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

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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.
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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

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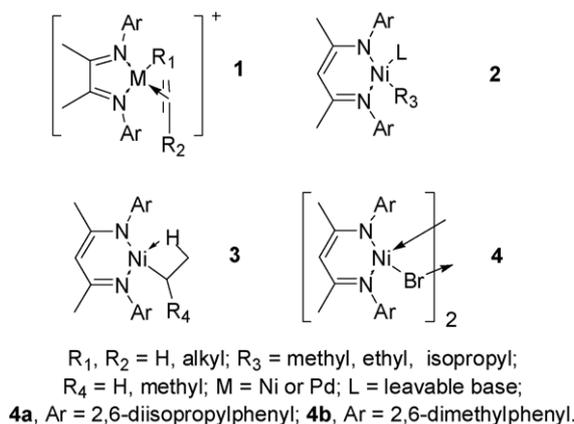 *E-mail address:* ceswuq@zsu.edu.cn (Q. Wu).

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

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

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$_6$H$_3$-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$_6$H$_3$-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
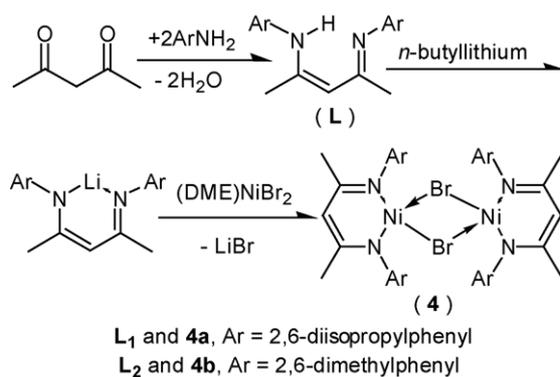
used. The uncertain assignments of the CH(CH$_3$)$_2$ (e) and the *m*-Ar (f) in **4a** [6c] were clarified by comparing the corresponding chemical shift of **4a** with **4b**. Compared with **4a**, small bulk complex **4b** is relative stable and likely to adopt dimer form in solution. Complexes **4a** and **4b** are noteworthy thermal-stable, but sensitive to air and moisture.

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
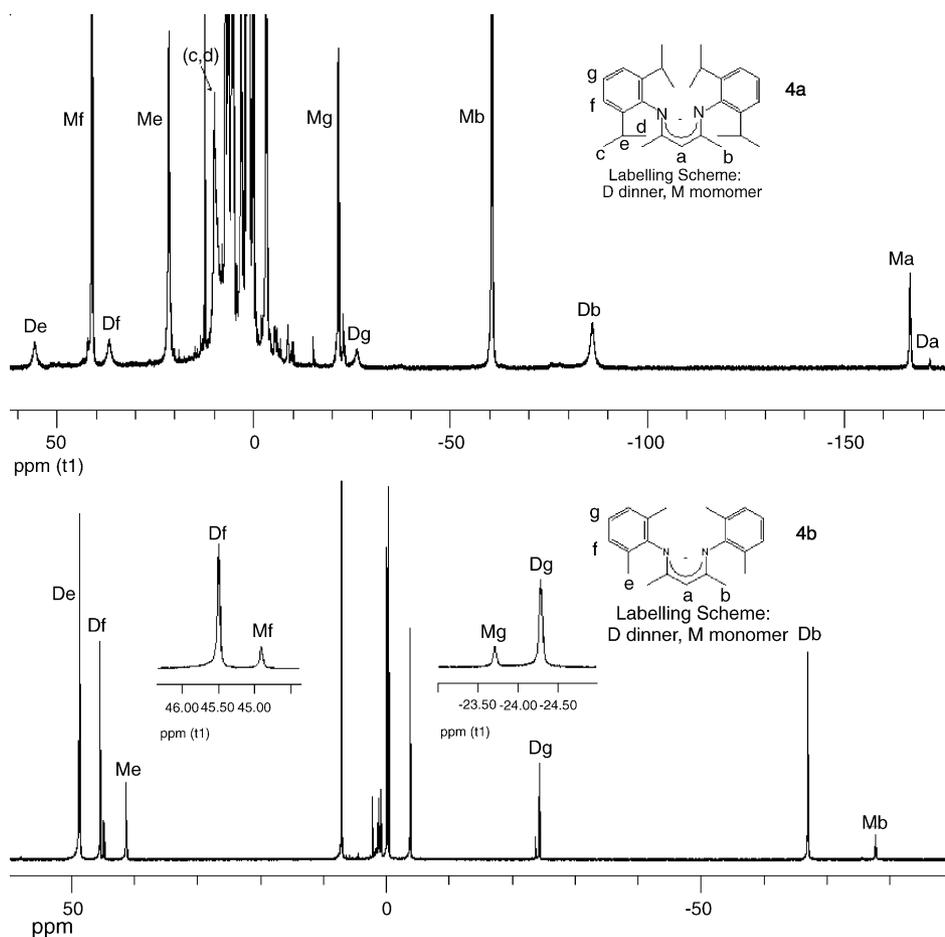
Fig. 2. ^{1}H NMR spectrum of complex **4a** and **4b** in C6D6 ($\sim$10 mmol/0.5 mL), at 30 °C.

