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New bi-nuclear and multi-nuclear α-diimine/nickel catalysts for ethylene polymerization

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Abstract

Bi-nickel-centre catalysts {[2,6-diisopropyl-C_6 H_3–N=C(CH_3)–(CH_3)C=N–3,5-di-R–C_6H_2–CH_2–3′,5′-di-R–C_6H_2–N=C(CH_3)–(CH_3)C=N–2,6-diisopropyl-C_6H_3][$NiCl_2$]$_2$; R, –CH(CH_3)$_2$, –CH_2CH_3, –CH_3} were prepared by Schiff-base condensation of 2,3-butanedione with 2,6-diisopropylaniline and substituted bis-aniline, and subsequent metathesis reaction with (DME)$NiCl_2$. Multi-nickel-centre catalysts {–[(–N=C(CH_3)–(CH_3)C=N–3,5-di-R–C_6H_2–CH_2–3′,5′-di-R–C_6H_2–)–$NiCl_2$]$_n$–; R, –CH(CH_3)$_2$, n = 4.0; R, –CH_2CH_3, n = 4.0; R, –CH_3, n = 2.5} were prepared by Schiff-base condensation of 2,3-butanedione with substituted bis-aniline, and subsequent metathesis reaction with (DME)$NiCl_2$. Comparing with mono-nickel-centre catalysts, the new catalysts have much bigger molecules, particularly the distance between every two active centres was controlled for bi-nickel-centre catalysts, and the distances among several active centres were controlled for multi-nickel-centre catalysts, resulting in the micro chemical environment of nickel centre being regulated. The catalytic evaluation clearly showed that this structural regulation had significant influence on catalytic activity. When the substitute was isopropyl or ethyl, the new catalysts demonstrated much higher catalytic activity than the corresponding mono-nickel-centre catalysts; but when the substitute was methyl, the new catalysts demonstrated lower catalytic activity than the corresponding mono-nickel-centre catalysts. The most efficient new catalyst was multi-nickel-centre catalyst with ethyl as substitute, which catalytic activity was high up to 3220 gPE/(gNi h) at 25 °C with Al(MAO)/Ni ratio at 500.

Keywords: α-Diimine; Nickel; Catalyst; Ethylene; Polyethylene

1. Introduction

Driven by industrial desire to obtain ever greater control over the properties of polyolefins to satisfy the increasing demands of human beings and market, the search for new highly active and selective catalysts for ethylene and α-olefins polymerization has always been an active research field in the past half century. Following the discovery and industrial application of multi-site Ziegler–Natta type catalysts, well-defined single-site catalysts have attracted extensive attention and have been developed very quickly in the past two decades because of their more excellent capability to control the microstructures of polyolefins by regulating the microstructures of well-defined transition metal complexes used as precatalysts [1–6].

Among well-defined catalysts, most attention has ever been focused on early transition metal d^o and lanthanide $d^o f^n$ systems [7–10]. But in the past several years, there has rapidly growing interest in the area of late-transition metal catalysts for ethylene and α-olefins polymerization. Recent developments have resulted in highly active late-transition metal catalysts [4–6]. In this field, the key milestones have been the discoveries of the α-diimine/Ni(II) and Pd(II) catalysts [11–19], and the 2,6-bis(imino)pyridine/Fe(II) and Co(II) catalysts [20–29], both of which are highly active catalysts for ethylene polymerization upon activation with methyl aluminoxane (MAO). Comparing with early transition metal catalysts,

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such as titanium, zirconium or chromium based catalysts with high oxophilicity including metallocene type and ligand incorporated complex type which are easily being poisoned by most functionalized olefins, late-transition metal catalysts have lower oxophilicity, and therefore, have greater functional group tolerance to polar monomers. Actually the α-diimine/Pd(II) catalysts could catalyze the copolymerization of ethylene with functionized olefins [30–33].

Among late-transition metal catalysts, the α-diimine/Ni(II) and Pd(II) catalysts [11–19] formed a new kind of highly active catalysts to convert ethylene to high molecular mass polyethylene. Regarding previous studies and application of nickel catalysts in industry, mostly producing α-olefins by oligomerization which is the basis of the SHELL higher olefin process (SHOP), this new α-diimine/Ni(II) and Pd(II) catalysts opened a new idea and understanding to search for new catalysts. The key is to use bulky substitute to reduce the competing β-hydrogen elimination. In particular, this new nickel(II) and palladium(II) based catalysts could convert ethylene directly to highly branched polyethylene without the addition of expensive α-olefins, such as 1-hexene and 1-octene [14].

After the α-diimine/Ni(II) and Pd(II) catalysts were firstly published in 1995 by Brookhart and co-workers [11], see (1) and (2) in Scheme 1, extensive interests have been aroused on these unque catalysts, up to now, some closely related catalyst systems have been reported in order to understand the mechanism more deeply and to develop new catalysts by Brookhart and some other groups. Brookhart and his co-workers subsequently developed a new kind of neutral nickel catalysts derived from bulky anilinotropone ligands [34–37], see (3) in Scheme 1, which also showed high activity for ethylene polymerization. Gibson and his co-workers developed some Ni(II) and Pd(II) catalysts containing iminopyridine ligands [38,39], see (4) in Scheme 1, which generally demonstrated greatly reduced ethylene polymerization activity because of lack of steric protection on one side of the axial position in the square-plannar active species. Besides these, some nickel catalysts containing diphosphine ligands [40], and [PO] ligands [41,42], are also active catalysts for ethylene polymerization. In our effort to search for new highly active α-diimine/Ni(II) catalysts for ethylene polymerization, we found that substituted bis-aniline could be used to prepared bi-nuclear and multi-nuclear diimine/Ni(II) catalysts, which have been proved to be highly active catalysts for ethylene polymerization. Here, we report the synthesis of these new ligands, the preparation of bi- and multi-nuclear Ni(II) based catalysts, and the catalytic studies for ethylene polymerization under the activation of methyl aluminoxane.

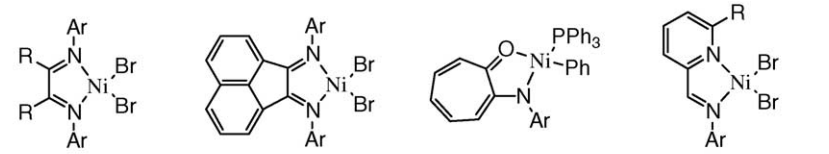
2. Experimental

2.1. General considerations

All manipulations involving air-sentive materials were carried out by using standard Schlenk techniques under an atmosphere of nitrogen. Dichloromethane was distilled from calcium hydride, toluene and hexane were distilled from sodium. Methyl aluminoxane solution (10%) in toluene was purchased from Aldrich to be used directly without any treatment. ^{1}H NMR and ^{13}C NMR were recorded on ARX200 spectrometer. (DME)$NiCl_2$ was prepared according to a reported method [43].

