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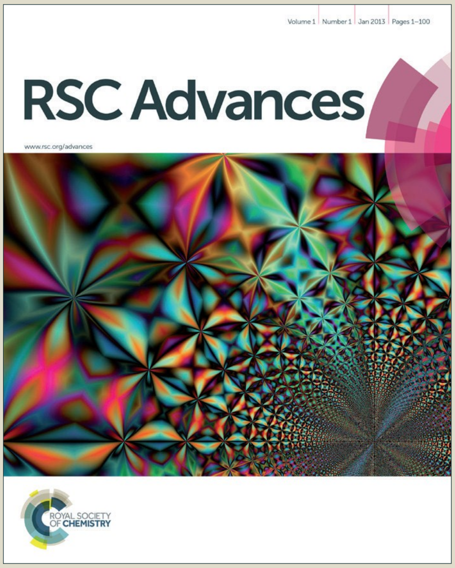

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ARTICLE

Enhancing thermo-stability to ethylene polymerization: Synthesis, characterization and the catalytic behavior of 1-(2,4-dibenzhydryl-6-chlorophenylimino)-2-aryliminoacenaphthylnickel halides

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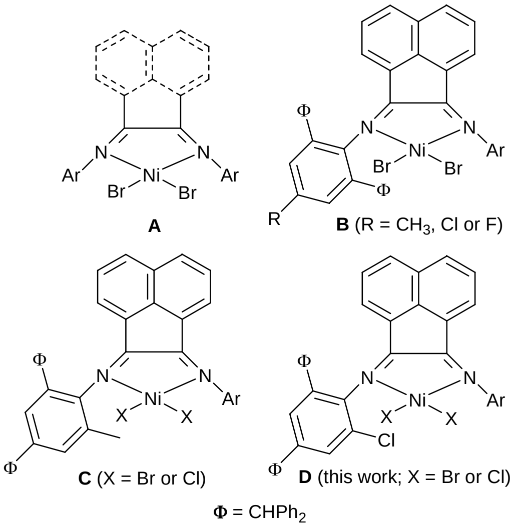
Linlin Fan,[a,b] Erlin Yue,[b] Shizhen Du,[b] Cun-Yue Guo,*[a] Xiang Hao,[b] and Wen-Hua Sun*[b,c]

A series of 1-(2,4-dibenzhydryl-6-chlorophenylimino)-2-aryliminoacenaphthylene derivatives (**L1–L5**) was synthesized and reacted with nickel halides to form the corresponding nickel complexes $LNiX_2$ (X = Br, **Ni1 – Ni5**; X = Cl, **Ni6 – Ni10**). The molecular structures of representative complexes **Ni2** and **Ni5** were determined by the single crystal X-ray diffraction, indicating the distorted square planar geometry around nickel atom of complex **Ni2** and the distorted tetrahedral geometry around nickel atom of complex **Ni5**, respectively. Upon activation with low amount of ethylaluminium sesquichloride($Et_3Al_2Cl_3$, EASC), all nickel complexes exhibited high activities up to 1.09×10^7 g of PE (mol of Ni)$^{-1}$h^{-1} toward ethylene polymerization, producing branched polyethylenes. Most importantly, these systems showed good thermo-stability, even at 80 °C maintaining the activity with 3.76×10^6 g of PE (mol of Ni)$^{-1}$h^{-1}.