Table 1
The isomerization and dimerization data of 1-hexene catalyzed with **4**/MAO system

Catalyst	1-Hexene (mL)	1-Hexene and isomers (%)	Dimers (%)	1-Hexene (%)	*Trans*-2-hexene (%)	*Cis*-2-hexene (%)
4a[a]	1	88.6	11.4	46.61	29.85 (55.91)	23.54 (44.09)
4a[b]	0.01	81.51	18.49	7.51	66.37 (71.77)	26.11 (28.23)
4b[b]	0.01	48.46	51.54	0.65	80.75 (81.29)	18.59 (18.71)

[a] Measured with GC–MS with DB-5MS column.

[b] Measured by GC with HP-5MS column; temperature 45 °C, Cat. **4a** and **4b** 7×10^{-5} mol, MAO 80 mg, 3 h; the value in parenthesis is the relative abundance of *cis*- and *trans*-isomers in 2-hexenes.
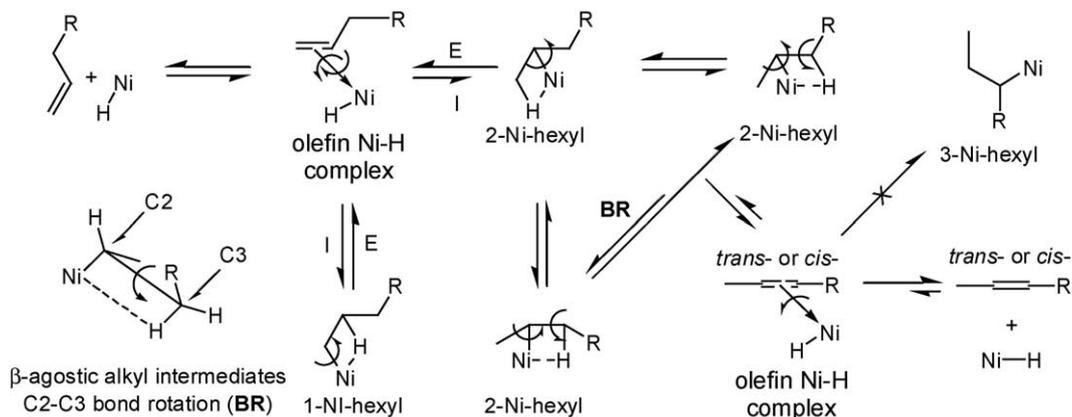
Scheme 2. Presumed relationships of the Ni-hexyl intermediates with hexene isomers (ligands were omitted for clarity, R = propyl).
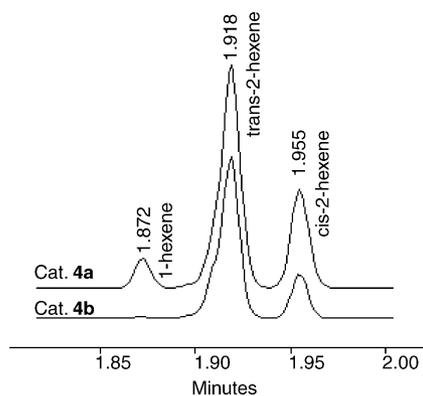
Fig. 3. GC spectrum of the hexene isomers (measured by GC with HP-5MS GC column, 1-hexene 0.01 mL, Cat. **4a** and **4b** = 7×10^{-5} mol, MAO 80 mg, temperature 45 °C, 3 h).

