

# Unsymmetrical $\alpha$ -Diimine Nickel (II) Complex with Rigid Bicyclic Ring Ligand: Synthesis, Characterization, and Ethylene Polymerization in the Presence of $\text{AlEt}_2\text{Cl}$

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**ABSTRACT:** Unsymmetrical  $\alpha$ -diimine ligand **1** was successfully synthesized via condensation of trimethylaluminum (TMA) metalated 2-methyl-6-isopropyl-aniline with rigid bicyclic aliphatic diketone camphorquinone. Syn- and anti-stereoisomers were detected by  $^{13}\text{C}$  NMR in the condensation product. The corresponding  $\alpha$ -diimine nickel (II) complex **1** was prepared from the exchange reaction of (DME)- $\text{NiBr}_2$  with the ligand **1**, and displayed high activity for ethylene polymerization in the presence of diethylaluminum

chloride ( $\text{AlEt}_2\text{Cl}$ ). The resultant polymers were confirmed by gel permeation chromatography and  $^{13}\text{C}$  NMR characterization to be broad molecular weight distribution polyethylene with various branches, and high degree of branching, even at low polymerization temperature  $-10^\circ\text{C}$ . © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 206–210, 2008

**Key words:**  $\alpha$ -diimine nickel (II) complexes; trimethylaluminum; branched polyethylene; isomerization

## INTRODUCTION

To obtain the good process ability of polyethylene, producing broad molecular distribution polyethylene or long-chain-branched polyethylene has received considerable attention.<sup>1–7</sup>

Recently,  $\alpha$ -diimine nickel (II) complexes have been disclosed owning great potential for the branching polymerization of ethylene through the modification of the ligands' steric and electronic properties.<sup>8–14</sup> No matter how different the coordination environment of these reported  $\alpha$ -diimine nickel (II) complexes was, the degree of branching of the obtained polyethylenes below  $0^\circ\text{C}$  was trace.<sup>13,14</sup>

The sym-substituted  $\alpha$ -diimine nickel (II) complexes are typical single-site catalysts for ethylene polymerization and afford polyethylene with narrow molecular weight distribution.<sup>15–18</sup> While Pellecchia<sup>15</sup> found that unsym-substituted  $\alpha$ -diimine nickel (II) complexes could exist either as syn-isomer with the same *o*-substituents on the aniline moieties orienting toward the virtual positions of the coordination plane in the same direction, or as anti-isomer with the same *o*-substituents in contrary direction. More-

over, two isomers could interconvert owing to partial rotation of the aryl and the conversion rate depending on steric bulk of the substituents and the temperature. In our research group's previous work,<sup>14</sup> the unsym- $\alpha$ -diimine nickel (II) complex of 2,3-bis(2-phenylphenyl)-butane diimine nickel (II) dibromide afforded broad molecular weight distribution polyethylene below  $0^\circ\text{C}$ .

Here we report a novel unsym- $\alpha$ -diimine nickel (II) complex, which is quite different from the previous  $\alpha$ -diimine nickel (II) complexes based on acenaphthenequinone or 2,3-butanedione. The unsymmetrical rigid  $\alpha$ -diimine ligand **1** was synthesized via the condensation of sterically bulky camphorquinone with 2-methyl-6-isopropyl-aniline metalated by TMA. It is reasonable to believe that the resultant ligand **1** and corresponding nickel (II) complex **1** exists as syn- and anti-isomers. The effect of the interconversion of both isomers on ethylene polymerization was investigated, and the obtained polymer was characterized by GPC,<sup>13</sup>  $^{13}\text{C}$  NMR, and DSC.