Introduction

Two decades have passed since the discovery of α-diiminonickel pre-catalysts in ethylene polymerization,[1] the rapid progress of the nickel complex pre-catalysts has been reviewed timely.[2] Regarding the foremost model of α-diiminonickel pre-catalysts (**A**, Scheme 1),[1,3] the catalytic activities of their nickel complexes were enhanced by using the bulky 2,3-bis(2,6-diarylphenylimino)butanes[4] as well as dibenzhydryl-substituted 2,3-diiminobutanes,[5] in addition, the good thermo-stable precatalysts were achieved.[5c] In parallel, the dibenzhydryl-substituted 1,2-bis(arylimino)acenaphthylene derivatives have also been developed and used to improve the catalytic activities of their nickel complexes (**B**, Scheme1);[6,7,8] besides higher activities achieved, the properties of resultant polyethylenes were tailored through changing substituents from methyl,[6] chloro-[7] and fluoro-group[8] with producing narrow polydispersion polyethylenes from low to high molecular weights. It is still far to meet the industrial demands regarding the thermo-stable precatalysts, fortunately the 1-(2,4-dibenzhydryl-6-methylphenylimino)-2-aryliminoacenaphthyl nickel complexes performed high ethylene polymerization at high temperature (**C**, Scheme 1)[9a] along with extensive analogous complexes.[9b,9c] The computational study clearly indicated the positive influence of the electron-withdrawing substituents to the late-transition metal precatalysts,[10] which were consistent to experimental observations.[5a,7,8] Instead of 2,4-dibenzhydryl-6-methylphenylamine[9a] by 2,4-dibenzhydryl-6-chlorophenylamine, subsequently the 1-(2,4-dibenzhydryl-6-chlorophenylimino)-2-aryliminoacenaphthylene derivatives were prepared and reacted with nickel halides to form the title nickel complexes (**D**, Scheme 1). These new nickel complexes exhibited high activities up to 1.09×10^7 g of PE (mol of Ni)$^{-1}$h^{-1} for ethylene polymerization at 50 °C in comparison to its analogs at 20 °C[9a], more importantly, the system maintained good thermal stability and high activity with 3.76×10^6 g of PE (mol of Ni)$^{-1}$ h^{-1} up to 80 °C. Therefore the title complex



Scheme 1. α-Diiminonickel complex precatalysts

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[a] School of Chemistry and Chemical Engineering, University of Chinese Academy of Sciences, Beijing 100049, China.
[b] Key Laboratory of Engineering Plastics and Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.
[c] State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China.

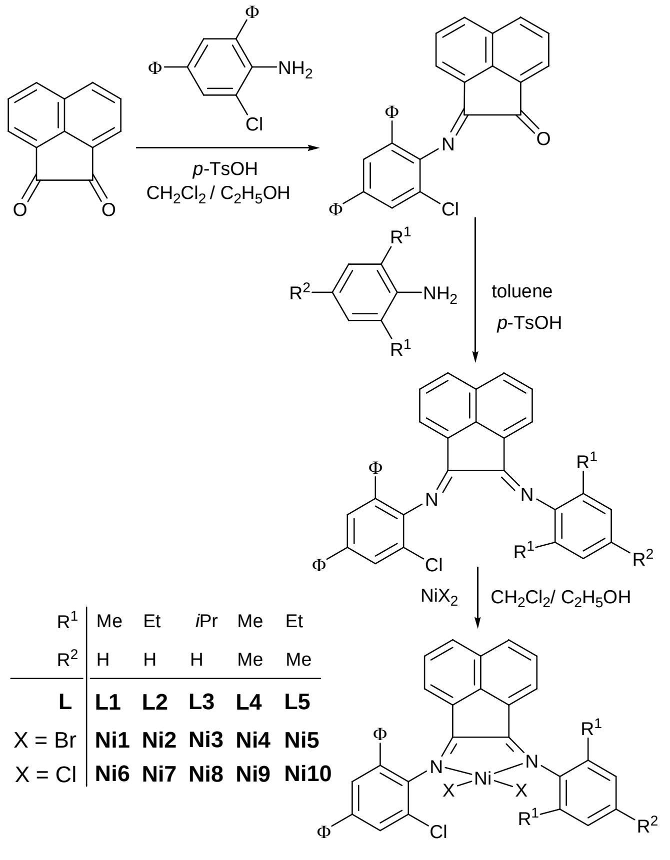
† Electronic supplementary information (ESI) available: CCDC 1422645 and 1422646 contain the supplementary crystallographic data for Ni2 and Ni5. These data can be obtained free of charge from The Cambridge Crystallographic Data www.ccdc.cam.ac.uk/data_request/cif

precatalysts would be potentially useful in industrial process, and further investigations remain to be interesting. The resulting polyethylenes possessed high molecular weights, but narrow polydispersity. The syntheses and characterization of the nickel complexes are reported in detail as well as their catalytic behavior toward ethylene polymerization, and the properties of the resultant polyethylenes were explored with regard to the molecular weight, polydispersity as well as branching.