Fig. 4. Nomenclature for the Ni-alkyl intermediates.

solution remained as 1-hexene, while 29% of them had been isomerized to internal olefin (2- and 3-hexenes) [11c]. Herein, The neutral Ni(II) active centers are hedged by the coordination wedge of the β-diketiminato ligands. Due to this configuration feature, the β-diketiminato Ni-alkyl species should be relative idle comparing with the cationic α-diimine M-alkyl species and likely to eliminate. Once the β-H elimination occurred and the hexene/Ni–H complexes formed, the reinsertion of these binding 2-hexenes into the Ni–H bond should be more difficult than that of 1-hexene (Scheme 2). Moreover, after being released, the rebinding probability of 2-hexene to the Ni–H intermediate should be lower than that of 1-hexene.
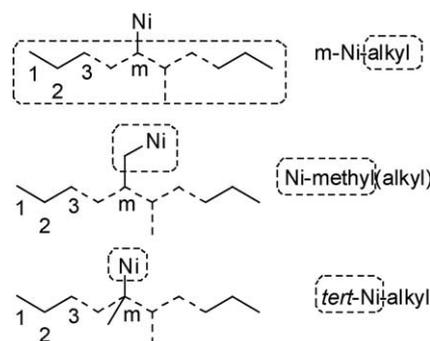
Hereby, the preponderance of 2-hexenes in the total hexenes is regarded as the result of this accumulation circle.

Since the 1,2 insertion of 1-hexene to Ni–H is favored by kinetics, the preponderance of 2-hexenes indicates that considerable parts of 2-Ni-hexyl intermediates are derived from 1-Ni-hexyl intermediate. These suggest that the isomerization from 1-Ni-hexyl to 2-Ni-hexyl is thermodynamically favored.

The distribution of the hexenes was also observed being greatly affected by the initial concentration of 1-hexene (see Table 1). Thermodynamic equilibrium cannot be reached within the experiment time scale (due to the bad stability of the active species). The *trans-/cis*-2-hexene ratio should be related to the stability of the respective β-agostic alkyl species and the freedom of C2–C3 bond rotation (see Scheme 2).
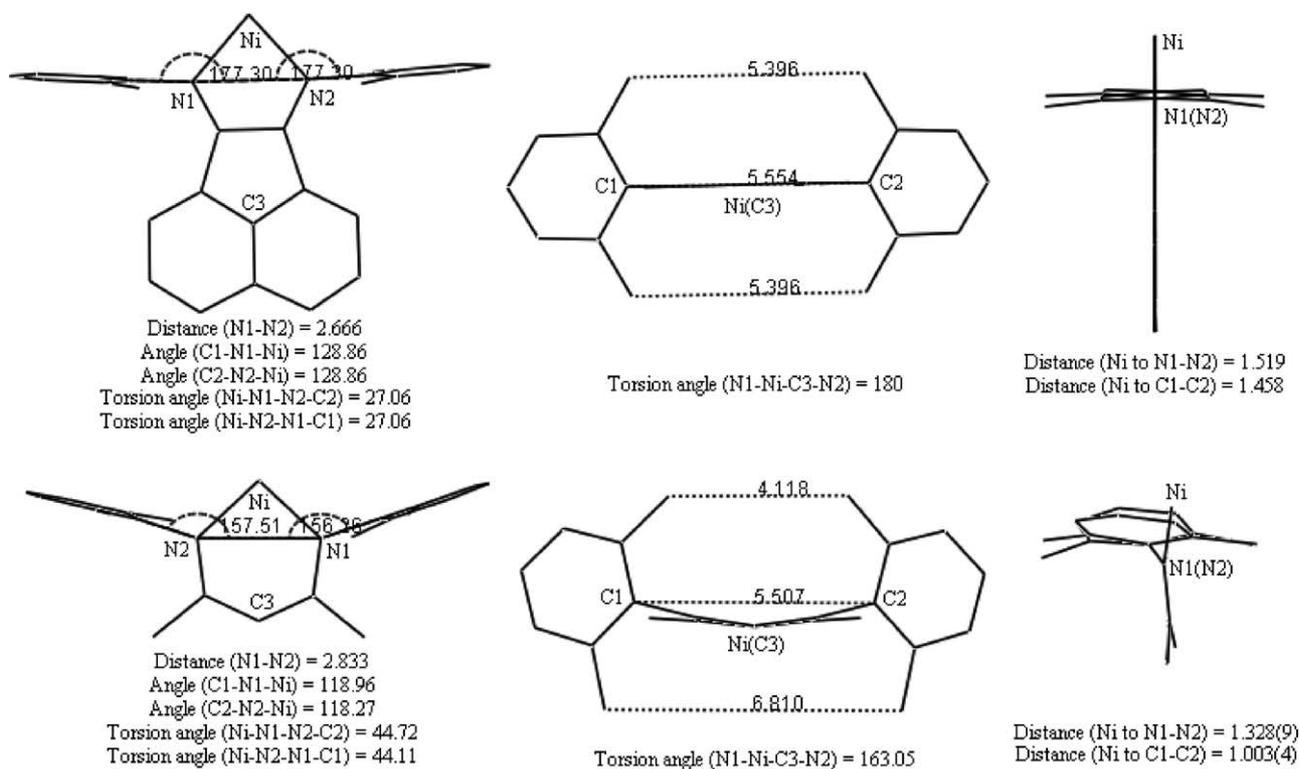