## EXPERIMENT

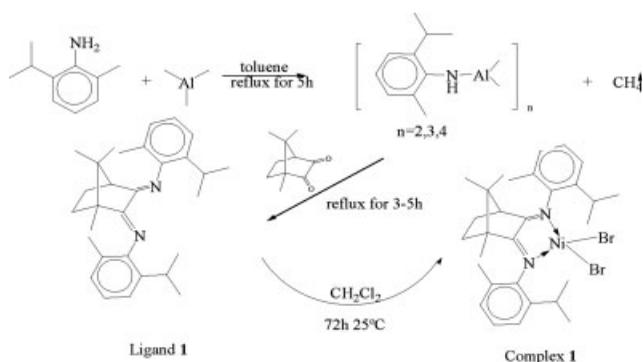
### General consideration

All manipulations involving air-sensitive materials were carried out by using standard Schlenk techniques under an atmosphere of extra-pure-grade nitrogen. Dichloromethane was distilled from  $\text{P}_2\text{O}_5$ , toluene was refluxed over metallic sodium for 48 h and

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**Scheme 1** The synthesis route of ligand 1 and complex 1.

distilled under nitrogen atmosphere before use. GPC of polymers was performed on a Water 150C at 135°C and 1,2,4-trichlorobenzene as solvent. The columns were calibrated with narrow molecular weight distribution polystyrene standards.  $^{13}\text{C}$  NMR spectra of polyethylene samples were recorded at 120°C in a 10-mm tube using an INOVA 500 MHz spectrometer. The samples were dissolved in *o*-dichlorobenzene/benzene- $d^6$  to form a 15 wt % solution.

### Preparation of ligand 1

A 100-mL Schlenk flask was charged with 1.00 g 2-isopropyl-6-methylaniline, equiv-molar TMA toluene solution, and 10-mL toluene under nitrogen atmosphere, refluxed for 2 h, and then the solution turned to pale yellow. Subsequently adding the required camphorquinone, immediately the solution turned into brownish red, and refluxed for 5 h. The crude product was poured into 25-mL water, and the organic phase was separated and washed with water ( $3 \times 25$  mL). The isolated organic phase was dried by anhydrous  $\text{MgSO}_4$  for 24 h, and then evaporated. The residue was eluted with acetate and petroleum ether (the volume ratio = 1 : 15) on the neutral aluminum column chromatography. Then eluted component was recrystallized in hexane in the refrigerator. Yield: 57.5%. Anal. Calculated for (%): C 84.14, H 8.96, N 6.18. Found (%): C 84.06, H 9.41, and N 6.54 (detected on a Vario EL).

### Preparation of complex 1

A 100-mL Schlenk flask was charged with nitrogen and stoichiometric amount of  $(\text{DME})\text{NiBr}_2$  and 0.708 g (1.55 mmol) ligand 1, to which 30-mL  $\text{CH}_2\text{Cl}_2$  was added, stirring for 72 h at 25°C. After being held for this time the mixture was filtrated to give a clear red solution that gave a clear red/brown solid by removing the solvent dichloromethane under reduced pressure. The red/brown solid product was washed with  $3 \times 5$  mL ether, and then dried in vac-

uum; 0.715 g product was obtained; yield, 71.0%. Anal. Calculated for (%): C 55.66, H 6.18, and N 4.33. Found (%): C 55.33, H 6.08, N 4.08 (detected on a Vario EL).

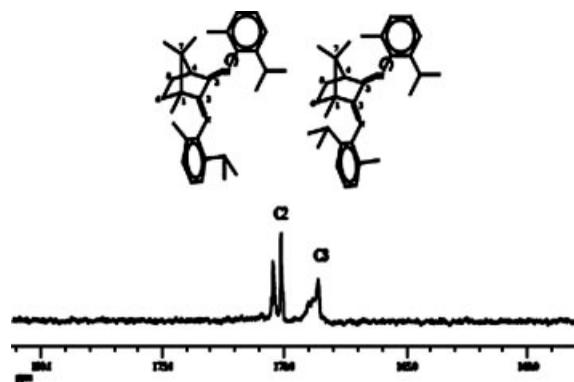
### Ethylene polymerization

The polymerization runs were carried out under an extra-pure-grade nitrogen atmosphere in 100-mL glass flask equipped with a magnetic stirrer. Toluene and  $\text{AlEt}_2\text{Cl}$  were introduced into the reactor, and then saturated with 4.5 psig ethylene; at last the complex 1 solution was added. After 30 min, the polymerizations were terminated by the addition of 10 wt % HCl in ethanol. The polymers were washed with ethanol and dried in vacuum at 60°C to constant weight.