Results and discussions

Synthesis of 1-(2,4-dibenzhydryl-6-chlorophenylimino)-2-arylimino acenaphthylenes (L1–L5) and their nickel complexes (Ni1–Ni10)

The stoichiometric condensation of acenaphtylene-1,2-dione with 2,4-dibenzhyldryl-6-chlorophenylamine was conducted to form the 2-(2,4-dibenzhydryl-6-chlorophenylimino)acenaphthylenone, which further reacted with various anilines to afford the 1-(2,4-dibenzhydryl-6-chlorophenylimino)-2-arylimino-acenaphthylene derivatives (**L1** – **L5**, Scheme 2). Then the routine reactions of these organic ligands (**L1** – **L5**) with either (DME)NiBr$_2$ (DME as dimethoxyethane) or NiCl$_2$·6H$_2$O formed their corresponding nickel complexes as bromides **Ni1** – **Ni5** or chlorides **Ni6** – **Ni10** (Scheme 2) in acceptable yields, respectively. Reflected by the FT-IR spectra, the stretching vibrations of C=N of the nickel halide complexes **Ni1 – Ni10** showed weaker intensities in the range of 1660 cm^{-1}–1630 cm^{-1} in comparing with the range of 1670 cm^{-1}–1650 cm^{-1} for the free organic compounds **L1–L5**, indicating effective coordination between cationic nickel and N$_{imino}$ atom. T confirm the absolute structure, the single crystals of representative complexes **Ni2** and **Ni5** were obtained and characterized by the single crystal X-ray diffraction.



R^1	Me	Et	*i*Pr	Me	Et
R^2	H	H	H	Me	Me
L	**L1**	**L2**	**L3**	**L4**	**L5**
X = Br	**Ni1**	**Ni2**	**Ni3**	**Ni4**	**Ni5**
X = Cl	**Ni6**	**Ni7**	**Ni8**	**Ni9**	**Ni10**

Scheme 2. Synthesis of ligands **L1–L5** and their nickel complexes **Ni1–Ni10**.

X-Ray crystallography

Single crystals of complexes **Ni2** and **Ni5** were obtained by layering diethyl ether onto their dichloromethane solution, respectively. There are two independent molecules of the complex **Ni2** together with free dichloromethane in the crystal cell adapting the distorted square planar geometry around the nickel, shown in Figure 1. The complex **Ni5** described the distorted tetrahedral geometry around the nickel, shown in Figure 2. The different configurations of complexes **Ni2** and **Ni5** may be caused by substituents and the solvent molecules in the crystal cells. Their selected bond lengths and angles ar tabulated in Table 1.

Table 1. Selected bond lengths (Å) and angles (°) for complexes **Ni2** and **Ni5**

Ni2		Ni5	
Bond lengths (Å)			
Ni(1)–Br(1)	2.5077(6)	Ni(1)–Br(1)	2.3172(8)
Ni(1)–Br(2)	2.4978(6)	Ni(1)–Br(2)	2.3360(8)
Ni(1)–N(1)	2.158(3)	Ni(1)–N(1)	2.031(3)
Ni(1)–N(2)	2.147(3)	Ni(1)–N(2)	2.010(3)
N(1)–C(12)	1.272(4)	N(1)–C(12)	1.277(5)
N(1)–C(23)	1.409(4)	N(1)–C(23)	1.435(4)
N(2)–C(11)	1.272(5)	N(2)–C(11)	1.282(5)
N(2)–C(1)	1.411(4)	N(2)–C(1)	1.440(5)
Cl(1)–C(28)	1.729(4)	Cl(1)–C(28)	1.724(4)
Bond angles (°)			
N(2)–Ni(1)–N(1)	79.52(11)	N(2)–Ni(1)–N(1)	82.70(13)
Br(1)–Ni(1)–Br(2)	102.34(2)	Br(1)–Ni(1)–Br(2)	125.62(3)
N(2)–Ni(1)–Br(1)	165.66(8)	N(2)–Ni(1)–Br(1)	105.90(10)
N(1)–Ni(1)–Br(1)	89.20(8)	N(1)–Ni(1)–Br(1)	114.83(9)
N(2)–Ni(1)–Br(2)	88.94(7)	N(2)–Ni(1)–Br(2)	115.66(10)
N(1)–Ni(1)–Br(2)	168.43(8)	N(1)–Ni(1)–Br(2)	104.13(9)