Fig. 5. The sketch map comparison of the literature α-diimine Ni(II) complex [14] and β-diketiminato Ni(II) complex [6c,6e] (hydrogen and some of methyl carbon atoms were omitted for clarity. Ni to A1–A2 means the distance of the nickel atom to the line through A1 atom and A2 atom).

Moreover, decreased steric bulk of the β-diketiminato ligand leads to increases in the portion of 2-hexenes and the *trans*-/*cis*-2-hexene ratio (see Fig. 3 and Table 1). These suggest that the rotations of Ni–C and C2–C3 bonds are relative free in less bulky **4b**/MAO system comparing with **4a**/MAO system.

The active species of the β-diketiminato Ni(II)/MAO system might adopt square planner structure or tetrahedral structure. In both cases, the Ni atoms of the β-diketiminato Ni(II) complexes [6] were deeply embodied into the ligands comparing with the α-diimine Ni(II) complexes [14] (see Fig. 5). The rotations [4c,15] and the reinsertion of the binding 2-hexenes to fit the formation of the 3-Ni-hexyl intermediate were thus not favored by the coordination wedge and became very difficult (see Scheme 2). The probability of deriving 3-hexenes was thus greatly lowered. This suggest that the migration (walking) of the Ni(II) atom from the second carbon to the third carbon along the hexyl chain is unfavorable in the β-diketiminato Ni(II)/MAO system.

GC–MS analysis confirmed that these marked peaks are the C12 inner olefin isomers (for these peaks: $e/m = 168$, see Fig. 6). These dimers should be the elimination products of the *m*-Ni-dodecyl intermediates ($m = 5$), which formed after the insertion of 1-hexene to the *m*-Ni-hexyl intermediates ($m = 1$ or 2) as the literature pathways [11a,b]. The *cis*- and *trans*-position isomers of these dimers should be derived after the β-H elimination of Ni with the β-H and β′-H (see Scheme 3). These C12 dimers include 7-methyl-*trans*-5-undecene (23.36 min), 7-methyl-*trans*-4-undecene (25.54 min), *trans*- or *cis*-4-dodecene (28.84 min), and *trans*-5-dodecene (30.31 min).