2.2. General procedure for ethylene polymerization

The polymerization of ethylene was carried out in a 1 l glass autoclave equipped with a mechanical stirrer which stirring rate is adjustable. The autoclave was heated by recycling hot water. Before reaction, the autoclave was dried by heating at 80 °C under vacuum for 2 h, during which period the autoclave was swept with dry N_2 at least three times. After the autoclave was dried completely and cooled down to room temperature, toluene, MAO and catalyst solution in dichloromethane were introduced in turn with syringes. The mixture was stirred for several minutes; then, the autoclave was vacuumed and ethylene was pressed in quickly, immediately the polymerization was initiated and was observed soon. The reaction pressure, the maxium flow rate of ethylene and the stirring rate were set up at 5.0 bar, 280 mg/min and 450 rpm, respectively. The catalytic polymerization was run for 30 min under 25 °C. After which time the pressure was vented and the polymerization was quenched with excess



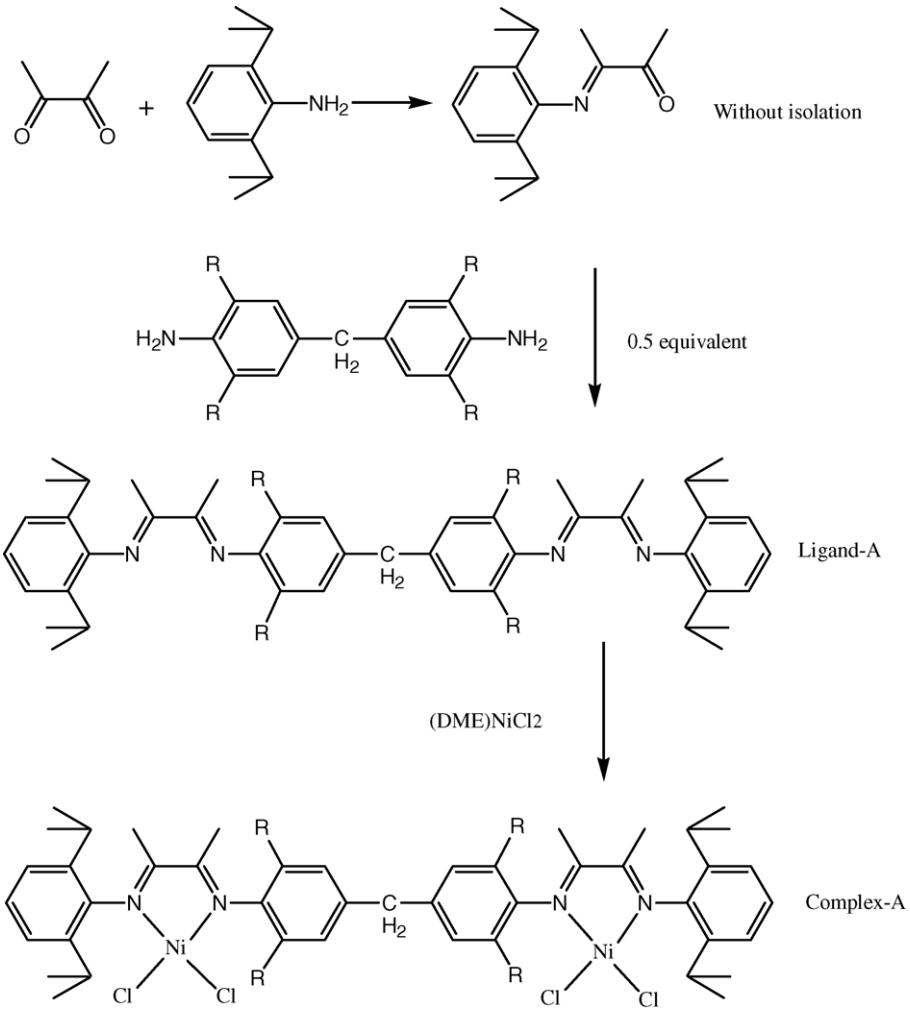
Scheme 1. Some reported nickel based catalysts for ethylene polymerization.

ethanol. The produced polymer was taken out by opening the autoclave, washed with diluted hydrochloric acid and then ethanol, and then dried in oven at 80 °C overnight. Finally, the polymer was weighed and the reaction rate was calculated in unit of g PE/(g Ni h).

2.3. Preparation of ligands and complexes

2.3.1. Preparation of ligand-A1

2, 6-Diisopropyl-C_6H_3–N=C(CH_3)–(CH_3)C=N–3,5-di-R–C_6H_2–CH_2–3′,5′-di-R–C_6H_2–N=C(CH_3)–(CH_3)C=N–2,6-diisopropyl-C_6H_3; R, –$CH(CH_3)_2$ (for the molecular structure, see Scheme 2). A 100 ml Schlenk flask was charged with 3.29 g (18.59 mmol) 2,6-diisopropylaniline, 1.60 g (18.59 mmol) 2,3-butanedione, 30 ml ethanol and 0.4 ml glacial acetic acid, the pale yellow solution was stirred for one day at room temperature. Then, 3.41 g (9.30 mmol) 4,4′-methylbis(2,6-diisopropylaniline) and more 30 ml ethanol was added. The final solution was stirred for one week at room temperature while yellow precipitate was produced. The yellow precipitate was isolated by filtration, washed with 2 × 10 ml ethanol, and dried in vacuum; 4.8 g yellow powder was obtained; yield, 63%. Anal. calculated for $C_{57}H_{80}N_4$ (%): C, 83.36; H, 9.82; N, 6.82. Found (%): C, 82.46; H, 10.10; N, 6.59. ^{1}H NMR ($CDCl_3$, δ): 1.23, 1.24, 1.26, 1.29 (–CH(C$\underline{H}_3$)$_2$), 2.15, 2.17 (–N=C(C$\underline{H}_3$)–C(C$\underline{H}_3$)=N–),



Ligand-A1, Complex-A1: R=$CH(CH_3)_2$

Ligand-A2, Complex-A2: R=CH_2CH_3

Ligand-A3, Complex-A3: R=CH_3

Scheme 2. The route for the preparation of ligand-A1–A3 and complex-A1–A3.