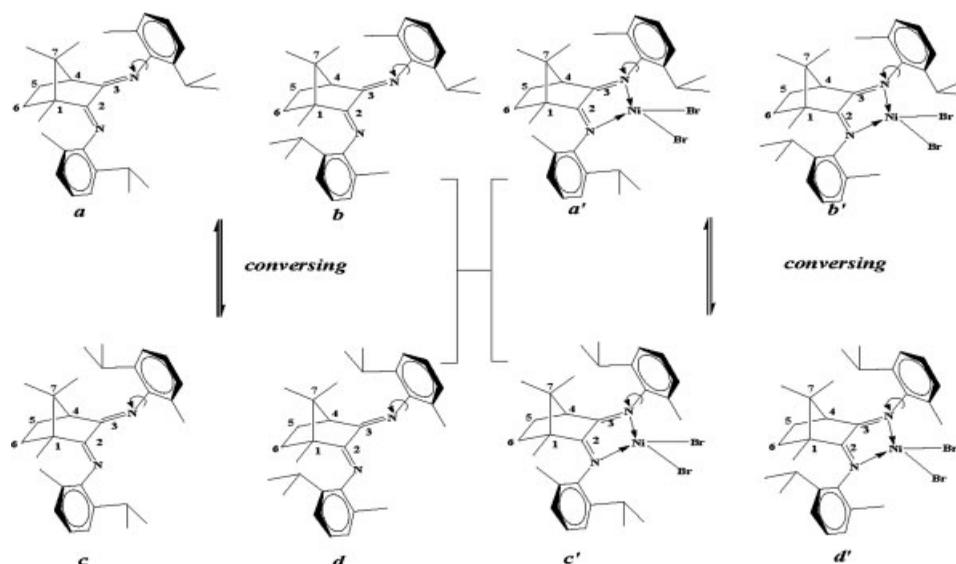
## RESULTS AND DISCUSSION

It is difficult to synthesize ligand 1 via the conventional condensation of camphorquinone with alkyl-substituted anilines catalyzed with formic acid,<sup>9-12</sup> *p*-toluenesulfonic acid,<sup>16</sup> or anhydrous  $\text{ZnCl}_2$ .<sup>17</sup> It is speculated that the rigid aliphatic bicyclic ring system results in the nitrogen donor atoms having little flexibility in their relative positions. Also Okuda<sup>19</sup> suggested that the bridgehead methyl group on the camphorquinone backbone hinder 2,6-alkyls-substituted aniline and camphorquinone from forming the  $\alpha$ -diimine ligand. Therefore, in this case, TMA was employed as the catalyst for the condensation to synthesize ligand 1 as shown in Scheme 1.<sup>18</sup>

As characterized by  $^{13}\text{C}$  NMR, the prepared ligand 1 existed syn- and anti-stereoisomers in terms of the characteristic chemical shift of the  $\text{C}=\text{N}$  carbon, as shown in Figure 1. It is reasonable to believe that these stereoisomers result from either the stereoselective condensation reaction of unsym-substituted aniline with camphorquinone or their interconversion owing to the rotation of aromatic ring (see Scheme 2). Bimodal resonances at 170.0 and 170.2 ppm



**Figure 1** The  $^{13}\text{C}$  NMR spectrum of ligand 1.



**Scheme 2** The interconversion of stereoisomers of ligand 1 and complex 1.

for C 2 (see Fig. 1) appear to imply stereo-selective condensation of the C 2 carbonyl with the TMA metalated 6-isopropyl-2-methyl aniline. The peak at 170.2 ppm derived from the C 2 indicates that the *o*-isopropyl is in the same orientation with bridged group, while the assignment of C 2 at 170.0 ppm displays that the *o*-isopropyl is on the opposite orientation of bridged group. Moreover, both structures cannot interconvert because the rotation of aromatic ring may be blocked by the bridgehead methyl. A broad resonance from 168.6 to 169.2 ppm assigned to C 3 is indicative of the rotation of the vicinal aromatic ring. Complex 1 was synthesized from (DME)-NiBr<sub>2</sub> by ligand exchange with the ligand 1. It can be assumed that the original geometry of the ligand 1 is substantially maintained in the complex 1.<sup>15</sup>