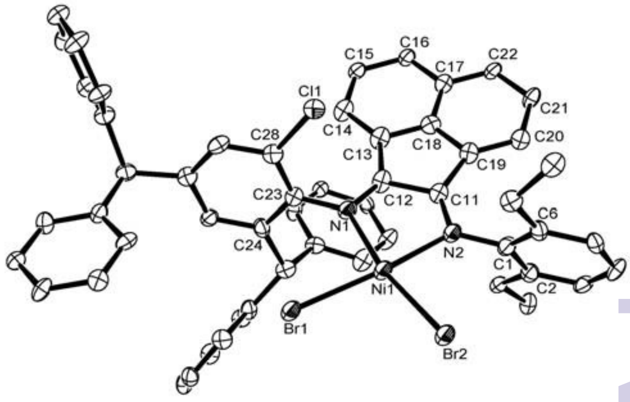


Figure 1. ORTEP drawing of **Ni2** with thermal ellipsoids at a 30% probability level. Hydrogen atoms and molecule of dichloromethane have been omitted for clarity.

According to Figure 1, the square plane was formed with the N1, N2, Br2 and Br1 atoms and the nickel atom having a deviation distance of 0.090 Å from the plane. The bond lengt of Ni1–N1 (2.158 Å) is slightly longer than the value corresponding Ni1–N2 (2.147 Å), indicating the steric hindrance of ligands and being consistent with their analogues.[6–9] The typical C=N double-bond character were observed within bonds N1–C12 (1.272 Å) and N2–C11 (1.272 Å), being significantly shorter than the typical C-N single bonds of the N1–C23 (1.409 Å) and N2–C1 (1.411 Å). Moreover, the Ni–Br bond lengths are 2.5077 Å (Ni1–Br1) and 2.4978 Å (Ni1–Br2).

Complex **Ni5**, with the distorted tetrahedral geometry around the nickel center being consistent to its analogous complexes,[6,9a] has the basal plane of the N1, N2 and Br1 atoms with the apical atom of the Br2. The distance between nickel atom and the basal plane is 0.939 Å. The dihedral angle between the plane formed by N1, N2 and Ni1, and the basal plane is 38.26°. The Ni–N bond lengths are 2.031 Å (Ni1–N1) and 2.010 Å (Ni1–N2). Similar to the complex **Ni2**, the bonds N1–C12 (1.277 Å) and N2–C11 (1.282 Å) have the typical C=N double-bond character, and are shorter than the single-bond N1–C23 (1.436 Å) and N2–C1 (1.441 Å). The Ni–Br bond lengths are 2.317 Å (Ni1–Br1) and 2.336 Å (Ni1–Br2). The dihedral angles between the chelate plane including N1, N2 and Ni1 and N1-aryl ring or N2-aryl ring are 82.64° and 77.43°, respectively.

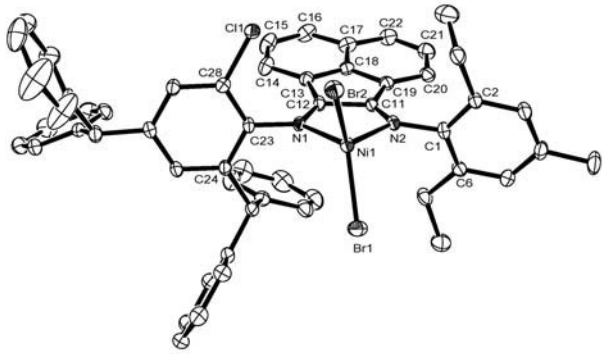


Figure 2. ORTEP drawing of **Ni5** with thermal ellipsoids at a 30% probability level. Hydrogen atoms have been omitted for clarity.