2.73, 2.77, 2.80, 2.83, 2.87 (–C<u>H</u>$(CH_3)_2$), 4.11 (–C=N–3,5-di-R–C_6H_2–C<u>H_2</u>–3′,5′-di-R–C_6H_2–N=C–), 7.09 (–C=N–3,5-di-R–C_6<u>H_2</u>–CH_2–3′,5′-di-R–C_6<u>H_2</u>–N=C–), 7.15–7.26 (2,6-diisopropyl–C_6<u>H_3</u>–N=C–). ^{13}C NMR ($CDCl_3$, δ): 16.53, 16.57 (–N=C(<u>C</u>H_3)–C(<u>C</u>H_3)=N–), 22.67, 22.79, 22.98, 23.06 (–CH(<u>C</u>H_3)$_2$), 28.48 (–<u>C</u>H$(CH_3)_2$), 41.42 (–C=N–3,5-di-R–C_6H_2–<u>C</u>H_2–3′,5′-di-R–C_6H_2–N=C–), 122.97, 123.16, 135.02, 146.18 (2,6-diisopropyl-<u>C</u>$_6$$H_3$–N=C–), 123.66, 134.97, 136.42, 144.02 (–C=N–3,5-di-R–<u>C</u>$_6$$H_2$–$CH_2$–3′,5′-di-R–<u>C</u>$_6$$H_2$–N=C–), 168.21, 168.45 (–N=<u>C</u>(CH_3)–<u>C</u>(CH_3)=N–).

2.3.2. Preparation of ligand-A2

2, 6-diisopropyl-C_6H_3–N=C(CH_3)–(CH_3)C=N–3, 5-di-R–C_6H_2–CH_2–3′,5′-di-R–C_6H_2–N=C(CH_3)–(CH_3)C=N–2,6-diisopropyl-C_6H_3; R, –CH_2CH_3 (for the molecular structure, see Scheme 2). The title compound was prepared by using the same procedure for the preparation of ligand-A1 by using 2.89 g (9.30 mmol) 4,4′-methylbis(2,6-diethylaniline) instead of 3.41 g 4,4′-methylbis(2,6-diisopropylaniline); 4.3 g yellow powder was obtained; yield, 61%. Anal. calculated for $C_{53}H_{72}N_4$ (%): C, 83.19; H, 9.48; N, 7.32. Found (%): C, 82.89; H,9.90; N, 7.30. ^{1}H NMR ($CDCl_3$, δ): 1.243, 1.256, 1.271 (–CH_2C<u>H</u>$_3$), 1.28, 1.29, 1.31, 1.33 (–CH(C<u>H</u>$_3$)$_2$), 2.17, 2.19 (–N=C(C<u>H</u>$_3$)–C(C<u>H</u>$_3$)=N–), 2.41, 2.45, 2.49, 2.52 (–C<u>H</u>$_2$$CH_3$), 2.74, 2.78, 2.82, 2.85, 2.89 (–C<u>H</u>$(CH_3)_2$), 4.01 (–C=N–3,5-di-R–C_6H_2–C<u>H</u>$_2$–3′,5′-di-R–C_6H_2–N=C–), 7.07 (–C=N–3,5-di-R–C_6<u>H</u>$_2$–CH_2–3′,5′-di-R–C_6<u>H</u>$_2$–N=C–), 7.15–7.24 (2,6-diisopropyl-C_6<u>H</u>$_3$–N=C–). ^{13}C NMR ($CDCl_3$, δ): 13.73 (–CH_2<u>C</u>H_3), 16.24, 16.52 (–N=C(<u>C</u>H_3)–C(<u>C</u>H_3)=N–), 22.67, 22.98 (–CH(<u>C</u>H_3)$_2$), 24.76 (–<u>C</u>H_2CH_3), 28.45 (–<u>C</u>H$(CH_3)_2$), 41.08 (–C=N–3,5-di-R–C_6H_2–<u>C</u>H_2–3′,5′-di-R–C_6H_2–N=C–), 122.94, 123.72, 134.99, 146.14 (2,6-diisopropyl-<u>C</u>$_6$$H_3$–N=C–), 126.79, 130.46, 136.49, 145.30 (–C=N–3, 5-di-R–<u>C</u>$_6$$H_2$–$CH_2$–3′, 5′ -di-R–<u>C</u>$_6$$H_2$–N=C–), 168.11, 168.16 (–N=<u>C</u>(CH_3)–<u>C</u>(CH_3)=N–).

