



2,6-Dibenzhydryl-*N*-(2-phenyliminoacenaphthylidene)-4-chloroaniline nickel dihalides: Synthesis, characterization and ethylene polymerization for polyethylenes with high molecular weights

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ARTICLE INFO

Article history:

Received 24 August 2012

Received in revised form

5 December 2012

Accepted 6 December 2012

Dedicated to Prof. Dr. Joachim W. Heinicke on the occasion of his 65th birthday.

Keywords:

α -Diimine nickel complex

Polymerization

High molecular weight

High branching

Theoretical calculations

ABSTRACT

A series of 2,6-dibenzhydryl-*N*-(2-phenyliminoacenaphthylidene)-4-chloroanilines (**L1–L5**) and their nickel halide complexes LNiX_2 ($X = \text{Br}$, **C1–C5**; $X = \text{Cl}$, **C6–C10**) were synthesized. All organic compounds were characterized by FT-IR and NMR spectroscopy and elemental analysis. The nickel complexes were characterized by FT-IR spectroscopy, elemental analysis and their structures were determined by single-crystal X-ray diffraction. Upon activation with MAO, all of these nickel complexes showed high activities (up to 10^7 g of PE ($\text{mol of Ni}^{-1} \text{ h}^{-1}$) for ethylene polymerization. The resulting polyethylenes possess high molecular weights (M_w up to 10^6 g mol^{-1}) and feature high degrees of branching. The MM-QEq method was employed to assess the ligands' effects on catalytic activities. The results show that higher net charges on the nickel core correlate directly with higher measured activities.

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1. Introduction

In 1995, it was discovered that α -diimino metal halides of Ni(II) and Pd(II) are highly active pre-catalysts for ethylene polymerization [1–3]. It is the significant feature of these catalysts that the sterically bulky ligands prevent the β -elimination chain termination leading to oligomers [4]. Such pre-catalysts with bidentate ligands of the types N'N [5–14], N'O [15–20], N'P [21–27], P'O [28–31], and also with tridentate ligands of the types N'N'N [32–40], N'N'O [8,41,42], and N'P'N [43,44] have since been extensively explored in ethylene polymerization, and some of them have been employed in co-polymerization with functional co-monomers [45,46]. The cationic α -diimino nickel systems have been attractive because of the easy variability of the ligands by the substitution pattern of

the parent ligand [47] and the unique properties of the resulting polyethylenes [48]. Moreover, adaptations of the reaction parameters not only change the catalytic activities but also significantly affect the microstructures of the resulting polymers [49–51]. Furthermore, extensive studies have explored ligands with modified back-bones [52–54] or different chelating atoms [55–58]. Among the studies of nickel pre-catalysts bearing α -diimine ligands, only a few papers employed unsymmetrical α -diimine ligands [59]. With the use of unsymmetrical α -diimine ligands, it is thought that one bulky *N*-imine prevents the β -elimination chain termination and that the other *N*-imine is helpful to produce highly branched polyethylene. For example, the use of 2,6-dibenzhydryl-4-methylaniline as one of the anilines in the formation of unsymmetrical α -diimine ligands produced diimino nickel bromides with one of the highest activities amongst reported diimino nickel halide pre-catalysts and produced highly branched polyethylene [60]. Pre-catalysts bearing ligands formed with the isomeric 2,4-dibenzhydryl-*N*-(2-aryliminoacenaphthylidene)-6-methylaniline also were successful [61].

In this paper we explore the effects of the replacement of the 4-methyl group of 2,6-dibenzhydryl-4-methylaniline by chlorine to

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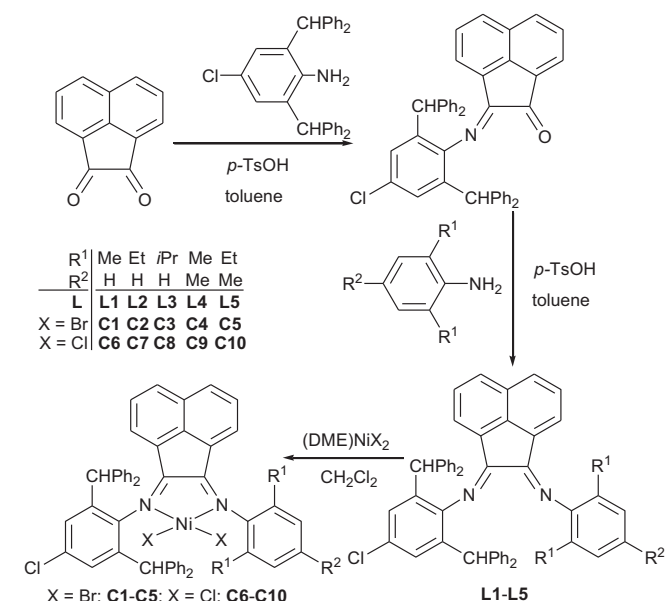
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further probe the relationship between the structures of the ligands and the catalytic activities of their complex pre-catalysts. Thus, the new α -diimines **L1–L5**, derivatives of 2,6-dibenzhydryl-*N*-(2-aryliminoacenaphthylidene)-4-chloroaniline, have been prepared and have been employed to synthesize the nickel halide complexes **C1–C10** (Scheme 1). Upon activation by the MAO co-catalyst, all nickel complexes were found to exhibit high activity for ethylene polymerization and to produce polyethylenes with high molecular weights and narrow polydispersity. Calculations by the metal atom net charge correlation (MANCC) method [62–65] are successfully employed to correlate the nature of the organic ligands and the catalytic activities of their corresponding complex pre-catalysts.

2. Results and discussion

2.1. Synthesis and characterization of diimines **L1–L5** and of their nickel complexes **C1–C10**

The syntheses of 2,6-dibenzhydryl-*N*-(2-aryliminoacenaphthylidene)-4-chloroaniline derivatives **L1–L5** and of their nickel halide complexes **C1–C10** are outlined in Scheme 1. The reaction of acenaphthylene-1,2-dione and 2,6-dibenzhydryl-4-chloroaniline produced 2-(2,6-dibenzhydryl-4-chlorophenylimino)acenaphthylone, which was further reacted with various anilines to afford the unsymmetrical α -diimines **L1–L5**. All organic compounds were well characterized by FT-IR and NMR spectroscopy and their elemental analyses were consistent with their formulas. Compounds **L1–L5** reacted with (DME)NiBr₂ or (DME)NiCl₂, respectively, in dichloromethane to form their corresponding bromide **C1–C5** or chloride **C6–C10** complexes, respectively. The complexes were identified by IR spectroscopy and elemental analysis. In their IR spectra, a band in the range 1580–1590 cm⁻¹ can be ascribed to the stretching vibration of C=N. As compared to the corresponding free ligand, the IR spectra of all compounds show a red shift of ν (C=N) by ca. 50–60 cm⁻¹, which reflects the coordination of the imine nitrogen atoms to the nickel atom. Furthermore, the structures of **C1**, **C3** and **C6** were determined by single-crystal X-ray diffraction analysis.



Scheme 1. Synthesis of ligands **L1–L5** and of their nickel complexes **C1–C10**.