GC–MS analysis confirmed that those unmarked peaks in the spectrum are also C12 inner olefin isomers (their MS fragment distributions are similar to that of C12 inner olefins). Some of them, such as 5-methyl-*trans*-4-undecene (27.57 min), should be related to the Ni-methyl(undecyl) intermediates (see Scheme 3). These multi-substituted olefin products suggest that the *tert*-Ni-dodecyl intermediates could originate from the 1,2 insertion of α-olefin, and this is direct evidence that the metal center can migrate from a primary carbon to the adjacent tertiary carbon. Hereby, we propose
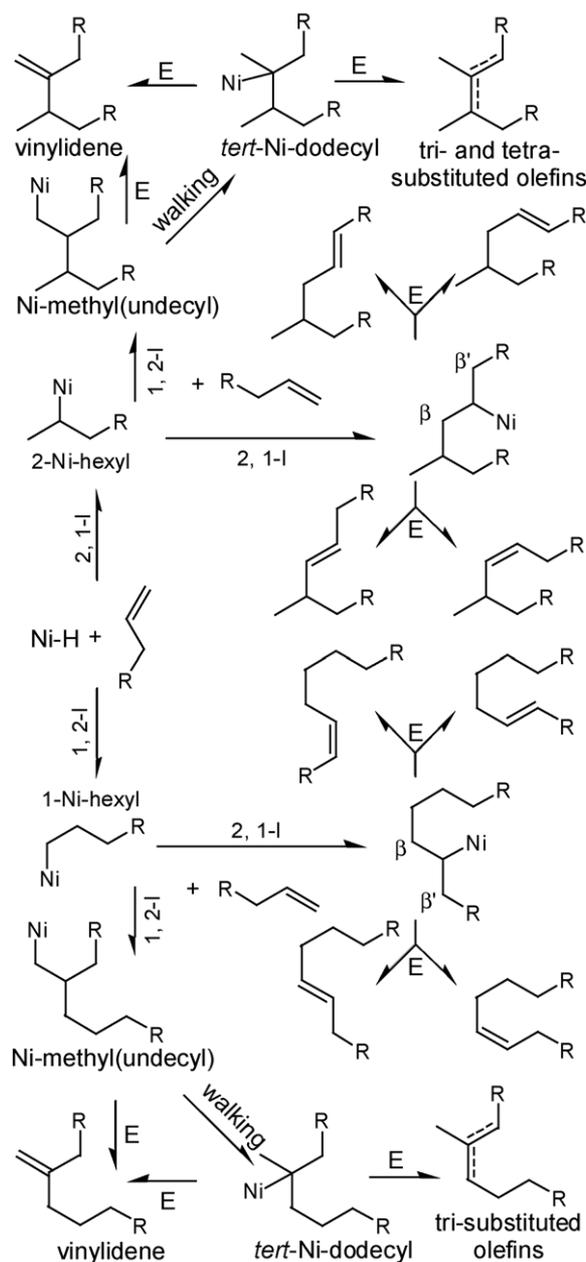
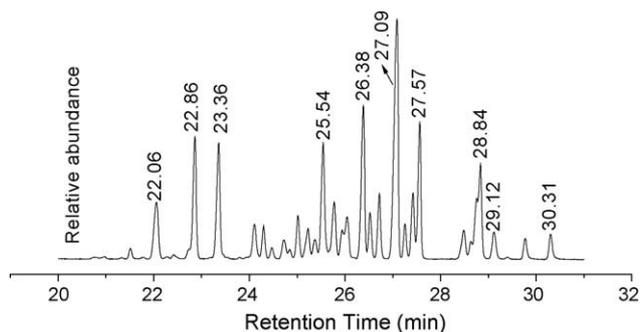Scheme 3. The formation pathways of the C12 dimer isomers (I = insertion, E = elimination, R = propyl).

Fig. 6. GC–MS spectrum of the C12 dimers (measured by GC–MS with DB-5MS column, Cat. **4a** 7×10^{-5} mol, MAO 80 mg, temperature 45 °C, 3 h).

an alternative pathway that would lead to the formation of the branch-on-branch structure in the ethylene polymerization process [2,13d,17] (see Scheme 4).