2.3.3. Preparation of ligand-A3

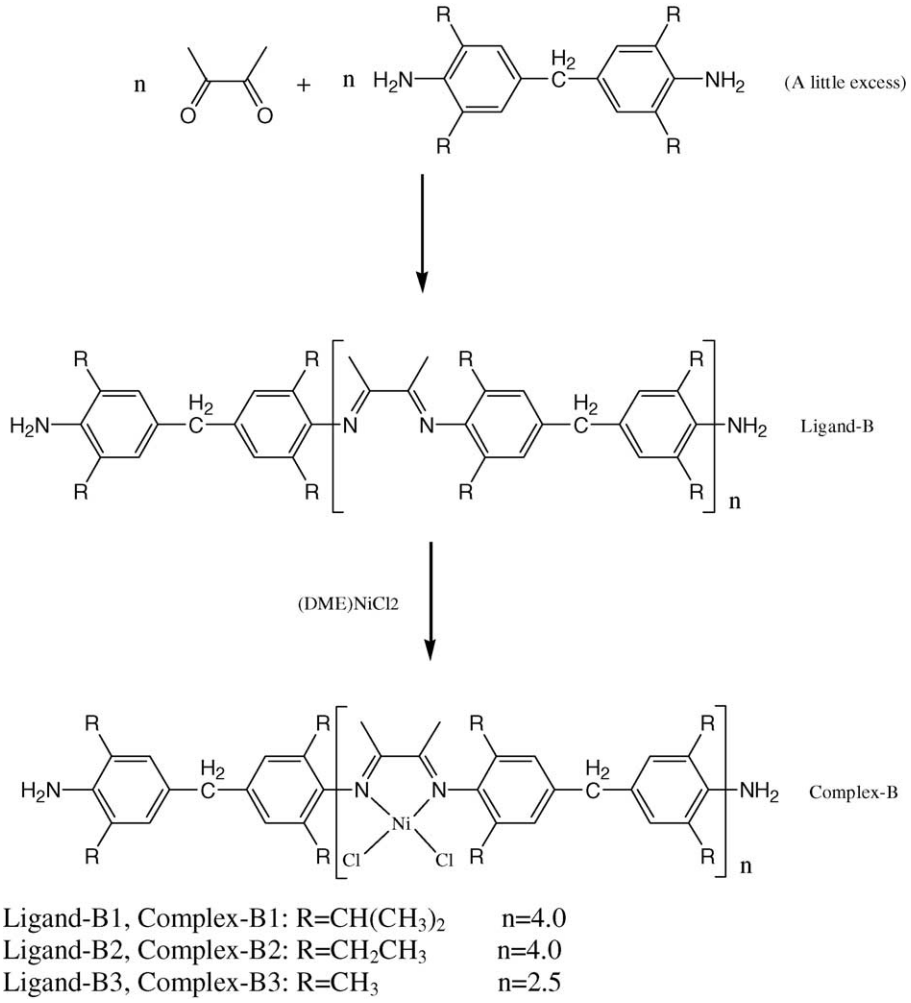
2, 6-Diisopropyl-C_6H_3–N=C(CH_3)–(CH_3)C=N–3, 5-di-R–C_6H_2–CH_2–3′,5′-di-R–C_6H_2–N=C(CH_3)–(CH_3)C=N–2,6-diisopropyl-C_6H_3; R, –CH_3 (for the molecular structure, see Scheme 2). The title compound was prepared by using the same procedure for the preparation of ligand-A1 by using 2.37 g (9.30 mmol) 4,4′-methylbis(2,6-dimethylaniline) instead of 3.41 g 4,4′-methylbis(2,6-diisopropylaniline); 2.24 g yellow powder was obtained; yield, 34%. Anal. calculated for $C_{49}H_{64}N_4$ (%): C, 83.00; H, 9.10; N, 7.90. Found (%): C, 82.52; H,9.44; N, 7.89. ^{1}H NMR ($CDCl_3$, δ): 1.22, 1.24, 1.26, 1.27 (–CH(C<u>H</u>$_3$)$_2$), 2.09 (–C=N–3,5-di-(C<u>H</u>$_3$)–C_6H_2–CH_2–3′,5′-di-(C<u>H</u>$_3$)–C_6H_2–N=C–), 2.13 (–N=C(C<u>H</u>$_3$)–C(C<u>H</u>$_3$)=N–), 2.74, 2.77, 2.79, 2.81, 2.84 (–C<u>H</u>$(CH_3)_2$), 3.93 (–C=N–3,5-di-R–C_6H_2–C<u>H</u>$_2$–3′,5′-di-R–C_6H_2–N=C–), 6.99 (–C=N–3,5-di-R–C_6<u>H</u>$_2$–CH_2–3′,5′-di-R–C_6<u>H</u>$_2$–N=C–), 7.11–7.24 (2,6-diisopropyl-C_6<u>H</u>$_3$–N=C–). ^{13}C NMR ($CDCl_3$, δ): 15.91, 16.45 (–N=C(<u>C</u>H_3)–C(<u>C</u>H_3)=N–), 17.79 (–C=N–3, 5-di-(<u>C</u>H_3)–C_6H_2–CH_2–3′, 5′ -di-(<u>C</u>H_3)–C_6H_2–N=C–), 22.67, 23.00 (–CH(<u>C</u>H_3)$_2$), 28.42 (–<u>C</u>H$(CH_3)_2$), 40.73 (–C=N–3, 5 -di-R–C_6H_2–<u>C</u>H_2–3′, 5′ -di-R–C_6H_2–N=C–), 122.95, 123.72, 135.00, 146.27 (2,6-diisopropyl-<u>C</u>$_6$$H_3$–N=C–), 124.59, 128.50, 136.32, 146.13 (–C=N–3,5-di-R–<u>C</u>$_6$$H_2$–$CH_2$–3′,5′-di-R–<u>C</u>$_6$$H_2$–N=C–), 168.00, 168.23 (–N=<u>C</u>(CH_3)–<u>C</u>(CH_3)=N–).

2.3.4. Preparation of ligand-B1

–[–N=C(CH_3)–(CH_3)C=N–3,5-di-R–C_6H_2–CH_2–3′,5′-di-R–C_6H_2-]$_n$–; R, –$CH(CH_3)_2$ (for the molecular structure, see Scheme 3). A 100 ml Schlenk flask was charged with 1.12 g (13.01 mmol) 2,3-butanedione, 5.25 g (14.32 mmol) 4,4′-methylbis(2,6-diisopropylaniline), 50 ml ethanol and 0.4 ml glacial acetic acid. The final mixture was stirred for one week at room temperature while yellow precipitate was produced. The yellow precipitate was isolated by filtration, washed with 3× 10 ml ethanol, and dried in vacuum; 5.29 g yellow powder was obtained; yield, 98%. Anal. calculated for repeating unit $C_{29}H_{40}N_2$ (%): C, 83.60; H, 9.68; N, 6.72. Found (%): C, 83.34; H, 10.78; N, 6.99. ^{1}H NMR ($CDCl_3$, δ): repeating unite: 1.18, 1.22 (–CH(C<u>H</u>$_3$)$_2$), 2.13 (–N=C(C<u>H</u>$_3$)–(C<u>H</u>$_3$)C=N–), 2.69, 2.72, 2.75, 2.79, 2.82 (–C<u>H</u>$(CH_3)_2$), 4.07 (–C=N–3,5-di-R–C_6H_2–C<u>H</u>$_2$–3′,5′-di-R–C_6H_2–), 7.05 (–C=N–3,5-di-R–C_6<u>H</u>$_2$–CH_2–3′,5′-di-R–C_6<u>H</u>$_2$–). End group: 1.30, 1.35 (–C=N–3,5-di-(($CH_3)_2$CH)–C_6H_2–CH_2–3′,5′-di-((CH_3)$_2$CH)–C_6H_2–NH_2), 2.90, 2.94, 2.98, 3.01, 3.04 (–C=N–3,5-di-(($CH_3)_2$CH)–C_6H_2–CH_2–3′,5′-di-(($CH_3)_2$C<u>H</u>)–C_6H_2–NH_2), 3.98 (–C=N–3,5-di-(($CH_3)_2$CH)–C_6H_2–C<u>H</u>$_2$–3′,5′-di-(($CH_3)_2$CH)–C_6H_2–NH_2), 6.92 (–C=N–3,5-di-(($CH_3)_2$CH)–C_6H_2–CH_2–3′, 5′ -di-(($CH_3)_2$CH)–C_6<u>H_2</u>–NH_2). ^{13}C NMR ($CDCl_3$, δ): repeating unite: 16.55 (–N=C(<u>C</u>H_3)–C(<u>C</u>H_3)=N–), 22.78, 23.04 (–CH(<u>C</u>H_3)$_2$), 27.93 (–<u>C</u>H$(CH_3)_2$), 41.40 (–C=N–3,5-di-R–C_6H_2–<u>C</u>H_2–3′,5′-di-R–C_6H_2–), 123.64, 134.97, 136.37, 144.03 (–C=N–3,5-di-R–<u>C</u>$_6$$H_2$–$CH_2$–3′,5′-di-R–<u>C</u>$_6$$H_2$–), 168.50 (–N=<u>C</u>$(CH_3)$–<u>C</u>$(CH_3)$=N–). End group: 22.51 (–C=N–3,5-di-(($CH_3)_2$CH)–C_6H_2–CH_2–3′,5′-di-(($\underline{C}H_3)_2$CH)–C_6H_2–NH_2), 27.84 (–C=N–3,5-di-(($CH_3)_2$CH)–C_6H_2–CH_2–3′,5′-di-(($CH_3)_2$<u>C</u>H)–C_6H_2–NH_2), 41.27 (–C=N–3,5-di-(($CH_3)_2$CH)–C_6H_2–<u>C</u>H_2–3′,5′-di-(($CH_3)_2$CH)–C_6H_2–NH_2), 123.16, 131.31, 132.52, 137.97 (–C=N–3,5-di-(($CH_3)_2$CH)–C_6H_2–CH_2– 3′, 5′ -di-(($CH_3)_2$CH)–<u>C</u>$_6$$H_2$–$NH_2$).