2.2. X-ray crystallographic studies

Single crystals of **C1**, **C3** and **C6** suitable for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into dichloromethane solutions. The solid-state structures of **C1**, **C3** and **C6** are shown in Figs. 1–3 and selected bond lengths and bond angles are provided in Table 1. Their molecular structures indicate distorted tetrahedral coordination of nickel and this is consistent with the structures of the 4-methyl analogs reported previously [60]. As an example, we discuss the crystal structure of **C1**. In **C1**, the atoms N1, N2 and Br2 form the basal plane, the apical position is occupied by atom Br1, and the Ni atom is placed 0.941 Å above the basal plane. The Ni–Br bond lengths are 2.350(7) Å (Ni–Br1) and 2.342(8) Å (Ni–Br2) and are quite similar. On the other hand, the Ni–N bond lengths of 2.048(3) Å (Ni–N1) and 2.010(3) Å (Ni–N2) differ slightly more and this reflects the different steric demand of the two aryl groups linked to the coordinating N atoms. The C=N bonds have bond lengths of d (N1–C12) = 1.283(5) Å and d (N2–C1) = 1.280(5) Å, respectively. The best planes of the two arenes linked to the imine-*N* atoms are nearly perpendicular with respect to the plane of the acenaphthylene; with dihedral angles of 87.63° for the arene at N2 (contains C45–C50) and of 87.53° for the arene at N1 (contains C13–C18).

2.3. Ethylene polymerization

Complex **C4** was screened under 10 atm ethylene with various alkylaluminum reagents as co-catalysts (Table 2) including methylaluminumoxane (MAO), modified methylaluminumoxane (MMAO), diethylaluminum chloride (AlEt₂Cl), and ethylaluminum sesquichloride (EASC). The best performance was observed with co-catalyst MAO (Entry 1 in Table 2). The polyethylene with highest molecular weight was obtained with MMAO (Entry 2 in Table 2). Seeking primarily high activities, MAO was used as activator in further optimizations of the reaction parameters.

On variation of the Al/Ni ratios from 2000 to 3500 at 20 °C (entries 1–4 in Table 3), the optimum activity of 1.10×10^7 g PE (mol Ni)⁻¹ h⁻¹ was observed with the Al/Ni ratio of 3000 and producing polyethylene with a relatively higher molecular weight. This phenomenon is consistent with observations of its analogs [60,61]. When reaction temperatures were varied within the range from 20 °C to 60 °C (entries 3, 5–7 in Table 3) with the Al/Ni ratio of 3000

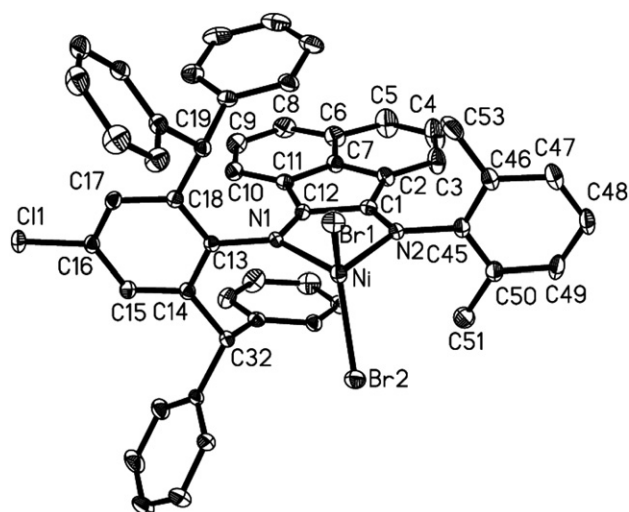


Fig. 1. ORTEP drawing of **C1**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.

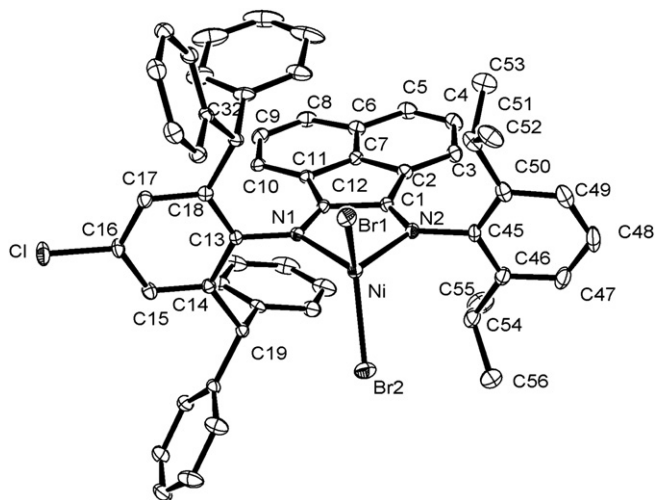


Fig. 2. ORTEP drawing of **C3**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.

under 10 atm ethylene, the catalytic activities decreased significantly and the resulting polyethylenes showed lower molecular weights. This observation also agrees with previous observations of α -diimino nickel analogs [49,60,61], and is ascribed to lower solubility of ethylene and higher chain termination at the elevated temperature. With lower pressure of ethylene (entries 3, 8, 9 in Table 3), reduced activities were observed due to lower concentration of ethylene monomer. With regard to the lifetime of active species (entries 3, 10–12 in Table 3), slight deactivations were observed which probably were caused by impurities in the ethylene source and the limitation of mass transfer due to the formation of insoluble polyethylene.

To assess any branching of the obtained PE samples, their IR spectra were recorded on a Perkin–Elmer System 2000 FT-IR spectrometer for samples with 0.2–0.6 mm thick membranes. The analysis of the spectra [66] indicated branched polyethylenes with over 40 branches for every 1000 carbons. For the polyethylene with a low molecular weight (Entry 7 in Table 3), the ^{13}C NMR measurement [67] (Fig. 4) shows branching of 98 branches/1000C and this result agrees closely with the IR analysis. Our measurements corroborate and agree with other reports of

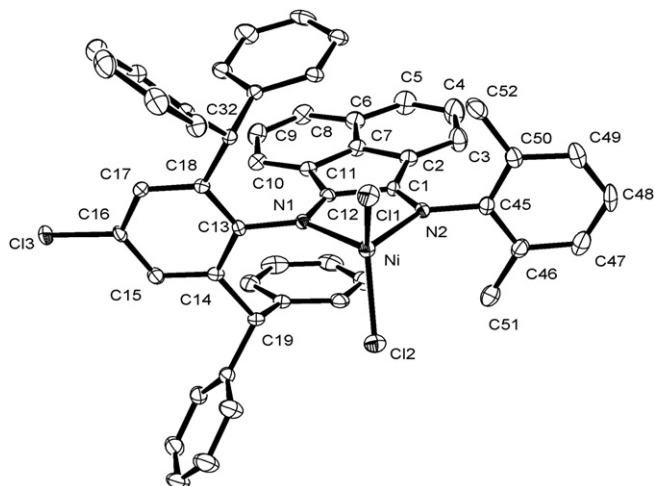


Fig. 3. ORTEP drawing of **C6**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for complexes **C1**, **C3** and **C6**.