In theory, the binding and the direct insertion of the 1-hexene to the *m*-Ni-dodecyl intermediates ($m = 5$) are difficult in both the β-diketiminato and α-diimine system. Due to the open configuration of their ligands, α-diimine catalysts are capable of polymerizing α-olefins via the chain-strengthen mechanism [1,2,11c,13] (see Scheme 5). However, in β-diketiminato catalyst systems, after β-H elimination and the formation of the dodecene/Ni–H complexes, the rotation and the reinsertion of these binding dodecenes were blocked by the coordination wedge. The *m*-Ni-dodecyl
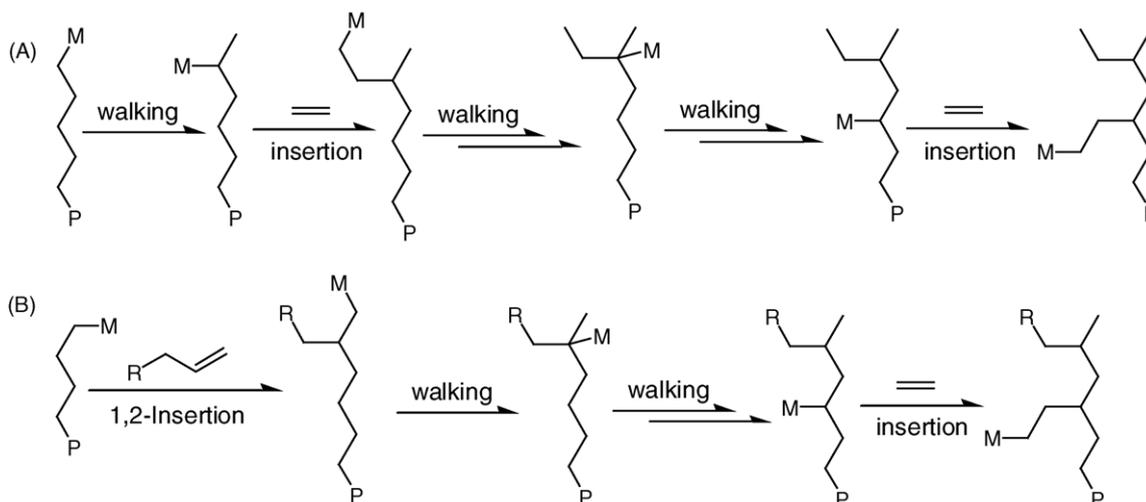
Scheme 4. Mechanism for the formation of the branch-on-branch structure in the ethylene polymerization, **A** mechanism in literature [2], **B** alternative pathway proposed here (R = methyl, propyl, amyl, etc.).
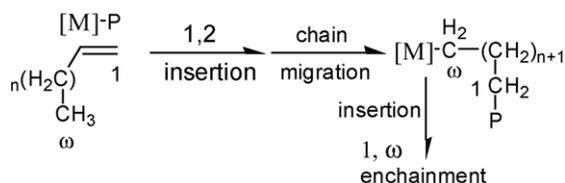
Scheme 5. "Chain-strengthen" mechanism of the 1-olefin polymerization catalyzed with α-diimine catalysts/MAO system (P = polymeric alkyl chain).

intermediates ($m = 1$ or 2), which are fitting for 1-hexene to insert, cannot be produced as the same mechanism occurred in the α-diimine catalyst systems. Thus, no trimers or higher oligomers were formed. In less bulky **4b**/MAO system, the portion of dimers is larger than that in **4a**/MAO system (see Table 1). Small bulk **4b**/MAO is more promising in α-olefin dimerization than **4a**/MAO.

In general, the obtained dimers are mainly inner olefin isomers that were derived from the direct β(or β')-H elimination of the m-Ni-dodecyl intermediates ($m = 5$). No corresponding olefin products of the m-Ni-dodecyl intermediates ($m < 4$) were detected by GC–MS. That is to say, the migration (walking) of the Ni(II) atom from a secondary carbon to another one along the alkyl chain of the m-Ni-dodecyl intermediates is blocked in the β-diketiminato Ni(II)/MAO system.

3. Conclusion

The β-diketiminato Ni(II) complex/MAO systems shows strong tendency of isomerizing the substrate 1-hexene. The preponderance of 2-hexene in all hexenes is the result of an accumulation circle. Due to the coordination wedge of the bulky β-diketiminato Ni(II) catalyst, 3-hexenes, trimers and higher oligomers were not produced. The walking of the Ni atom from a primary carbon to the adjacent secondary or

tertiary carbon of the alkyl chain is thermodynamically favored. However, the walking of the Ni atom from the a secondary carbon to another one along the alkyl chain of the Ni-alkyl intermediates is unfavorable in the β-diketiminato Ni(II)/MAO systems. Small bulk **4b**/MAO is more promising on the purpose of α-olefin isomerization and dimerization than **4a**/MAO.