Ethylene polymerization

Complex **Ni1** was used to optimize the ethylene polymerization parameters to find a suitable co-catalyst. The ethylene polymerization trials were conducted through using various alkylaluminium reagents such as methylaluminoxane (MAO), modified methylaluminoxane (MMAO), dichloride ethylaluminium ($AlEtCl_2$) and ethylaluminium sesquichloride ($Et_3Al_2Cl_3$, EASC) as activators at 30 °C under 10 atm ethylene; their results are summarized in Table 2. In general, the **Ni1**/EASC system exhibited the highest activity toward ethylene polymerization (entries 1–4, Table 2). Therefore further extensive investigations were explored with EASC as co-catalyst.

In presence of EASC, the complex **Ni1** was explored to optimize the polymerization parameters including the Al/Ni molar ratio, reaction temperature and reaction period (Table 3). At 20 °C, the catalytic activities gradually increased with variations of the Al/Ni molar ratio from 200 to 500 (entries 1–4, Table 3), then slightly decreased with further higher Al/Ni molar ratio as 600 (entry 5, Table 3), indicating the optimum Al/Ni ratio at 500.

Table 2. Selection of a suitable co-catalyst based on **Ni1**.[a]

Entry	Co-cat.	Al/Ni	Act.[b]	T_m[c] / °C	M_w[d]	M_w/M_n[d]
1	MAO	3000	2.64	120.5	33.36	2.3
2	MMAO	3000	1.25	131.0	2.67	1.9
3	$EtAlCl_2$	500	1.97	131.4	5.85	2.5
4	EASC	500	5.68	122.2	18.51	2.6

[a] Conditions: 2.0 μmol of **Ni1**; 10 atm of ethylene; 30 °C; 30 min; 100 ml toluene. [b] 10^6 g of PE (mol of Ni)$^{-1}$ h^{-1}. [c] Determined by DSC. [d] Determined by GPC, 10^4 g·mol^{-1}.

Fixing the Al/Ni ratio at 500, the reaction temperatures were increased from 20 to 80 °C (entries 4, 6–11, Table 3); the highest activity of 1.09 × 10^7 g of PE (mol of Ni)$^{-1}$h^{-1} was observed at 50 °C (entry 8, Table 3). It is worthily mentioned that the polymerization at 80 °C (entry 11, Table 3) maintained a high activity with 3.76 × 10^6 g of PE (mol of Ni)$^{-1}$h^{-1}, meaning that the current system possessed better thermal-stability than their analogous pre-catalysts.[5a,6,7,9a] Regarding the GPC curves of obtained polyethylenes (Figure 3), the higher molecular weights of polyethylenes were obtained at the lower reaction temperatures (entries 4, 6–11, Table 3), the chain transfer and termination would easily take place at the elevated temperature.

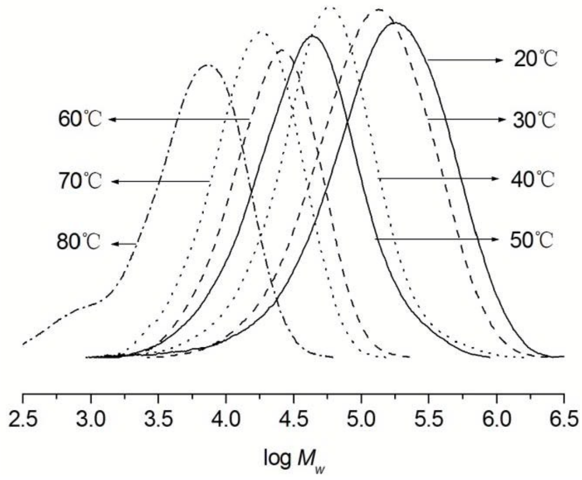


Figure 3. GPC curves of polyethylenes by the **Ni1**/EASC system at different temperature (entries 4, 6–11 in Table 3)