X	C1	C3	C6
	Br	Br	Cl
<i>Bond lengths (Å)</i>			
Ni–X(1)	2.350(7)	2.351(8)	2.209(13)
Ni–X(2)	2.342(8)	2.325(10)	2.216(13)
Ni–N(1)	2.048(3)	2.037(3)	2.049(3)
Ni–N(2)	2.010(3)	2.015(3)	2.015(9)
N(1)–C(12)	1.283(5)	1.293(4)	1.291(5)
N(1)–C(13)	1.446(5)	1.437(4)	1.451(5)
N(2)–C(1)	1.280(5)	1.282(4)	1.282(5)
N(2)–C(45)	1.451(5)	1.450(4)	1.442(5)
Cl(1)–C(16)	1.738(4)	1.740(3)	1.745(4)
<i>Bond angles (°)</i>			
N(2)–Ni–N(1)	83.16(12)	82.89(12)	83.27(14)
X(2)–Ni–X(1)	122.41(3)	124.72(3)	124.92(5)
N(1)–Ni–X(2)	113.66(8)	115.11(8)	112.26(11)
N(1)–Ni–X(1)	111.65(9)	106.61(8)	110.18(10)
N(2)–Ni–X(1)	111.60(9)	109.91(8)	112.06(10)
N(2)–Ni–X(2)	107.34(9)	109.75(9)	106.31(11)

the formation of branched polyethylenes by active nickel species through β -hydrogen migration [48,51,60,61].

To understand the influence of the nature of ligands on the catalytic behavior of their nickel complexes, all bromide complexes were employed for ethylene polymerization under the same reaction conditions with an Al/Ni molar ratio of 3000, at 20 °C and under 10 atm ethylene pressure (entries 3, 13–16 in Table 3). The current classes of pre-catalysts showed relatively higher activities in comparison to the catalytic behavior of their 4-methyl analogs [60]. The activities were highest for **C4** (with 2,4,6-trimethylphenylamino-) and the activity decreased in the order **C4** > **C1** (with 2,6-dimethylphenylamino-) > **C5** (with 2,6-diethyl-4-methylphenylamino-) > **C2** (with 2,6-diethylphenyl-amino-) > **C3** (with 2,6-diisopropylphenylamino-). This ordering is consistent with the observations that low steric demand of the *ortho*-substituent and of the methyl substituent in the *para*-position enhance the catalytic activities of their pre-catalysts [60,68–70]. Pre-catalysts with bulky R^1 substituents result in polyethylenes with higher molecular weights but with near constant polydispersity. This observation indicates that the bulky ligands hinder the chain termination during the polymerization and produce polyethylenes with higher molecular weights.

As for the chloride complexes, the optimization of the catalytic parameters was tried with complex **C9**, the chloride analog of the bromide complex **C4** (entries 1–6 in Table 4). The results indicate that the chloride pre-catalyst required a smaller amount of co-catalyst MAO. The assessment of the influence of the nature of ligands on the catalytic behavior was repeated with all of the chloride complex pre-catalysts.

Comparison of the two data sets obtained for bromide and chloride complexes showed no significant effect of the nature of the halide on the catalytic activities under the optimal conditions.

Table 2
Ethylene polymerization by pre-catalyst **C4** with various co-catalysts^a.

Entry	Co-cat.	Al/Ni	T/°C	Activity ^b	$T_m^c/^\circ\text{C}$	$M_w^d/10^5 \text{ g mol}^{-1}$	M_w/M_n^d
1	MAO	3000	20	11.0	94.6	6.33	2.9
2	MMAO	3000	20	2.71	93.0	18.6	2.7
3	Et_2AlCl	600	20	4.07	89.8	3.23	2.2
4	EASC	600	20	3.10	90.4	2.37	2.2

^a Conditions: 1.5 μmol of **C4** 30 min; 10 atm of ethylene; total volume 100 mL.

^b $10^6 \text{ g of PE (mol of Ni)}^{-1} \text{ h}^{-1}$.

^c Determined by DSC.

^d Determined by GPC.

Table 3
Results of ethylene polymerization catalyzed by C1–C5 with MAO^a.

Entry	Pre-cat.	Al/Ni	T/°C	t/min	P(C ₂ H ₄)/atm	Activity ^b	T _m ^c /°C	M _w ^d /10 ⁵ g mol ⁻¹	M _w /M _n ^d	Branches/1000C ^e
1	C4	2000	20	30	10	3.98	99.0	3.15	2.5	35
2	C4	2500	20	30	10	6.31	98.0	4.79	2.4	43
3	C4	3000	20	30	10	11.0	94.6	6.40	2.8	50
4	C4	3500	20	30	10	8.17	92.8	6.33	2.9	28
5	C4	3000	30	30	10	8.33	93.6	4.68	2.3	53
6	C4	3000	40	30	10	6.96	69.8	3.46	2.5	80
7	C4	3000	60	30	10	3.79	47.8	2.97	3.2	90
8	C4	3000	20	30	5	6.70	87.2	4.34	2.4	80
9	C4	3000	20	30	1	0.74	31.4	4.32	5.4	160
10	C4	3000	20	10	10	14.8	98.8	5.98	2.3	37
11	C4	3000	20	20	10	12.3	96.7	5.96	2.9	44
12	C4	3000	20	60	10	6.81	102.5	9.80	2.8	46
13	C1	3000	20	30	10	9.80	94.8	4.38	2.4	53
14	C2	3000	20	30	10	8.21	94.1	5.44	2.5	50
15	C3	3000	20	30	10	7.20	88.6	12.9	2.5	40
16	C5	3000	20	30	10	9.10	91.2	6.43	2.6	66

^a Conditions: 1.5 μmol of Ni; total volume 100 mL.

^b 10⁶ g of PE (mol of Ni)⁻¹ h⁻¹.

^c Determined by DSC.

^d Determined by GPC.

^e Determined by FT-IR.

The active species derived from both halide pre-catalysts should be very similar and halogen abstraction is facile in both cases [71]. There was a halide effect and different Al/Ni ratio effect on the properties of their resulting polyethylenes in that the polyethylenes produced with the chloride pre-catalysts (entries 5, 7–10 in Table 4) showed relatively higher molecular weights than those produced with the bromide pre-catalysts (entries 3, 13–16 in Table 3). In this work, the halide effect can be seen clearly. For example, on fixing the Al/Ni ratio to 2500 (entry 2 in Table 3, entry 4 in Table 4), the bromide and chloride complexes show similar activity ($6.31\text{--}7.65 \times 10^6$ g of PE (mol of Ni)⁻¹ h⁻¹), while the resultant polyolefin obtained from chloride compounds displayed higher molecular weight and wider PDI.

2.4. Theoretical calculation of catalyst activity

MANCC calculations were performed to investigate the correlation between the nature of the ligands (i.e., their substituents) and the catalytic activities of the complex pre-catalysts [62–65]. The MANCC method combines a molecular mechanics (MM) approach with QEq charge distributions. The method is applied

here to the complex pre-catalysts and assuming that the ligand binding in the electronic ground state of the complex pre-catalysts parallels the ligand binding in the active species. In previous studies, the experimentally determined catalytic activities were shown to correlate with metal charges computed by the MANCC method for catalytic systems of Ti [62], Ni [63,64] and Fe [65].