Ethylene polymerizations catalyzed by complex 1 in the presence of AlEt<sub>2</sub>Cl displayed high activity up

to 10<sup>6</sup> g PE/molNi h at the polymerization temperatures from -10 to 70°C in toluene (Table I). All the products were polymers, not oligomers. It is notable that the resultant polyethylenes had broad molecular weight distribution. The results implied that the unsym- $\alpha$ -diimine nickel (II) complex 1 exist various isomers and provide multiactive species for ethylene polymerization when activated by AlEt<sub>2</sub>Cl. As depicted in Scheme 2, it is reasonable to postulate that the complex 1 possessed two syn-isomers (*a'* and *b'*) and two anti-isomers (*c'* and *d'*), which may result in multiactive species with different steric bulk for ethylene polymerization under appropriate conditions. In syn-isomers, two bigger substituents are oriented toward the virtual positions of the coordination plane in the same direction, which has bigger steric bulk for chain propagation when compared with the opposite direction. Moreover, the iso-

**TABLE I**  
The Results of Ethylene Polymerization with Unsymmetrical  $\alpha$ -Diimine Nickel (II) and AlEt<sub>2</sub>Cl<sup>a</sup>

Run	Temperature (°C)	Activity $\times 10^{-6}$ (g PE/mol Ni·h)	$M_w^b \times 10^{-4}$	$M_w/M_n^b$	Branch/1000 C <sup>c</sup>
1	-10	0.93	2.18	9.22	50
2	0	1.58	2.49	5.53	n.d. <sup>d</sup>
3	10	1.14	3.01	4.63	n.d. <sup>d</sup>
4	30	1.70	1.66	3.24	115
5 <sup>e</sup>	30	1.81	1.64	4.14	103
6	50	1.87	1.33	3.17	n.d. <sup>d</sup>
7	70	0.71	n.d. <sup>d</sup>	n.d. <sup>d</sup>	n.d. <sup>d</sup>

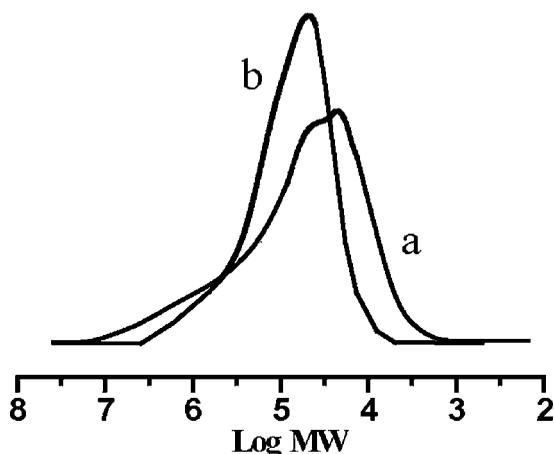
<sup>a</sup> Polymerization conditions: [Ni] = 1.0  $\times 10^{-4}$  mol/L,  $n_{Al}/n_{Ni}$  = 690,  $P(C_2H_4)$  = 0.15 MPa,  $t_p$  = 0.5 h, toluene used as solvent.

<sup>b</sup> Measured by GPC with polystyrene standards.

<sup>c</sup> Degree of branching (branching numbers of 1000 carbon atoms in polyethylene main chain) determined by <sup>13</sup>C NMR.

<sup>d</sup> Not determined.

<sup>e</sup>  $n_{Al}/n_{Ni}$  = 205.