Regarding the lifetime of the active species, the ethylene polymerization was conducted over different periods such as 15, 30, 45 and 60 min (entries 8 and 12–14, Table 3). The highest activity was observed within 15 min (entry 12, Table 3), probably reflecting that the active species were quickly formed upon the addition of EASC. The catalytic activities gradually decreased with prolonging the reaction time, meanwhile the resultant polyethylene possessed the higher molecular weight along with a longer reaction time (Figure 4), indicating some

Table 3. Ethylene polymerization by **Ni1–Ni10** / EASC[a]

Entry	Pre-cat.	Al/Ni	T/°C	t/ min	Act.[b]	T_m[c]/ °C	M_w[d]	M_w/M_n[d]
1	**Ni1**	200	20	30	1.87	131.7	35.72	2.3
2	**Ni1**	300	20	30	4.03	124.8	24.55	3.1
3	**Ni1**	400	20	30	4.19	125.0	24.47	3.6
4	**Ni1**	500	20	30	4.49	123.0	25.11	3.3
5	**Ni1**	600	20	30	3.77	124.5	26.69	3.3
6	**Ni1**	500	30	30	5.68	122.2	18.51	2.6
7	**Ni1**	500	40	30	7.83	107.6	8.07	2.4
8	**Ni1**	500	50	30	10.86	101.0	5.43	2.5
9	**Ni1**	500	60	30	10.30	79.2	2.90	1.8
10	**Ni1**	500	70	30	9.24	79.2	2.07	1.7
11	**Ni1**	500	80	30	3.76	72.4	0.75	2.5
12	**Ni1**	500	50	15	16.48	88.9	4.74	2.1
13	**Ni1**	500	50	45	9.17	98.0	6.46	2.5
14	**Ni1**	500	50	60	8.69	111.6	7.70	2.0
15	**Ni2**	500	50	30	8.07	96.7	7.97	2.4
16	**Ni3**	500	50	30	6.62	59.9	8.78	2.1
17	**Ni4**	500	50	30	8.54	97.0	4.71	2.2
18	**Ni5**	500	50	30	7.88	83.1	6.91	2.1
19	**Ni6**	500	50	30	6.47	98.7	5.55	2.2
20	**Ni7**	500	50	30	5.62	97.4	9.41	2.3
21	**Ni8**	500	50	30	3.11	62.6	9.42	2.2
22	**Ni9**	500	50	30	6.05	107.2	5.97	2.4
23	**Ni10**	500	50	30	3.54	96.5	7.28	2.6
24[e]	**Ni1**	500	50	30	0.69	52.9	17.63	2.6
25[f]	**Ni1**	500	50	30	4.72	95.7	8.75	2.0

[a] Conditions: 2.0μmol of **Ni1**; ethylene pressure 10 atm；total volume 100 ml. [b] 10^6 g of PE (mol of Ni)$^{-1}$h^{-1}. [c] Determined by DSC. [d] Determined by GPC, 10^4 g·mol^{-1}. ethylene pressure 1 atm. [f] ethylene pressure 5 atm.

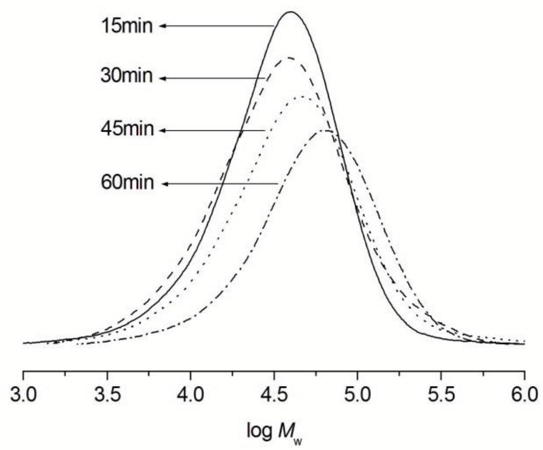


Figure 4. GPC curves of polyethylenes by the **Ni1**/EASC system at different times (entries 8 and 12–14 in Table 3)

catalytic species remained active[11] and consistent with the literature observations.[6,7,9a,12]