Molecular models were built using Material Studio software and then optimized with molecular mechanics (MM). We chose the Dreiding force field [72] for its advantage of relatively simple parameters and the ease of its extension to other metals. For the present study, atom types were added into the force field files for nickel atom and the atoms bonded to nickel and their parameters were derived from our X-ray crystal data as described previously [64]. The nonbonded potential truncation was performed using the spherical cutoff method for van der Waals potentials and electrostatic interactions, with the cutoff distance of 1.85 nm. To obtain net charge on each atom of the pre-catalysts, the MANCC method combines the MM and QEq theoretical methods as follows. In the first step, charges were distributed on each atom by QEq on a given pre-catalyst molecule and MM structure optimizations were performed until the energy had converged. In the second step, net charges on each atom were refined by the QEq method and using the optimized structure obtained in the first step.

The net charges of all of the nickel complexes were calculated by the MANCC method and the results are tabulated in Table 5 and plots are shown in Fig. 5. Within the two groups of the bromide or chloride nickel complexes, respectively, the experimentally measured catalytic activities increased with the net charges of the nickel centers in the pre-catalysts. This trend is in line with previous calculation results for other nickel complex pre-catalysts [63,64], and also in line with expectation based on the plausible mechanism of polymerization.

In the olefin polymerization mechanism, the olefin coordination to the central metal or its insertion into the M–R bond (R alkyl chain) is the most likely turnover limiting step, and both are considered to be directly and closely related to the electrophilicity of the central metal [3,5,49,73]. Thus, a higher net charge of the metal core would enhance its coordination ability and thereby increase the catalyst's activity. Ligand effects on catalytic activities should be especially pronounced for electron-rich transition metal complexes and these include complexes of Ni²⁺ ion (3d⁸). In particular, this interpretation also is consistent with and accounts

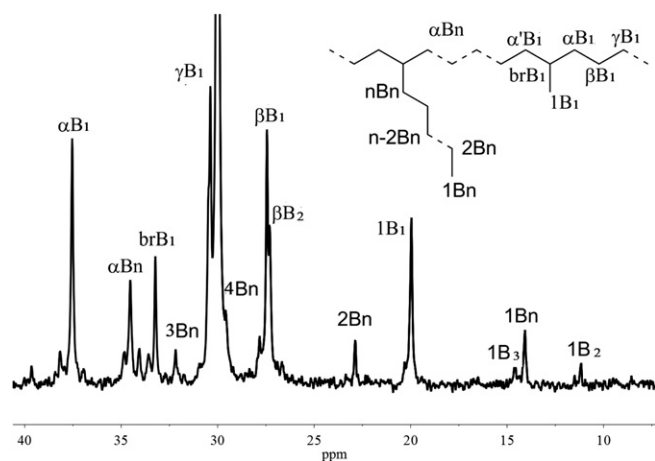


Fig. 4. ¹³C NMR spectrum of the polyethylene formed by C4/MAO at 60 °C (Entry 7 in Table 3).

Table 4
Results of ethylene polymerization catalyzed by C6–C10 with MAO^a.

Entry	Pre-cat.	Al/Ni	T/ ^o C	Activity ^b	T _m ^c / ^o C	M _w ^d /10 ⁵ g mol ⁻¹	M _w /M _n ^d	Branches/1000C ^e
1	C9	1000	20	5.42	104.3	4.17	2.6	30
2	C9	1500	20	9.86	92.2	5.63	3.0	64
3	C9	2000	20	7.91	89.5	6.78	3.8	57
4	C9	2500	20	7.65	97.9	6.89	3.2	48
5	C9	3000	20	6.48	103.3	7.89	4.6	36
6	C9	1500	30	4.02	77.8	4.31	3.4	70
7	C6	1500	20	9.81	95.7	5.49	3.3	53
8	C7	1500	20	7.89	95.6	12.5	3.2	50
9	C8	1500	20	5.68	102.3	24.1	2.9	25
10	C10	1500	20	8.10	96.6	22.9	3.3	44

^a Conditions: 1.5 μmol of Ni; 30 min; 10 atm of ethylene; total volume 100 mL.^b 10⁶ g of PE (mol of Ni)⁻¹ h⁻¹.^c Determined by DSC.^d Determined by GPC.^e Determined by FT-IR.

for the finding that the current pre-catalysts with 4-chloro groups show higher activities than their analogs with 4-methyl groups [60].

3. Conclusions

A series of bulky unsymmetrical α-diimines was synthesized and reacted with (DME)NiX₂ (X = Br, Cl) to form bromide or chloride nickel complexes, respectively. Activated by the co-catalyst MAO, all of these nickel complex pre-catalysts showed high catalytic activity for the polymerization of ethylene (up to 1.48 × 10⁷ g of PE (mol of Ni)⁻¹ h⁻¹) leading to polyethylenes with high molecular weights and with narrow polydispersity. The results suggest that ligands that increase of the net charge on the nickel center enhance the catalytic activities of the pre-catalysts in ethylene polymerization.

4. Experimental section

4.1. General procedures

All work involving air- and/or moisture-sensitive compounds was performed using standard Schlenk techniques under a nitrogen atmosphere. Toluene was refluxed over sodium benzophenone and distilled under nitrogen prior to use. Methylaluminoxane (MAO, 1.46 mol/L solution in toluene) and modified methylaluminoxane (MMAO, 1.93 mol/L in heptane, 3A) were purchased from Akzo Nobel Corp. Diethylaluminium chloride (Et₂AlCl, 0.79 mol/L in toluene) and ethylaluminium sesquichloride (EASC, 0.87 mol/L in toluene) were purchased from Acros Chemicals. High-purity ethylene was purchased from Beijing Yanshan Petrochemical Co. and used as received. Other reagents were purchased from Aldrich, Acros, or local suppliers. NMR spectra were recorded on a Bruker DMX 400 MHz instrument at ambient temperature using TMS as an internal standard; δ values are given in ppm and J values in Hz. IR spectra were recorded on a Perkin–Elmer System 2000 FT-IR spectrometer. Elemental analysis was carried out using a Flash EA 1112 micro-analyzer. Molecular weights and molecular weight distribution (MWD) of polyethylene were determined by

PL-GPC220 at 150 °C, with 1,2,4-trichlorobenzene as the solvent. The melting points of polyethylene were measured from the second scanning run on a Perkin–Elmer TA-Q2000 differential scanning calorimetry (DSC) analyzer under a nitrogen atmosphere. In the procedure, a sample of about 2.0–4.0 mg was heated to 150 °C at a rate of 20 °C/min and kept for 5 min at 150 °C to remove the thermal history and then cooled at a rate of 20 °C/min to –20 °C. ¹³C NMR spectra of the polyethylenes were recorded on a Bruker DMX 300 MHz instrument at 135 °C in deuterated 1,2-dichlorobenzene with TMS as an internal standard.