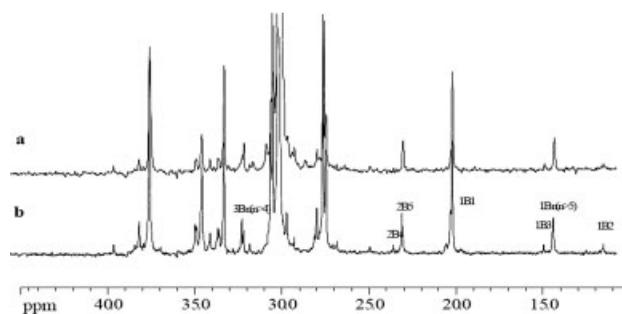


**Figure 2** The GPC plots of polyethylene obtained at  $-10^{\circ}\text{C}$  (a) and  $30^{\circ}\text{C}$  (b) from Run 1 and Run 4 in Table I.

mers with the orientation having smaller steric bulk should be preferential for chain propagation and provide polyethylene with lower molecular weight. For anti-isomers, two bigger substituents are in different directions. It is reasonable to believe that anti-isomers have bigger steric bulk for chain propagation than syn-isomers, and can synthesize higher molecular weight polyethylene. Furthermore, we were also interested in that the  $M_w/M_n = 9.22$  of polyethylene synthesized at  $-10^{\circ}\text{C}$  was much broader than 3.24 of that done at  $30^{\circ}\text{C}$  (Fig. 2), and on the other hand polyethylene yielded at  $-10^{\circ}\text{C}$  had lower molecular than that at  $30^{\circ}\text{C}$ . A possible explanation of the peculiar result is that there are more isomers related to multiactive species for ethylene polymerization at lower temperature. As elevating temperature, syn-isomers (isomer  $a'$  and  $b'$  in Scheme 2) will convert into anti-isomers (isomer  $c'$  and  $d'$  in Scheme 2), which are steadier at high temperature.<sup>14,15</sup> Therefore, the higher molecular weight polyethylene with narrow molecular weight distribution could be synthesized at the higher polymerization temperature. With respect to the higher polymerization temperature ( $>30^{\circ}\text{C}$ ) making the molecular weight of polyethylene obtained decrease (Table I), it is can be understandable because of fasten  $\beta$ -hydride elimination, while the chain propagation slow down for the lower monomer concentration.

The influence of the  $\text{AlEt}_2\text{Cl}$  on the polymerizations have also been studied. At lower  $n_{\text{Al}}/n_{\text{Ni}}$ , the distribution of the obtained polyethylene was broader, indicating the broad molecular weight distribution resulting from the multiactive species rather than the transfer to the  $\text{AlEt}_2\text{Cl}$ .

The  $^{13}\text{C}$  NMR as shown in Figure 3 characterized the polyethylene samples prepared at different polymerization temperature. According to the assign-



**Figure 3**  $^{13}\text{C}$  NMR spectra of polyethylene obtained at  $-10^{\circ}\text{C}$  (a) and  $30^{\circ}\text{C}$  (b) from Run 1 and Run 4 in Table I.

ments of each resonance peak, based on chemical shift calculations performed with the method of Linderman and Adams,<sup>20</sup> the polyethylene contained primarily methyl branches but also ethyl, propyl, butyl, amyl, and long branches (longer than six carbons) (Table II). The nomenclature used to designate the different carbon types is that of Usami and Takayama.<sup>27</sup> The carbon in branches is denoted  $x\text{B}_n$ , where  $n$  is the length of the branch and  $x$  is the carbon number starting with the methyl group as 1.  $x\text{B}_n$  is also used to mark the carbon of the methylene or branch point in the main chain, whereas  $x$  is