2.3.5. Preparation of ligand-B2

–[–N=C(CH_3)–(CH_3)C=N–3,5-di-R–C_6H_2–CH_2–3′,5′-di-R–C_6H_2-]$_n$–; R, –CH_2CH_3 (for the molecular structure, see Scheme 3). The title compound was prepared by using the same procedure for the preparation of ligand-B1 by using 1.07 g (12.43 mmol) 2,3-butanedione and 4.25 g (13.69 mmol) 4,4′-methylbis(2,6-diethylaniline); 3.57 g yellow powder was obtained; yield, 80%. Anal. calculated for repeating unit $C_{25}H_{32}N_2$(%): C, 83.29; H, 8.95; N, 7.77.

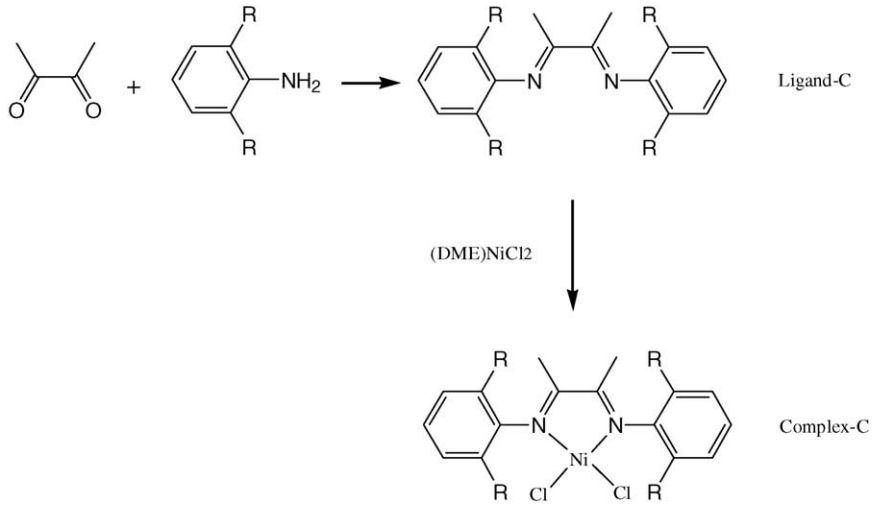


Scheme 3. The route for the preparation of ligand-B1–B3 and complex-B1–B3.

Found (%): C, 82.51; H, 9.51; N, 7.67. ^{1}H NMR ($CDCl_3$, δ): repeating unite: 1.21, 1.25, 1.28 (–$CH_2C\underline{H}_3$), 2.19 (–N=C($C\underline{H}_3$)–($C\underline{H}_3$)C=N–), 2.35, 2.45, 2.48, 2.56 (–$C\underline{H}_2CH_3$), 4.05 (–C=N–3,5-di-R–C_6H_2–$C\underline{H}_2$–3′,5′-di-R–C_6H_2–), 7.07 (–C=N–3,5-di-R–$C_6\underline{H}_2$–CH_2–3′,5′-di-R–$C_6\underline{H}_2$–). End group: 1.34, 1.38 (–C=N–3,5-di-(CH_3CH_2)–C_6H_2–CH_2–3′,5′-di-($C\underline{H}_3CH_2$)–C_6H_2–NH_2), 2.60, 2.63 (–C=N–3,5-di-(CH_3CH_2)–C_6H_2–CH_2–3′,5′-di-($CH_3C\underline{H}_2$)–C_6H_2–NH_2), 3.97 (–C=N–3,5-di-(CH_3CH_2)–C_6H_2–$C\underline{H}_2$–3′,5′-di-(CH_3CH_2)–C_6H_2–NH_2), 6.93 (–C=N–3,5-di-(CH_3CH_2)–C_6H_2–CH_2–3′,5′-di-(CH_3CH_2)–$C_6\underline{H}_2$–NH_2). ^{13}C NMR ($CDCl_3$, δ): repeating unite: 13.71 (–$CH_2\underline{C}H_3$), 16.13 (–N=C($\underline{C}H_3$)–C($\underline{C}H_3$)=N–), 24.72 (–$\underline{C}H_2(CH_3)$), 41.03 (–C=N–3,5-di-R–C_6H_2–$\underline{C}H_2$–3′,5′-di-R–C_6H_2–), 126.71, 130.41, 136.43, 145.28 (–C=N–3,5-di-R–$\underline{C}_6H_2$–CH_2–3′,5′-di-R–$\underline{C}_6H_2$–), 168.14 (–N=$\underline{C}(CH_3$)–$\underline{C}(CH_3$)=N–). End group: 13.11 (–C=N–3,5-di-(CH_3CH_2)–C_6H_2–CH_2–3′,5′-di-($\underline{C}H_3CH_2$)–C_6H_2–NH_2), 24.32(–C=N–3,5-di-(CH_3CH_2)–C_6H_2–CH_2–3′,5′-di-($CH_3\underline{C}H_2$)–C_6H_2–NH_2), 40.87 (–C=N–3,5-di-(CH_3CH_2)–C_6H_2–$\underline{C}H_2$–3′,5′-di-(CH_3CH_2)–C_6H_2–NH_2), 126.50, 127.71, 129.88, 139.38 (–C=N–3,5-di-(CH_3CH_2)–C_6H_2–CH_2–3′,5′-di-(CH_3CH_2)–$\underline{C}_6H_2$–NH_2).