4.2. Syntheses and characterization

4.2.1. 2-(2,6-Dibenzhydryl-4-chlorophenylimino)acenaphthylene

A solution of 2,6-diphenylmethyl-4-chloroaniline (1.29 g, 2.8 mmol), acenaphthylene-1,2-dione (0.51 g, 3.3 mmol), and a catalytic amount of p-toluenesulfonic acid in toluene (120 mL) were stirred and refluxed for 3 h. After solvent evaporation at reduced pressure, the crude product was dissolved in a minimum amount of CH₂Cl₂. The CH₂Cl₂ solution was mixed with petroleum ether, and a yellow powder was obtained upon standing at room temperature. Yield: 1.33 g (78%). Mp: 236–237 °C. ¹H NMR (400 MHz, CDCl₃, TMS): δ 8.03 (d, J = 5.82 Hz, 2H), 7.71 (m, 2H), 7.26–7.23 (m, 4H), 7.19 (t, J = 6.72 Hz, 2H), 7.06 (m, 5H), 6.97 (s, 2H), 6.84 (d, J = 7.36 Hz, 5H), 6.60 (t, J = 7.28 Hz, 3H), 6.43 (t, J = 7.21 Hz, 2H), 6.17 (d, J = 6.97 Hz, 1H), 5.43 (s, 2H). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 189.47, 162.67, 146.95, 142.74, 142.11, 141.01, 134.22, 132.11, 130.05, 129.97, 129.72, 129.48, 129.00, 128.53, 128.24, 128.16, 127.86, 127.38, 126.81, 126.74, 126.00, 123.98, 121.88, 52.29. IR (KBr; cm⁻¹): 3026 (w), 1722 (s), 1659 (m), 1594 (s), 1491 (s), 1431 (s), 1273 (m), 1072 (m), 1029 (s), 889 (m), 826 (m), 777 (s), 737 (s), 694 (vs). Anal. Calcd for C₄₄H₃₀ClNO (624.17): C, 84.67; H, 4.84; N, 2.24. Found: C, 84.31; H, 4.88; N, 2.21.

4.2.2. Synthesis of 2,6-dibenzhydryl-N-(2-phenylimino)acenaphthyl-nylidene)-4-chlorobenzeneamine (L1–L5)

4.2.2.1. 2,6-Dibenzhydryl-N-(2-(2,6-dimethylphenylimino)acenaphthyl-nylidene)-4-chlorobenzeneamine (L1). To a solution of 2-(2,6-dibenzhydryl-4-chlorophenylimino)acenaphthylene (0.30 mg,

Table 5
Calculated charge of nickel atom in complexes C1–C10.

	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
Charge on Ni	0.393	0.389	0.387	0.394	0.390	0.443	0.440	0.429	0.445	0.442
Obs. activity ^a	9.80	8.21	7.20	11.0	9.10	9.81	7.89	5.68	9.86	8.10

^a Values in units of 10⁶ g of PE (mol of Ni)⁻¹ h⁻¹.

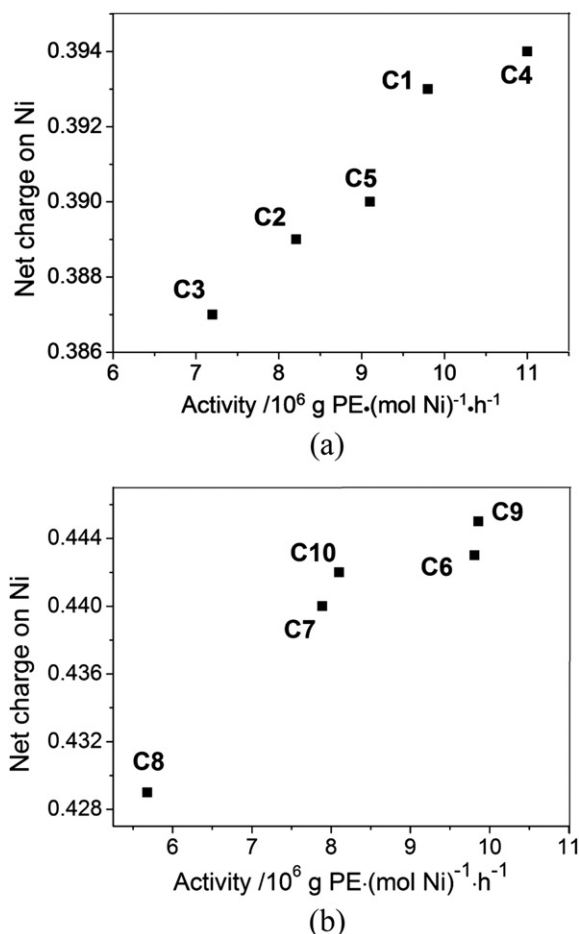


Fig. 5. Variation between calculated net charge on Ni and polymerization activity: (a) for complexes C1–C5 and (b) for C6–C10.

0.48 mmol), 2,6-dimethylaniline (0.089 g, 0.72 mmol), and a catalytic amount of *p*-toluenesulfonic acid in 70 mL of toluene at 120 °C were stirred for 9 h, then the solvent was removed by vacuum evaporation. The residue was further purified by silica column chromatography (40/1 petroleum ether/ethyl acetate) to afford 0.19 g of **L1** (yellow, 60% yield). Mp: 218–219 °C. ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.74 (d, *J* = 8.24 Hz, 1H), 7.62 (d, *J* = 8.26 Hz, 1H), 7.28–7.25 (m, 5H), 7.19 (m, 4H), 7.10 (d, *J* = 7.26 Hz, 5H), 7.04 (m, 1H), 6.08 (s, 2H) 6.92 (d, *J* = 7.52 Hz, 4H), 6.61 (t, *J* = 7.60 Hz, 4H), 6.54 (d, *J* = 7.10 Hz, 1H), 6.43 (t, *J* = 7.34 Hz, 2H), 6.14 (d, *J* = 7.12 Hz, 1H), 5.61 (s, 2H), 2.21 (s, 6H). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 163.98, 161.39, 149.27, 147.79, 142.40, 141.14, 140.14, 134.71, 129.98, 129.90, 129.61, 129.08, 128.97, 128.74, 128.51, 128.39, 128.30, 128.07, 127.79, 127.04, 126.65, 125.93, 124.88, 124.30, 124.00, 122.03, 52.39, 18.32, 17.78. IR (KBr; cm⁻¹): 3025 (w), 2913 (w), 1976 (w), 1733 (m), 1666 (s), 1593 (s), 1492 (s), 1427 (s), 1239 (s), 1078 (m), 1036 (s), 922 (m), 890 (m), 766 (s), 700 (vs). Anal. Calcd. for C₅₂H₃₉ClN₂ (727.33): C, 85.87; H, 5.40; N, 3.85. Found: C, 85.60; H, 5.49; N, 3.85.

4.2.2.2. 2,6-Dibenzhydryl-N-(2-(2,6-diethylphenylimino)acenaphthylidene)-4-chlorobenzenamine (L2). The synthetic procedure of **L2** was similar to that for **L1**, except that 2,6-diethylaniline (0.11 g, 0.72 mmol) was used in place of 2,6-dimethylaniline. Yellow solid of **L2** were collected in a yield of 61% (0.22 g). Mp: 228–229 °C. ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.71 (d, *J* = 8.06 Hz, 1H), 7.57 (d, *J* = 8.39 Hz, 1H), 7.25–7.20 (m, 10H), 7.09 (d, *J* = 7.20 Hz,

4H), 6.98 (m, 3H), 6.91 (d, *J* = 7.36 Hz, 4H), 6.60 (t, *J* = 7.52 Hz, 4H), 6.52 (d, *J* = 6.93 Hz, 1H), 6.42 (t, *J* = 6.66 Hz, 2H), 6.05 (d, *J* = 7.20 Hz, 1H), 5.62 (s, 2H), 2.68 (m, 2H), 2.51 (m, 2H), 1.16 (m, 6H). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 163.91, 161.60, 148.26, 147.83, 142.57, 140.99, 140.08, 134.65, 130.67, 129.87, 129.78, 129.54, 129.00, 128.71, 128.39, 128.30, 128.03, 127.46, 126.98, 126.56, 126.27, 125.89, 124.29, 122.51, 52.27, 24.54, 14.28. IR (KBr; cm⁻¹): 3027 (w), 2966 (w), 1661 (m), 1588 (m), 1491 (s), 1426 (s), 1266 (w), 1181 (m), 1079 (m), 1032 (s), 919 (w), 887 (w), 736 (s), 694 (vs). Anal. Calcd for C₅₄H₄₃ClN₂ (755.39): C, 85.86; H, 5.74; N, 3.71. Found: C, 85.44; H, 5.98; N, 3.75.