**TABLE II**  
The Chemical Shifts and Assignments to the Peaks in the Figure 3

Chemical shift	Assignments
10.85	$1\text{B}_2$
13.55	$1\text{B}_{4-n}, 1,4-1\text{B}_1$
14.08	$1\text{B}_3$
19.46	$1\text{B}_1, 1,5-\text{B}_1, 1,6-\text{B}_1, 1,4-\text{B}_1$
19.81	$2\text{B}_3$
22.42	$2\text{B}_{6-n}$
22.88	$2\text{B}_5, 1,4-2\text{B}_n$
24.13	$1,5-\beta'\text{B}_1$
26.06	$2\text{B}_2$
26.76	$\beta\text{B}_2$
26.94	$\text{B}_{3-n}, (n-1)\text{B}_n, 1,4-\beta\text{B}_2,$ $1,4-(n-1)\text{B}_n$
27.40	$1,6-\beta'\text{B}_1$
28.32	$3\text{B}_4$
28.65	$4\text{B}_n, 1,4-4\text{B}_n$
29.02	$\delta\text{B}_{1-n}$
29.55	Back bone $\text{CH}_2$
29.83	$\gamma\text{B}_n, 1,4-\gamma\text{B}_1,$ $1,5-\gamma\text{B}_1, 1,6-\gamma\text{B}_1,$ $1,4-\gamma\text{B}_n, 1,4-(n-2)\text{B}_n$
31.17	$1,4-\alpha\text{B}_1$
31.60	$3\text{B}_5$
32.07	$\text{brB}_1, 1,5-\text{brB}_1, 1,6-\text{brB}_1$
32.74	$1,4-\text{brB}_1$
32.93	$\alpha\text{B}_2$
33.01	$4\text{B}_4$
33.56	$\alpha\text{B}_{3-n}$

replaced by Greek letters or *br*, respectively. For paired-branch prefixes, 1 and *m* are used, where *m* is the number of carbons between two tertiary carbons, 1 being the first tertiary carbon and *m* the next. The backbone carbons between branches are designated by Greek letters with primes. The result strongly suggests the possibility of chain walking. It seems significant that the obtained polyethylene had high degree of branching and high content of long branches, even at low polymerization temperature  $-10^{\circ}\text{C}$  approaching 45. The structures and properties of the obtained polyethylenes were quite different from those synthesized with the previously reported unsym- $\alpha$ -diimine nickel (II) catalysts, which provided linear polyethylenes below  $0^{\circ}\text{C}$  and branched polyethylene with few long branches at higher temperatures ( $>25^{\circ}\text{C}$ ).<sup>13–18</sup> An hypothesis for the branching is that the sterically bicyclic aliphatic frame retards the monomer coordinating to the active species affording the intermediates of the chain propagation; meanwhile, the sterically bicyclic aliphatic frame has scarcely any effects on the chain walking, as the chain walking only involves the metal-alkyl species. The high olefin disassociation energy barrier disfavor the polymer chain disbond, thus the chain reinsert forming various branches. The more difficult the monomer coordinate to the active species, the farther the active species walk along the propagation chain and more multifarious branches are formed.<sup>20–25</sup> Moreover, less electronic flexible active species is propitious to the chain propagation. According to Fujita, electronically flexible ligands are capable of receiving electrons from the coordinating olefin through the metal atom and releasing electrons whenever required to expedite the olefin insertion.<sup>26</sup>

## CONCLUSIONS

Trimethylaluminum assisted condensation reaction of carbonyl functionalities with primary amines is a very convenient method, which is especially useful for electronically deactivated and sterically bulky systems. The bridgehead methyl could only block the rotation of one aryl. Therefore, the unsymmetrical  $\alpha$ -diimine nickel (II) complex **1** may not only exist as syn- and anti-isomers, but also they can interconvert owing to the rotation of the other aryl and the conversion velocity resting with temperature, and providing multiactive species with different steric bulk for synthesizing polyethylene with broad molecular weight distribution. Compared with the classical acenaphthenequinone or 2,3-butanedione backboned  $\alpha$ -diimine nickel (II) catalysts, the

complex **1** has greater probability of chain walking and the chain termination when activated for ethylene polymerizations, thus the resultant polyethylene had low molecular weight and high degree of branching. To obtain “constrained geometry”  $\alpha$ -diimine nickel catalysts, the both bridge-H substituted rigid ligand shall be designed and synthesized in our future work.

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