2.3.6. Preparation of ligand-B3

–[–N=C(CH_3)–(CH_3)C=N–3,5-di-R–C_6H_2–CH_2–3′,5′-di-R–C_6H_2-]$_n$–; R, –CH_3 (for the molecular structure, see Scheme 3). The title compound was prepared by using the same procedure for the preparation of ligand-B1 by using 1.16 g (13.47 mmol) 2,3-butanedione and 3.77 g (14.82 mmol) 4,4′-methylbis(2,6-dimethylaniline); 3.60 g yellow powder was obtained; yield, 88%. Anal. calculated for repeating unit $C_{21}H_{24}N_2$ (%): C, 82.85; H, 7.95; N, 9.20. Found (%): C, 80.78; H, 7.46; N, 9.31. ^{1}H NMR ($CDCl_3$, δ): repeating unite: 2.13 (–C=N–3,5-di-($C\underline{H}_3$)–C_6H_2–CH_2–3′,5′-di-($C\underline{H}_3$)–C_6H_2–), 2.24 (–N=C($C\underline{H}_3$)–($C\underline{H}_3$)–C=N–), 3.96 (–C=N–3,5-di-R–C_6H_2–$C\underline{H}_2$–3′,5′-di-R–C_6H_2–), 7.03 (–C=N–3,5-di-R–$C_6\underline{H}_2$–CH_2–3′,5′-di-R–$C_6\underline{H}_2$–). End group: 2.17 (–C=N–3,5-di-(CH_3)–C_6H_2–CH_2–3′,5′-di-($C\underline{H}_3$)–C_6H_2–NH_2), 3.88 (–C=N–3,5-di-



Ligand-C1, Complex-C1: R=$CH(CH_3)_2$
Ligand-C2, Complex-C2: R=CH_2CH_3
Ligand-C3, Complex-C3: R=CH_3

Scheme 4. The route for the preparation of ligand-C1–C3 and complex-C1–C3.

(CH_3)–C_6H_2–$C\underline{H}_2$–3′,5′-di-(CH_3)–C_6H_2–NH_2), 6.90 (–C=N–3,5-di-(CH_3)–C_6H_2–CH_2–3′,5′-di-(CH_3)–$C_6\underline{H}_2$–NH_2). ^{13}C NMR ($CDCl_3$, δ): repeating unite: 15.76 (–N=C($\underline{C}H_3$)–C($\underline{C}H_3$)=N–), 17.73 (–C=N–3,5-di-($\underline{C}H_3$)–C_6H_2–CH_2–3′,5′-di-($\underline{C}H_3$)–C_6H_2–), 40.61 (–C=N–3,5-di-(CH_3)–C_6H_2–$\underline{C}H_2$–3′,5′-di-(CH_3)–C_6H_2–), 124.52, 128.39, 136.22, 146.24 (–C=N–3,5-di-(CH_3)–$\underline{C}_6H_2$–CH_2–3′,5′-di-(CH_3)–$\underline{C}_6H_2$–), 168.09 (–N=$\underline{C}$(CH_3)–$\underline{C}$(CH_3)=N–). End group: 17.51 (–C=N–3,5-di-(CH_3)–C_6H_2–CH_2–3′,5′-di-($\underline{C}H_3$)–C_6H_2–NH_2), 40.32 (–C=N–3, 5-di-(CH_3)–C_6H_2–$\underline{C}H_2$–3′, 5′ -di-(CH_3)–C_6H_2–NH_2), 121.63, 128.58, 130.97, 140.55 (–C=N–3,5-di-(CH_3)–C_6H_2–CH_2–3′,5′-di-(CH_3)–$\underline{C}_6H_2$–NH_2).

Ligand-C1–C3 were prepared accoding to literature [44], see Scheme 4.

2.3.7. Preparation of complex-A1

{[2,6-Diisopropyl-C_6H_3–N=C(CH_3)–(CH_3)C=N–3,5-di-R–C_6H_2–CH_2–3′, 5′ -di-R–C_6H_2–N=C(CH_3)–(CH_3)-C=N–2,6-diisopropyl-C_6H_3][$NiCl_2$]$_2$; R, –$CH(CH_3)_2$} (for the molecular structure, see Scheme 2). A 50 ml Schlenk flask was charged with 0.55 g (2.50 mmol) (DME)$NiCl_2$, to which a solution of 1.07 g (1.30 mmol) ligand-A1 in 30 ml dichloromethane was added under stirring. The resulting red/brown mixture was stirred under room temperature over night. After which time the mixture was filtrated to give a clear red/brown solution which gave a red/brown solid by removing the solvent dichloromethane under reduced pressure. The red/brown solid product was washed with 3× 10 ml hexane, then dried in vacuum; 1.30 g product was obtained; yield, 92%. Anal. calculated for $C_{57}H_{80}N_4Ni_2Cl_4$ (%): C, 63.36; H, 7.46; N, 5.19. Found (%): C, 61.78; H, 7.47; N, 5.04.

2.3.8. Preparation of complex-A2

{[2,6-Diisopropyl-C_6H_3–N=C(CH_3)–(CH_3)C=N–3,5-di-R–C_6H_2–CH_2–3′, 5′ -di-R–C_6H_2–N=C(CH_3)–(CH_3)-C=N–2,6-diisopropyl-C_6H_3][$NiCl_2$]$_2$; R, –CH_2CH_3} (for the molecular structure, see Scheme 2). The title compound was prepared with the same procedure for the preparation of complex-A1 by using 1.13 g (5.14 mmol) (DME)$NiCl_2$ and 1.98 g (2.59 mmol) ligand-A2; 2.06 g red/brown solid product was obtained; yield, 78%. Anal. calculated for $C_{53}H_{72}N_4$ Ni_2Cl_4 (%): C, 62.14; H, 7.08; N, 5.47. Found (%): C, 60.38; H, 7.51; N, 5.46.

2.3.9. Preparation of complex-A3

{[2,6-Diisopropyl-C_6H_3–N=C(CH_3)–(CH_3)C=N–3,5-di-R–C_6H_2–CH_2–3′,5′-di-R–C_6H_2–N=C(CH_3)–(CH_3)-C=N–2,6-diisopropyl-C_6H_3][$NiCl_2$]$_2$; R, –CH_3} (for the molecular structure, see Scheme 2). The title compound was prepared with the same procedure for the preparation of complex-A1 by using 0.85 g (3.87 mmol) (DME)$NiCl_2$ and 1.38 g (1.95 mmol) ligand-A3; 1.26 g red/brown solid product was obtained; yield, 67%. Anal. calculated for $C_{49}H_{64}N_4Ni_2Cl_4$ (%): C, 60.78; H, 6.66; N, 5.79. Found (%): C, 59.73; H, 7.09; N, 5.39.