4.2.2.3. 2,6-Dibenzhydryl-N-(2-(2,6-diisopropylphenylimino)acenaphthylidene)-4-chlorobenzenamine (L3). Using the same procedure as for the synthesis of **L1**, except that 2,6-diisopropylaniline (0.13 g, 0.72 mmol) was in place of 2,6-dimethylaniline, **L3** was obtained as a yellow powder in 56% (0.21 g). Mp: 226–227 °C. ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.69 (d, *J* = 8.24 Hz, 1H), 7.54 (d, *J* = 8.30 Hz, 1H), 7.36–7.26 (m, 7H), 7.21 (d, *J* = 7.05 Hz, 3H), 7.09 (d, *J* = 7.20 Hz, 4H), 6.99 (s, 2H), 6.91 (d, *J* = 7.23 Hz, 5H), 6.58 (t, *J* = 7.36 Hz, 4H), 6.45–6.38 (m, 3H), 5.95 (d, *J* = 6.98 Hz, 1H), 5.63 (s, 2H), 3.15 (m, *J* = 6.64 Hz, 2H), 1.28 (d, *J* = 6.66 Hz, 6H), 1.01 (d, *J* = 6.70 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 164.11, 162.09, 147.92, 147.08, 142.75, 140.94, 140.17, 135.79, 134.78, 129.82, 129.62, 129.06, 128.88, 128.61, 128.43, 128.37, 128.13, 127.16, 127.05, 126.60, 125.97, 124.78, 124.41, 123.76, 123.18, 53.57, 52.26, 28.67, 24.39, 23.87. IR (KBr; cm⁻¹): 3059 (w), 3025 (w), 2960 (s), 1736 (w), 1661 (s), 1594 (s), 1492 (s), 1428 (s), 1267 (s), 1184 (s), 1077 (m), 1037 (s), 923 (m), 886.3 (m), 739 (s), 699 (vs). Anal. Calcd for C₅₆H₄₇ClN₂ (783.44): C, 85.85; H, 6.05; N, 3.58. Found: C, 85.55; H, 6.34; N, 3.55.

4.2.2.4. 2,6-Dibenzhydryl-N-(2-(2,4,6-trimethylphenylimino)acenaphthylidene)-4-chlorobenzenamine (L4). The synthetic procedure for **L4** was analogous to that for **L1**, except that 2,4,6-trimethylaniline (0.12 g, 0.72 mmol) was used in place of 2,6-dimethylaniline. Yellow solid of **L4** were collected in a yield of 58% (0.21 g). Mp: 238–239 °C. ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.72 (d, *J* = 8.25 Hz, 1H), 7.60 (d, *J* = 8.25 Hz, 1H), 7.29–7.23 (m, 5H), 7.19 (t, *J* = 6.92 Hz, 2H), 7.10 (d, *J* = 7.45 Hz, 4H), 7.02 (t, *J* = 7.46 Hz, 1H), 6.98 (s, 4H), 6.92 (d, *J* = 7.58 Hz, 4H), 6.60 (t, *J* = 7.18 Hz, 5H), 6.42 (t, *J* = 7.28 Hz, 2H), 6.14 (d, *J* = 7.11 Hz, 1H), 5.60 (s, 2H), 2.38 (s, 3H), 2.17 (s, 6H). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 163.95, 161.55, 147.85, 146.46, 142.41, 141.15, 140.12, 134.73, 133.20, 129.99, 129.91, 129.61, 129.22, 129.02, 128.87, 128.49, 128.27, 128.06, 127.77, 127.00, 126.63, 125.91, 124.64, 122.06, 52.38, 21.11, 18.24. IR (KBr; cm⁻¹): 3025 (w), 2963 (w), 1665 (s), 1644 (s), 1597 (m), 1491 (s), 1448 (s), 1427 (s), 1270 (m), 1183 (m), 1076 (m), 1032 (s), 920 (s), 889 (s), 737 (s), 700 (vs). Anal. Calcd for C₅₃H₄₁ClN₂ (741.36): C, 85.86; H, 5.57; N, 3.78. Found: C, 85.51; H, 5.56; N, 3.79.

4.2.2.5. 2,6-Dibenzhydryl-N-(2-(2,6-diethyl-4-methylphenylimino)acenaphthylidene)-4-chlorobenzenamine (L5). Using the same procedure as for the synthesis of **L1**, except that 2,6-diethyl-4-methylaniline (0.12 g, 0.72 mmol) was in place of 2,6-dimethylaniline, **L5** was obtained as yellow powder in 69% (0.26 g). Mp: 227–228 °C. ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.71 (d, *J* = 8.27 Hz, 1H), 7.57 (d, *J* = 8.30 Hz, 1H), 7.28–7.25 (m, 5H), 7.21–7.28 (m, 2H), 7.09 (d, *J* = 7.44 Hz, 4H), 7.03 (s, 2H), 6.98 (m, 3H), 6.91 (d, *J* = 7.56 Hz, 4H), 6.59 (t, *J* = 7.28 Hz, 5H), 6.41 (t, *J* = 7.39 Hz, 2H), 6.07 (d, *J* = 7.10 Hz, 1H), 5.62 (s, 2H), 2.62 (m, 2H), 2.47 (m, 2H), 2.43 (s, 3H), 1.14 (t, *J* = 7.56 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 164.02, 161.81, 147.92, 145.77, 142.63, 141.04, 140.10, 134.72, 133.50, 130.54, 129.84, 129.60, 128.98, 128.85,

128.71, 128.44, 128.32, 128.07, 127.48, 127.10, 126.60, 125.91, 122.53, 52.30, 24.58, 21.39, 14.69. IR (KBr; cm^{-1}): 3026 (w), 2963 (m), 1672 (m), 1650 (s), 1596 (m), 1492 (m), 1423 (s), 1264 (s), 1184 (m), 1079 (s), 1033 (s), 918 (m), 889 (s), 735 (s), 699 (vs). Anal. Calcd for $\text{C}_{55}\text{H}_{45}\text{ClN}_2$ (769.41): C, 85.86; H, 5.90; N, 3.64. Found: C, 85.75; H, 6.18; N, 3.34.

