminato Ni(II) systems.

© 2006 Elsevier B.V. All rights reserved.

Keywords: β -Diketiminato Ni(II) complexes; Ethylene; Polymerization; Oligomerization; Triphenylphosphine

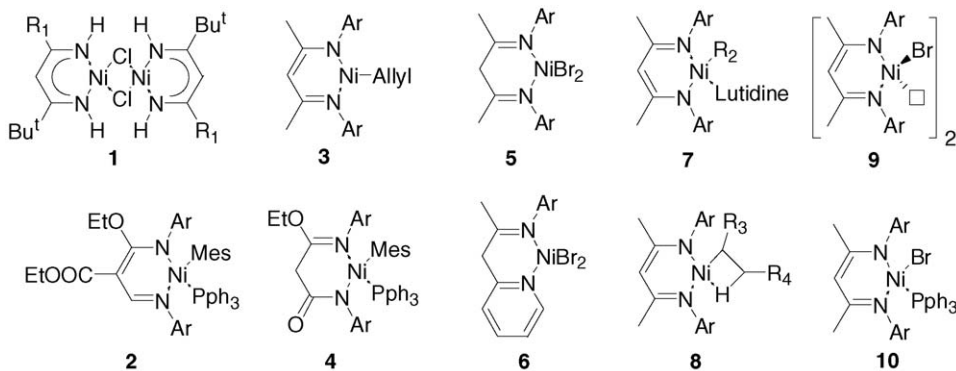
1. Introduction

The early report of the late transitional metal (LTM) catalyst can be traced back to the polymerization of butadiene catalyzed with diethyl bis(2,2'-bipyridyl)iron complexes developed by Yamamoto et al. in 1965 [1]. Later, Keim's researches founded base of the shell higher olefin process (SHOP) [2]. Due to the strong β -H elimination tendency of the LTM systems, rare LTM catalysts were found to produce solid ethylene polymers efficiently [3]. Until that, Brookhart and co-workers reported the cationic bulky α -diimine catalysts in 1995 [4]. Then, in 1998, Grubbs and co-workers reported the neutral salicylaldimine catalysts, which were capable of co-polymerizing the polar olefin monomers even in the polar solvent [5]. In the past decade, many researches on these two kinds of catalyst systems were carried out on topics including ligand structure [4,6], polymerization and branching mechanism [7]. The axial bulky aryl groups of the α -diimine ligands retard the chain transfer, and thus lead to

higher molecular weight polymers. This axial steric bulk concept had been validated with and extended to many kinds of fine contrived LTM catalyst systems, such as pyridine bis(imine) (PBI) Fe and Co catalyst systems, which produce high molecular weight linear ethylene polymers [8].

The researches on β -diketiminato metal complexes went afresh hot in the middle of 1990s [9]. The chemistry of the unsaturated three coordinate β -diketiminato LTM complexes were studied effectively by Holland and co-workers [10] and Warren and co-workers [11]. The works on the olefin polymerization with β -diketiminato transition metal catalysts, were recently reviewed in details by Gibson [12]. However, the researches on the ethylene polymerization by using β -diketiminato and analogous six-member-chelate-ring LTM catalyst systems are rare in the past decade [11a,13–15] (Fig. 1). The activities of these reported catalyst systems and corresponding characterization were listed in Table 1. Complexes of type **2** showed no activity either with methylaluminoxane (MAO) or with ethylaluminum sesquichloride (EASC) as cocatalyst. The amidoiminomalonate complex **4** shows high activities in the presence of MAO as cocatalyst, yielding oligomers with prevailing dimers (88.7%). Neither **3a**/BPh₃ nor **3a**/PMMAO are productive in catalyzing

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



a : Ar = 2,6-diisopropylphenyl; **b** : Ar = 2,6-dimethylphenyl; Allyl = CH₂C(CO₂Me)CH₂, CH₂CHCH₂; Mes = mesityl; R₁ = piperidino; R₂ = methyl, ethyl, n-propyl, isopropyl; R₃ = H, methyl; R₄ = H, methyl, ethyl;

Fig. 1. Reported Ni(II) complexes of bidentate nitrogen ligand with six-membered chelating ring (**1–8**) and β -diketiminato Ni(II) bromide complexes (**9** and **10**) discussed.