2.3.10. Preparation of complex-B1

{–[(–N=C(CH_3)–(CH_3)C=N–3, 5 -di-R–C_6H_2–CH_2–3′,5′-di-R–C_6H_2–)$NiCl_2$]$_n$–; R, –$CH(CH_3)_2$} (for the molecular structure, see Scheme 3). The title compound was prepared with the same procedure for the preparation of complex-A1 by using 0.62 g (2.82 mmol) (DME)$NiCl_2$ and 1.19 g (2.86 mmol repeating unit) ligand-B1; 1.04 g red/brown solid product was obtained; yield, 66%. Anal. calculated for repeating unit $C_{29}H_{40}N_2NiCl_2$ (%): C,

63.76; H, 7.38; N, 5.13. Found (%): C, 62.76; H, 8.21; N, 5.03.

2.3.11. Preparation of complex-B2

{–[(–N=C(CH_3)–(CH_3)C=N–3,5-di-R–C_6H_2–CH_2–3′,5′-di-R–C_6H_2–)$NiCl_2$]$_n$–; R, –CH_2CH_3} (for the molecular structure, see Scheme 3). The title compound was prepared with the same procedure for the preparation of complex-A1 by using 0.87 g (3.96 mmol) (DME)$NiCl_2$ and 1.44 g (3.99 mmol repeating unit) ligand-B2; 0.91g red/brown solid product was obtained; yield, 46%. Anal. calculated for repeating unit $C_{25}H_{32}N_2NiCl_2$ (%): C, 61.26; H, 6.58; N, 5.72. Found (%): C, 60.21; H, 7.18; N, 5.81.

2.3.12. Preparation of complex-B3

{–[(–N=C(CH_3)–(CH_3)C=N–3,5-di-R–C_6H_2–CH_2–3′,5′-di-R–C_6H_2–)$NiCl_2$]$_n$–; R, –CH_3} (for the molecular structure, see Scheme 3). The title compound was prepared with the same procedure for the preparation of complex-A1 by using 1.23 g (5.60 mmol) (DME)$NiCl_2$ and 1.73 g (5.68 mmol repeating unit) ligand-B3; 0.35 g red/brown solid product was obtained; yield, 14%. Anal. calculated for repeating unit $C_{21}H_{24}N_2NiCl_2$ (%): C, 58.11; H, 5.57; N, 6.45. Found (%): C, 54.73; H, 5.54; N, 6.07.

Complex-C1–C3 were prepared accoding to literature [11], see Scheme 4.

3. Results and discussions

3.1. Synthesis of new ligands and complexes

The aim of this paper is to develop a convenient and practical method to prepare new highly active α-diimine/nickel catalysts to regulate the catalytic performances for ethylene polymerization. The basic idea is to utilize substituted bis-anline instead of half or all the substituted anline to prepare new ligands and corresponding complexes. By this way, the molecular structures of the new catalysts were modified, in particular, the distance between every two active centres was controlled for bi-nickel-centre catalysts, in a similar way, the distances among several active centres were controlled for multi-nickel-centre catalysts, resulting in the micro chemical environment of nickel centre being regulated. This structural regulation may strongly influence the catalytic performances, such as catalytic activity. Under the guide of this basic idea, two kinds of new catalysts including bi-nickel-centre catalysts {[2,6-diisopropyl-C_6H_3–N=C(CH_3)–(CH_3)C=N–3,5-di-R–C_6H_2–CH_2–3′,5′-di-R–C_6H_2–N=C(CH_3)–(CH_3)C=N–2,6-diisopropyl-C_6H_3][$NiCl_2$]$_2$; R, –$CH(CH_3)_2$, –CH_2CH_3, –CH_3} and multi-nickel-centre catalysts {–[(–N=C(CH_3)–(CH_3)C=N–3,5-di-R–C_6H_2–CH_2–3′,5′-di-R–C_6H_2–)$NiCl_2$]$_n$–; R, –$CH(CH_3)_2$, n = 4.0; R, –CH_2CH_3, n = 4.0; R, –CH_3, n = 2.5}, were prepared and studied for catalytic ethylene polymerization in toluene using MAO as cocatalyst.

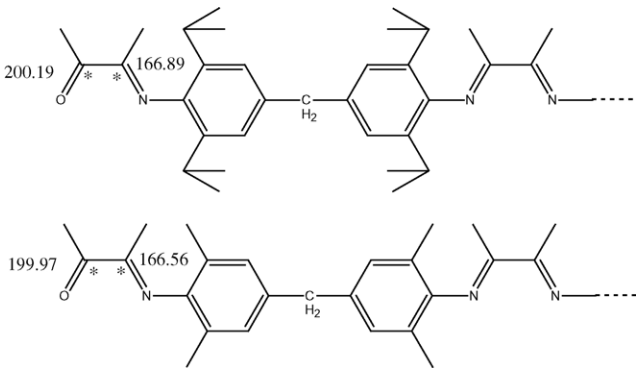
New ligands were synthesized by Schiff-base condensation using a little glacial acetic acid as promoter in ethanol. Ligands A1–A3 were synthesized by first condensation of 2,3-butanedione with one equivalent 2,6-diisopropylaniline to give an intermediate 3-(2,6-diisopropylphenylimino)-2-butanone [45], without isolation which were then condensed with 0.5 equivalent of substituted bis-aniline 4,4′-methylbis(2,6-diisopropylaniline), 4,4′-methylbis(2,6-diethylaniline) or 4,4′-methylbis(2,6-dimethylaniline), respectively, see Scheme 2; ligands B1–B3 were synthesized straightforward by condensation of 2,3-butanedione with one equivalent substituted bis-aniline 4,4′-methylbis(2,6-diisopropylaniline), 4,4′-methylbis(2,6-diethylaniline) or 4,4′-methylbis(2,6-dimethylaniline), respectively, see Scheme 3. Once the ligands were obtained, the corresponding complexes can be prepared conveniently according to a literature method [11].

In the preparation of ligands B1–B3, a little excess (10%) of substituted bis-anilines were used to make the main end groups of the obtained ligand to be aniline-type end group (see Scheme 3). ^{13}C NMR showed that, when the substituted bis-aniline was 4,4′-methylbis(2,6-diethylaniline), only aniline-type end groups were found; but when the substituted bis-aniline was 4,4′-methylbis(2,6-diisopropylaniline) or 4,4′-methylbis(2,6-dimethylaniline), besides aniline-type end groups, a little amount of ketone-type end groups were found (see Scheme 5). The number of the repeating unit can be calculated from ^1H NMR integration of –CH_2– group in –C=N–3,5-di-R–C_6H_2–C$\underline{H_2}$–3′,5′-di-R–C_6H_2–. In ligands B1–B3, n is 4.0, 4.0 and 2.5, respectively.