4.2.3. Preparation of the bidentate nickel complexes **C1**–**C10**

4.2.3.1. *2,6-Dibenzhydryl-N-(2-(2,6-dimethyl-phenylimino)acenaphthylidene)-4-chlorobenzenaminonickel dibromide (C1)*. The procedure for **C1** is described as follows. A mixture of the ligand **L1** (0.15 g, 0.20 mmol) and (DME)NiBr₂ (0.062 g, 0.20 mmol) in dried dichloromethane (10 mL) was stirred for 24 h at room temperature in a Schlenk tube, then absolute diethyl ether (10 mL) was added to precipitate the complex. The deposit was washed with diethyl ether and dried under vacuum to obtain a red powder of **C1** in 76% (0.14 g) yield. IR (KBr; cm^{-1}): 3025 (w), 2922 (w), 1646 (m), 1579 (s), 1492 (m), 1450 (m), 1427 (s), 1264 (m), 1180 (m), 1082 (m), 1032 (m), 921 (m), 892 (s), 773 (vs), 702 (vs). Anal. Calcd for $\text{C}_{52}\text{H}_{39}\text{ClBr}_2\text{N}_2\text{Ni}$ (945.83): C, 66.03; H, 4.16; N, 2.96. Found: C, 65.91; H, 4.14; N, 2.98.

4.2.3.2. *2,6-Dibenzhydryl-N-(2-(2,6-diethylphenylimino)acenaphthylidene)-4-chlorobenzenaminonickel dibromide (C2)*. Using the same procedure as for the synthesis of **C1**, except that **L2** (0.15 g, 0.20 mmol) was used in place of **L1** (0.15 g, 0.20 mmol), **C2** was obtained as red powder in 86% (0.17 g). IR (KBr; cm^{-1}): 3027 (w), 2967 (w), 1646 (s), 1595 (s), 1492 (s), 1429 (s), 1266 (w), 1181 (s), 1079 (s), 1033 (s), 920 (s), 892 (s), 769 (vs), 701 (vs). Anal. Calcd for $\text{C}_{54}\text{H}_{43}\text{ClBr}_2\text{N}_2\text{Ni}$ (973.89): C, 66.60; H, 4.45; N, 2.88. Found: C, 66.50; H, 4.51; N, 2.64.

4.2.3.3. *2,6-Dibenzhydryl-N-(2-(2,6-diisopropylphenylimino)acenaphthylidene)-4-chlorobenzenaminonickel dibromide (C3)*. The synthetic procedure for **C3** was analogous to that for **C1**, except that **L3** (0.16 g, 0.20 mmol) was used in place of **L1** (0.15 g, 0.20 mmol). Red solid of **C3** were collected in a yield of 88% (0.18 g). IR (KBr; cm^{-1}): 3058 (w), 3025 (w), 2967 (m), 1645 (s), 1620 (s), 1581 (s), 1492 (s), 1427 (s), 1290 (m), 1181 (s), 1079 (m), 1037 (s), 922 (m), 892 (s), 768 (vs), 701 (vs). Anal. Calcd for $\text{C}_{56}\text{H}_{47}\text{ClBr}_2\text{N}_2\text{Ni}$ (1001.94): C, 67.13; H, 4.73; N, 2.80. Found: C, 66.83; H, 4.63; N, 2.68.

4.2.3.4. *2,6-Dibenzhydryl-N-(2-(2,4,6-trimethylphenylimino)acenaphthylidene)-4-chlorobenzenaminonickel dibromide (C4)*. The synthetic procedure for **C4** was analogous to that for **C1**, except that **L4** (0.15 g, 0.20 mmol) was used in place of **L1** (0.15 g, 0.20 mmol). Red powder of **C4** was collected in a yield of 87% (0.18 g). IR (KBr; cm^{-1}): 3059 (w), 3025 (w), 2919 (w), 1647 (s), 1621 (s), 1584 (s), 1491 (s), 1451 (m), 1427 (s), 1270 (m), 1181 (m), 1076 (m), 1032 (m), 892 (m), 859 (m), 770 (s), 701 (vs). Anal. Calcd for $\text{C}_{53}\text{H}_{41}\text{ClBr}_2\text{N}_2\text{Ni}$ (959.86): C, 66.32; H, 4.31; N, 2.92. Found: C, 65.97; H, 4.44; N, 2.90.

4.2.3.5. *2,6-Dibenzhydryl-N-(2-(2,6-diethyl-4-methylphenylimino)acenaphthylidene)-4-chlorobenzenaminonickel dibromide (C5)*. Using the same procedure as for the synthesis of **C5**, except that **L5** (0.15 g, 0.20 mmol) was used in place of **L1** (0.15 g, 0.20 mmol), **C5** was obtained as red powder in 86% (0.26 g). IR (KBr; cm^{-1}): 3025 (m), 2968 (m), 1645 (s), 1619 (s), 1595 (s), 1494 (s), 1428 (s), 1294 (m), 1183 (m), 1079 (s), 1033 (s), 918 (m), 827 (s), 769 (s), 701 (vs). Anal. Calcd for $\text{C}_{55}\text{H}_{45}\text{ClBr}_2\text{N}_2\text{Ni}$ (987.91): C, 66.87; H, 4.59; N, 2.84. Found: C, 66.65; H, 4.62; N, 2.81.

4.2.3.6. *2,6-Dibenzhydryl-N-(2-(2,6-dimethylphenylimino)acenaphthylidene)-4-chlorobenzenaminonickel dichloride (C6)*. The

synthesis of **C6** was carried out in a manner identical with that for **C1**. A mixture of the ligand **L1** (0.15 g, 0.20 mmol) and (DME)NiCl₂ (0.044 g, 0.20 mmol) in dried dichloromethane (10 mL) was stirred for 24 h at room temperature in a Schlenk tube, then absolute diethyl ether (10 mL) was added to precipitate the complex. The deposit was washed with diethyl ether and dried under vacuum to obtain a red powder of **C6** in 80% (0.14 g). IR (KBr; cm^{-1}): 3026 (m), 2925 (w), 1646 (m), 1581 (s), 1493 (m), 1448 (m), 1428 (s), 1292 (m), 1180 (m), 1082 (m), 1033 (m), 921 (m), 893 (s), 774 (vs), 703 (vs). Anal. Calcd for $\text{C}_{52}\text{H}_{39}\text{Cl}_2\text{N}_2\text{Ni}$ (856.93): C, 72.88; H, 4.59; N, 3.27. Found: C, 72.61; H, 4.56; N, 3.22.

4.2.3.7. *2,6-Dibenzhydryl-N-(2-(2,6-diethylphenylimino)acenaphthylidene)-4-chlorobenzenaminonickel dichloride (C7)*. The synthetic procedure of **C7** was similar to that for **C6**, except that **L2** (0.15 g, 0.20 mmol) was used in place of **L1** (0.15 g, 0.20 mmol). Red powder of **C7** was collected in a yield of 78% (0.13 g). IR (KBr; cm^{-1}): 3025 (w), 2969 (w), 1625 (s), 1588 (s), 1492 (s), 1426 (s), 1264 (w), 1183 (s), 1079 (m), 1032 (s), 922 (w), 893 (s), 769 (s), 701 (vs). Anal. Calcd for $\text{C}_{54}\text{H}_{43}\text{Cl}_2\text{N}_2\text{Ni}$ (884.99): C, 73.29; H, 4.90; N, 3.17. Found: C, 73.10; H, 4.65; N, 3.22.