4. Experimental

4.1. General remarks

All manipulations were performed by standard Schlenk techniques under nitrogen atmosphere or in a M. Braun glovebox. All the containers were thoroughly dried by heating under vacuum. Hexane and toluene were thoroughly dried over phosphorus pentoxide and sodium respectively. MAO solid was prepared by the controlled hydrolyzation of the trimethylaluminum (TMA) at 0–60 °C by using $Al_2(SO_4)_3 \cdot 18H_2O$ ($H_2O/Al = 1.3$) that was dispersed in toluene. $(DME)NiBr_2$ was prepared according to the reported literature [16]. 2,6-Diisopropylaniline, 2,6-dimethylaniline, n-butyllithium were purchased from Aldrich Chemical Co. Other commercially available reagents were purchased and used as received.

4.2. H{N(C₆H₃ⁱPr₂-2,6)C(Me)}₂CH (L₁)

The synthetic routes of β-diketiminato ligand (**L**) had been reviewed in literature [5]. In this work, the β-diketiminato ligand was synthesized via the direct condensation of 2,6-diisopropylaniline with acetylacetone. 2,6-Diisopropylaniline (0.05 mol) and acetylacetone (0.02 mol) in 100 mL toluene were refluxed in a 250 mL flask for 3 h. After that, the flask was equipped with a Dean–Stark apparatus, and the mixture was further refluxed until no water

found. The solution was distilled under vacuum to remove the by-products (amines and β-keto-amines). The remains were recrystallized in methanol. Colorless crystal was obtained, 1.356 g (yield 16.2%). ^{1}H NMR (CDCl$_3$) (ppm): 12.11 (1H, H−N), 7.12 (6H, *o*- and *p*-Ar), 4.86 (1H, H-backbone), 3.11 (4H, CH(CH$_3$)$_2$), 1.70 (6H, CH$_3$), 1.21 (2H, CH(CH$_3$)$_2$), 1.17 (2H, CH(CH$_3$)$_2$). Anal. Calcd. for C$_{29}$H$_{42}$N$_2$: C 83.20, H 10.11, N 6.69. Found: C 83.08, H 9.93, N 6.64.

4.3. H{N(C$_6$H$_3$Me$_2$-2,6)C(Me)}$_2$CH (L$_2$)

The synthesis of **L$_2$** was preformed as in the case of **L$_1$**, using 0.05 mol 2,6-dimethylaniline, 0.02 mol acetylacetone and 100 mL toluene, and a refluxing time of 3 h. The product was obtained as colorless crystal, 1.189 g (yield 19.4%). ^{1}H NMR (CDCl$_3$) (ppm): 12.19 (1H, H−N), 7.03 (2H, *p*-Ar), 6.94 (4H, *m*-Ar), 4.87 (1H, H-backbone), 2.16 (12H, *o*-CH$_3$Ar), 1.69 (6H, CH$_3$). Anal. Calcd. for C$_{21}$H$_{26}$N$_2$: C 82.31, H 8.55, N 9.14. Found: C 82.30, H 8.55, N 9.14.