3.2. Catalytic studies for ethylene polymerization

The catalytic evaluation of new catalysts was carried out in toluene using MAO as cocatalyst. Comparative studies were also performed with mono-nickel-centre catalysts. The results were shown in Table 1.

The results showed that the catalytic activity varied significantly for catalysts of different kinds and for the same



Scheme 5. Ketone-type end groups in ligand-B1 (the first) and ligand-B3 (the second). (*) ^{13}C NMR data.

Table 1
Catalytic results of new catalysts for ethylene polymerization

Entry	Complex	Yield (g)	Activity (g/gNi h)	Colour			Polymerization status
				1	2	3	
1	A1	9.2	1840	Orange	Green	Green	Gooey
2	A2	8.3	1660	Orange	Green	Green	Gooey
3	A3	13.1	2620	Orange	Green	Green	Slurry
4	B1	6.7	1340	Orange	Pale green	Pale green	Gooey
5	B2	16.1	3220	Orange	Pale green	Pale green	Slurry
6	B3	12.4	2480	Orange	Pale green	Pale green	Slurry
7	C1	3.5	700	Yellow	Green	From green to pale white	Gooey
8	C2	7.1	1420	Yellow	Green	Green	Solution[a]
9	C3	16.7	3320	Yellow	Pale yellow	From pale yellow to orange	Solution[a]

Reaction conditions: 1 l glass autoclave, 150 ml toluene as solvent, 0.01 mmol Ni in 5 ml dichloromethane, 3.3 ml MAO as co-catalyst; stirring rate, 400/min; 25 °C; set point of ethylene pressure, 5.0 bar; maximum flow of ethylene, 280 mg/min; polymerization for 30 min. (1) Solution of precatalyst in dichloromethane (0.002 mmol Ni/ml); (2) after combination with MAO; (3) during polymerization.

[a] Polyethylene precipitated out after the polymerization was quenched with excess ethanol. But for A1–A3 and B1–B3 complexes, polyethylene precipitated out quickly during the polymerization.

kind catalyst with different substitutes. Among bi-nickel-centre catalysts, the highest activity was achieved when the substitute is methyl. Amongst multi-nickel-centre catalysts, the highest activity was achieved when the substitute is ethyl; Among mono-nickel-centre catalysts, the highest activity was achieved when the substitute is methyl. Comparing the new catalysts, including bi-nickel-centre catalysts and multi-nickel-centre catalysts, with mono-nickel-centre catalysts, it could be found that both bi-nickel-centre catalysts and multi-nickel-centre catalysts demonstrated much higher catalytic activity for ethylene polymerization when the substitute was isopropyl or ethyl; but when the substitute was methyl, the new catalysts demonstrated lower catalytic activity than mono-nickel catalysts. The most active new catalyst was multi-nickel-centre catalyst with ethyl as substitute with the catalytic activity high up to 3220 gPE/(gNi h) (run no. 5), which is comparable with the highest catalytic activity 3320 g/(gNi h) (run no. 9) of mono-nickel-centre catalyst with methyl as substitute under the same reaction conditions. Furthermore, the polymerization status could be observed clearly because the reactor is transparent glass autoclave. The results showed that the polymerization status was quite different for different kind of catalyst and for the same kind catalyst with different substitutes, see Table 1. For run nos. 3, 5, 6, the polymerization system is slurry; for run nos. 1, 2, 4, 7, the polymerization system is gooey; For run nos. 8 and 9, the polymerization system is solution, polyethylene emerged after the reaction was quenched with excess ethanol.

The prime difference between new catalysts and mono-nickel-centre catalysts is that the new catalysts have much bigger molecules than the mono-nickel-centre catalysts. Particularly, the distance between every two nickel centres was controlled for bi-nickel-centre catalysts, and the distances among several nickel centres were controlled for multi-nickel-centre catalysts. The experimental results in Table 1 clearly showed that this structural difference resulted in significant influence on catalytic activity for ethylene polymerization. Therefore, highly active bi- and multi-nuclear di-imine/nickel catalysts for ethylene polymerization, were developed successfully.

It has been proved that the scale of the substituted aryl group is one of the key factors of Ni(II) catalyst by reducing the competitive β-H elimination [11]. Comparing with the mono-nickel-centre catalysts, in bi-nickel-centre catalysts, it can be considered that one of the two phenyl rings around each nickel centre was introduced a bulky group at para position; In multi-nickel-centre catalysts, it can be considered that each of the two phenyl rings around each nickel centre was introduced a bulky group at para position. Although generally bulky substitutes at ortho positions of the phenyl rings have great influence on catalytic activity [11], these bulky substitutes at para positions could also have influence on catalytic activity by affecting the competitive β-H elimination in some extent. On the other hand, these bulky substitutes at para positions could also make the phenyl ring more electron-enriched, and therefore, they could slightly affect the coordination between chelating atom (N) and nickel centre, and probably they could make the coordination bond a little stronger, through which the catalytic performances, such as catalytic activity could be regulated. This might be the reason why the bi-nickel-centre catalysts, the multi-nickel-centre catalysts and the mono-nickel-centre catalysts demonstrated different catalytic activity even if the substitutes were the same.

4. Conclusions

A convenient method was developed to prepare new α-diimine/nickel catalysts using substituted bis-aniline. Thus two kinds of new catalysts, including bi-nickel-centre catalysts {[2,6-diisopropyl-C_6H_3–N=C(CH_3)–(CH_3)C=N–3, 5′-di-R–C_6H_2–CH_2–3′, 5′-di-R–C_6H_2–N=C(CH_3)–(CH_3)C=N–2,6-diisopropyl-C_6H_3][$NiCl_2$]$_2$; R, –CH(CH_3)$_2$, –CH_2CH_3, –CH_3} and multi-nickel-centre catalysts {–[(–N=C(CH_3)–(CH_3)C=N–3,5-di-R–C_6H_2–CH_2–3′,5′-

di-R–C_6H_2–)$NiCl_2$]$_n$–; R, –$CH(CH_3)_2$, $n = 4.0$; R, –CH_2CH_3, $n = 4.0$; R, –CH_3, $n = 2.5$}, were prepared. The catalytic studies showed the new catalysts had highly catalytic activity for ethylene polymerization. Comparing with mono-nickel-centre catalysts, the new catalysts demonstrated much higher catalytic activity when the substitute was isopropyl or ethyl; But when the substitute was methyl, the new catalysts demonstrated lower catalytic activity than mono-nickel-centre catalysts. The most active new catalyst was multi-nickel-centre catalyst with ethyl as substitute, which catalytic activity was high up to 3220 gPE/(gNi h) at 25 °C with Al(MAO)/Ni ratio at 500.

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