4.2.3.8. *2,6-Dibenzhydryl-N-(2-(2,6-diisopropylphenylimino)acenaphthylidene)-4-chlorobenzenaminonickel dichloride (C8)*. Using the same procedure as for the synthesis of **C8**, except that **L3** (0.16 g, 0.20 mmol) was in place of **L1** (0.15 g, 0.20 mmol), **C8** was obtained as red powder in 79% (0.14 g). IR (KBr; cm^{-1}): 3060 (w), 3027 (w), 2967 (m), 1653 (s), 1625 (s), 1591 (s), 1492 (s), 1430 (s), 1291 (m), 1181 (s), 1077 (m), 1032 (m), 921 (m), 892 (s), 768 (vs), 701 (vs). Anal. Calcd for $\text{C}_{56}\text{H}_{47}\text{Cl}_2\text{N}_2\text{Ni}$ (913.04): C, 73.67; H, 5.19; N, 3.07. Found: C, 73.55; H, 5.01; N, 2.95.

4.2.3.9. *2,6-Dibenzhydryl-N-(2-(2,4,6-trimethylphenylimino)acenaphthylidene)-4-chlorobenzenaminonickel dichloride (C9)*. The synthetic procedure of **C9** was similar to that for **C6**, except that **L4** (0.15 g, 0.20 mmol) was used in place of **L1** (0.15 g, 0.20 mmol). Red powder of **C9** was collected in a yield of 86% (0.15 g). IR (KBr; cm^{-1}): 3059 (w), 3026 (w), 2920 (w), 1651 (s), 1624 (s), 1594 (s), 1492 (s), 1492 (m), 1430 (s), 1270 (m), 1180 (m), 1033 (m), 892 (m), 858 (m), 771 (s), 701 (vs). Anal. Calcd for $\text{C}_{53}\text{H}_{41}\text{Cl}_2\text{N}_2\text{Ni}$ (870.96): C, 73.09; H, 4.74; N, 3.22. Found: C, 72.92; H, 4.79; N, 3.00.

4.2.3.10. *2,6-Dibenzhydryl-N-(2-(2,6-diethyl-4-methylphenylimino)acenaphthylidene)-4-chlorobenzenaminonickel dichloride (C10)*. Using the same procedure as for the synthesis of **C6**, except that **L5** (0.15 g, 0.20 mmol) was in place of **L1** (0.15 g, 0.20 mmol), **C10** was obtained as red powder in 77% (0.14 g). IR (KBr; cm^{-1}): 3024 (m), 2968 (m), 1652 (s), 1625 (s), 1589 (s), 1492 (s), 1426 (s), 1291 (m), 1182 (m), 1077 (s), 1032 (m), 920 (m), 827 (s), 771 (s), 701 (vs). Anal. Calcd for $\text{C}_{55}\text{H}_{45}\text{Cl}_2\text{N}_2\text{Ni}$ (899.01): C, 73.48; H, 5.05; N, 3.12. Found: C, 73.32; H, 5.02; N, 3.00.

4.3. X-ray crystallographic studies

Single-crystal X-ray diffraction studies for **C1**, **C3** and **C6** were carried out on a Rigaku RAXIS Rapid IP diffract meter with graphite-monochromatic Mo K α radiation ($\lambda = 0.71073$ Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 . All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package [74].

Crystal data and processing parameters for **C1**, **C3** and **C6** are summarized in Table 6.

4.4. Ethylene polymerization

4.4.1. Ethylene polymerization under 1 atm ethylene

The pre-catalyst **C4** was dissolved in toluene using standard Schlenk techniques, and the reaction solution was stirred with a magnetic stir bar under ambient ethylene atmosphere. The require amount of co-catalyst (MAO) was added by a syringe. After the reaction was carried out for the required period, the reaction solution was quenched with 10% hydrochloric acid in ethanol. The precipitated polymer was collected by filtration, washed with ethanol and water, and dried in a vacuum at 60 °C until constant weight.

4.4.2. Ethylene polymerization under 10/5 atm ethylene

A 300 mL stainless steel autoclave, equipped with a mechanical stirrer and a temperature controller, was employed for the reaction. Firstly, 30 mL toluene (freshly distilled) was injected to the clave which is full of ethylene. When the temperature rooted as we wanted, another 20 mL toluene which dissolved the complex (1.5 μmol), the require amount of co-catalyst (MAO, MMAO, EASC, Et₂AlCl), the residual toluene were added by syringe successively. The reaction mixture was intensively stirred for the desired time under corresponding pressure of ethylene through the entire experiment. The reaction was terminated and analyzed using the same method as above for ethylene polymerization at ambient pressure.

Table 6
Crystal data and structure refinement for **C1**, **C3** and **C6**.

Identification code	C1	C3	C6
Empirical formula	C ₅₂ H ₃₉ Br ₂ ClN ₂ Ni	C ₅₆ H ₄₇ Br ₂ ClN ₂ Ni	C ₅₂ H ₃₉ Cl ₃ N ₂ Ni
Formula weight	945.83	1001.94	856.91
Temperature/K	173(2)	173(2)	173(2)
Wavelength/Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	P2(1)/n	P-1	P2(1)/n
a/Å	15.16(3)	10.721(2)	15.144(3)
b/Å	15.983(3)	12.113(2)	16.012(3)
c/Å	17.646(4)	19.925(4)	17.305(4)
Alpha/°	90	84.22	90(3)
Beta/°	97.01(3)	79.05(3)	97.23(3)
Gamma/°	90	81.33(3)	90(3)
Volume/Å ³	4243.7(15)	2504.6(9)	4162.6(14)
Z	4	2	4
D calcd/(g cm ⁻³)	1.48	1.329	1.367
m/mm ⁻¹	2.442	2.073	0.698
F(000)	1920	1024	1776
Crystal size/mm	0.37 × 0.36 × 0.27	0.41 × 0.40 × 0.37	0.22 × 0.20 × 0.16
θ range (°C)	1.72–27.48	1.04–27.48	2.71–27.48
Limiting indices	-13 ≤ h ≤ 19 -20 ≤ k ≤ 20 -20 ≤ l ≤ 22	-13 ≤ h ≤ 13 -15 ≤ k ≤ 15 -25 ≤ l ≤ 25	-19 ≤ h ≤ 16 -20 ≤ k ≤ 14 -19 ≤ l ≤ 22
No. of rflns collected	18,530	22,365	18,294
No. unique rflns	9591	11,360	9420
R(int)	0.0402	0.0384	0.0546
No. of params	523	559	523
Completeness to θ [%]	98.6%	98.9%	98.6%
Goodness of fit on F ²	1.16	1.185	1.118
Final R indices [I > 2σ(I)]	R1 = 0.0599 wR2 = 0.1322	R1 = 0.0514 wR2 = 0.1407	R1 = 0.0852 wR2 = 0.1995
R indices (all data)	R1 = 0.0741 wR2 = 0.1429	R1 = 0.0633 wR2 = 0.1471	R1 = 0.1063 wR2 = 0.2166
Largest diff. peak and hole/(e Å ⁻³)	0.563 and -0.481	0.661 and -0.7904	0.360 and -0.599

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 20874105) and the President Fund of GUCAS.

Appendix A. Supplementary material

CCDC 883744–883746 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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