4.4. Ni{(N(C$_6$H$_3$^{i}Pr$_2$-2,6)C(Me))$_2$ CH}Br (4a)

The complex (**4a**) was prepared as the literature method [6c]. Ligand lithium salt was used as prepared in toluene without further isolation. (DME)NiBr$_2$ was used as Ni(II) source. The **L$_1$** 1.20 g (0.003 mol) was dissolved in 50 mL toluene, and cooled to −78 °C. *n*-Butyllithium 1.1 mL (hexane solution 2.6 M) was injected. The solution was allowed warm up to room temperature overnight. After that, (DME)NiBr$_2$ 1.08 g (0.0035 mol) were added, and the slurry were stirred at 80 °C for 12 h. After hot filtration, the filtrate was condensed by vacuum to 5–8 mL and the complexes were precipitated and washed twice with hexane. Grey blue solid was obtained, 0.86 g (yield 54.1%). ^{1}H NMR (C$_6$D$_6$) (ppm, ∼5 mM): dimer 55.59 (4H, *m*-Ar), 36.67 (4H, CH(CH$_3$)$_2$), −26.27 (2H, *p*-Ar), −88.08 (6H, CH$_3$); monomer 41.10 (4H, *m*-Ar), 21.57 (4H, CH(CH$_3$)$_2$), 8.29 (24H, CH(CH$_3$)$_2$), −21.51 (2H, *p*-Ar), −60.54 (6H, CH$_3$); monomer/dimer ≈5/1. ^{1}H NMR (CD$_2$Cl$_2$) (ppm, ∼10 mM): dimer 56.12 (4H, *m*-Ar), 36.87 (4H, CH(CH$_3$)$_2$), −26.64 (2H, *p*-Ar), −88.03 (6H, CH$_3$); monomer 40.31 (4H, *m*-Ar), 22.17 (4H, CH(CH$_3$)$_2$), 8.95 (24H, CH(CH$_3$)$_2$), −22.77 (2H, *p*-Ar), −59.09 (6H, CH$_3$); monomer/dimer ≈2/1.

4.5. Ni{(N(C$_6$H$_3$Me$_2$-2,6)C(Me))$_2$ CH}Br (4b)

The synthesis of complex **4b** was preformed as in the case of complex **4a**, using **L$_2$** 0.92 g (0.003 mol), *n*-butyllithium 1.1 mL (hexane solution 2.6 M) and 50 mL toluene, (DME)NiBr$_2$ 1.08 g (0.0035 mol) and a stirring time of 12 h at 80 °C. Product was obtained as dark blue solid, 0.85 g (yield 67.3%). ^{1}H NMR (C$_6$D$_6$) (ppm, ∼10 mM): dimer 50.49 (12H, *o*-CH$_3$Ar), 47.74 (4H, *m*-Ar), −22.96 (2H, *p*-Ar), −65.97 (6H, CH$_3$); monomer 47.62 (4H, *m*-Ar), 43.52 (12H, *o*-CH$_3$Ar), −22.28 (2H, *p*-Ar), −77.08 (6H, CH$_3$); monomer/dimer ≈1/4.5. ^{1}H NMR (CD$_2$Cl$_2$) (ppm,

∼10 mM): dimer 48.47 (12H, *o*-CH$_3$Ar), 45.73 (4H, *m*-Ar), −24.97 (2H, *p*-Ar), −67.98 (6H, CH$_3$); monomer 45.60 (4H, *m*-Ar), 41.50 (12H, *o*-CH$_3$Ar), −24.29 (2H, *p*-Ar), −79.09 (6H, CH$_3$); monomer/dimer ≈1/2.5.

4.6. Isomerization and dimerization of 1-hexene

Under nitrogen atmosphere, MAO (∼80 mg) was dissolved in toluene (2 mL) in a 20 mL glass tube, which was sealed with rubber cap and equipped with magnetic bar. 1-Hexene (toluene solution, 0.01 mL/mL) and β-diketiminato Ni(II) complexes **4** (7×10^{-5} mol dissolved in 1 mL toluene) were injected into the tube in sequence. After stirring at 45 °C for 3 h, the mixture was cooled to −20 °C in cooling bath, and terminated with 3 mL ethanol (NaOH solution in 95% ethanol). Additional water was added and the tube was sealed after CH$_4$ bubbling out. The upper colorless and transparent toluene part was collected for GC or GC–MS analysis.

4.7. Measurement

^{1}H NMR spectra were recorded on a Varian INOVA 500NB NMR spectrometer. Elemental analysis was determined with a Vario EL Series Elemental Analyzer from Elementar. The GC–MS data were recorded by a Finnigan Voyager GC-8000Top Series GC–MS System with DB-5MS GC column. The GC spectrum were recorded by a Varian CP3800 Series GC System with a HP-5MS GC column.

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at 10.1016/j.molcata.2004.12.024.

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