Table 1
Ethylene oligomerization and polymerization catalyzed by compounds **2–8** in literature [11a,13–15]

Cat.	Cat. mol ($\times 10^{-6}$)	Co-cat. (ratio/type)	P_E (atm)	t (h)	TON	M_n	Refs.
1	~5.3	~55/MAO	0.375	1	1120	–	[15b]
2	10	MAO or EASC	29.6	–	Inactive	–	[14]
4	10	300/MAO	23.7	–	20530	(C4–C16)	[14]
3a	60	2/BPh ₃	6.9	18	81	–	[15a]
3a	110	PMAO	0.3	12	88	–	[15a]
5a	80	60/MAO	19	3.5	1800	–	[13a]
6a	2000	200/MAO	1	0.5	0.06 (g)	–	[13b]
8b	–	None	6.9	10	–	(C8–C18)	[11a]

ethylene polymerization to form solid polyethylene. Without the present of MAO, only ethylene oligomers (C8–C14) were obtained with complex **8a** at 6.9 atm ethylene pressure.

Bulky β -diketiminato complexes are catalyst precursors characterized by their axial steric bulk as α -diimine catalysts [4] and the neutral active center as salicylaldimine catalysts [5]. The ligand of the β -diketiminato complexes adopts a wedge shape configuration as compared with the open ligand configuration of the α -diimine complexes [6d]. In previous report, 1-hexene isomerization and dimerization were investigated by using **9**/MAO catalyst systems [16]. Result shows that the migration (chain-walking) of Ni(II) center on the alkyl chain were restrained by the coordination wedge of the β -diketiminato ligands. Here, β -diketiminato Ni(II) bromide complexes **9** and **10** were used as catalyst precursors in the presence of MAO for ethylene polymerization. Neutral ligand β -diimine Ni(II) complexes **5** were synthesized following the literature method [13a] and also used as catalyst precursors for comparison.

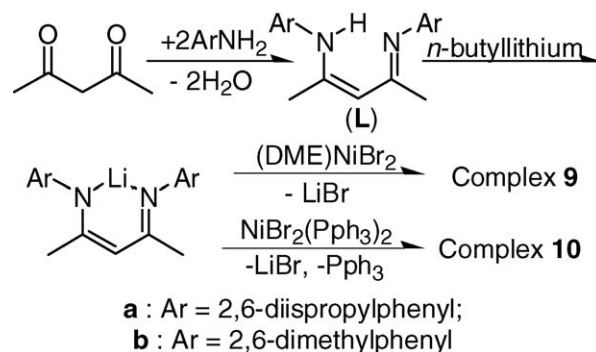
2. Result and discussion

2.1. Synthesis of β -diketiminato nickel complexes (**9** and **10**)

The synthetic routes of β -diketiminato Ni(II) complexes **9** and **10** are shown in Scheme 1. Complex **9** was synthesized according to the method in our previous report [16].

Ni{(N(C₆H₃R₂-2,6)C(Me)₂CH)}(PPh₃)Br (R = isopropyl **10a**, methyl **10b**) were readily obtained from reaction of lithium β -diketiminato salts with NiBr₂(PPh₃)₂. Hexane used to precipitate the target complex **10a** and **10b** should be enough to dissolve the PPh₃ released. These complexes are noteworthy thermal-stable, but sensitive to air and moisture.

The ¹H chemical shifts of these β -diketiminato complexes are paramagnetically induced by the unpaired spin of the Ni atom [17]. ¹H NMR spectra of **10a** and **10b** show that the equilibrium [10b,16] which shifts between monomer and dimer in the solution of **9a** and **9b** is interrupted by the introduction of PPh₃. ³¹P{¹H}NMR spectra of **10a** and **10b** show a single peak value around 135–136 ppm, and the sig-



Scheme 1. Synthesis of ligands and β -diketiminato Ni(II) complexes.

Download English Version:

<https://daneshyari.com/en/article/69006>

Download Persian Version:

<https://daneshyari.com/article/69006>

[Daneshyari.com](https://daneshyari.com)