Regarding the ethylene pressure, the polymerization experiments were conducted under different pressures such as the 1 atm, 5 atm and 10 atm (entries 8 and 24–25 in Table 3). Higher molecular weights of the resulting polyethylenes were achieved under lower ethylene pressures (Figure 5), which is quite unusual and differing from the common conclusion that the polyethylenes obtained at higher ethylene pressures showed higher molecular weights. Two competitive reactions as chain propagation and migration parallel exist within polymerization of ethylene. The current system results the faster chain migration than propagation at higher pressures, therefore, polyethylenes with lower molecular weights were obtained at higher ethylene pressure, meanwhile the termination and reformation of active species happened. Such phenomena were previously observed also with precatalysts of palladium[13a,b] and cobalt complexes.[13c]

Under the optimum conditions with an Al/Ni ratio of 500 at 50 °C, other bromide complexes were also investigated (entries 15–18 in Table 3) and showed high activities toward ethylene polymerization. The activities decrease in the order **Ni1** [2,6-di(Me)] > **Ni4** [2,4,6-tri(Me)] > **Ni2** [2,6-di(Et)] > **Ni5** [2,6-di(Et)-4-Me] > **Ni3** [2,6-di(i-Pr)]. Less bulky ortho-substituents (R1 group; Scheme 2) in the complexes, the higher catalytic activities; it was considered of the bulky 2,4-dibenzhydryl-6-

chlorophenyl group already occupying some space around nickel site.[7,8,9c]

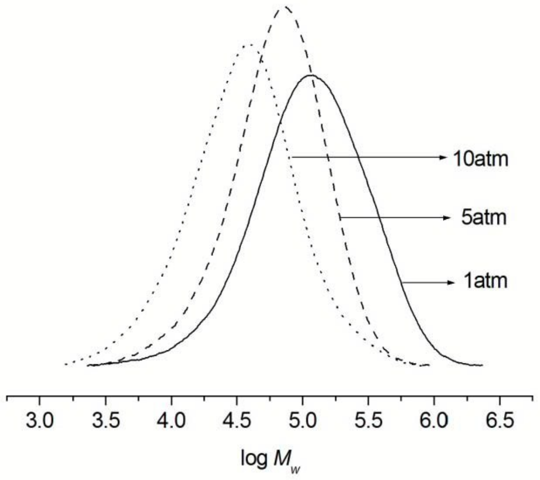


Figure 5. GPC curves of polyethylenes by the **Ni1**/EASC system at different pressures (entries 8 and 24–25 in Table 3)

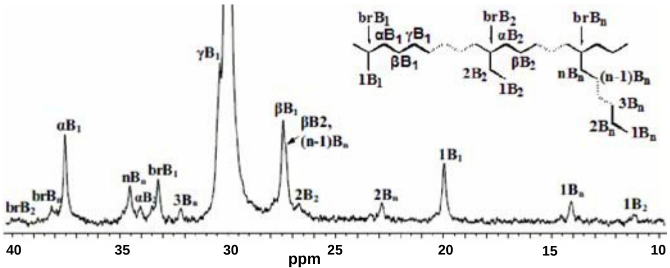


Figure 6. ^{13}C NMR spectrum of the polyethylenes obtained with Ni1/EASC at 50 °C (entry 8, Table 3)

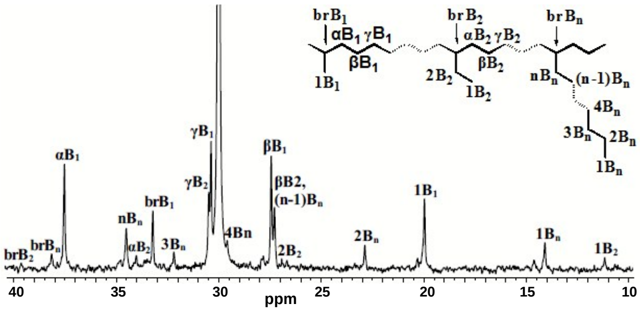


Figure 7. ^{13}C NMR spectrum of the polyethylenes obtained with **Ni1**/EASC at 60 °C (entry 9, Table 3)

Besides the molecular weights and polydispersity measured by the GPC measurement, the DSC data were measured and showed most of the T_m values higher than 100 °C, being generally higher than these of the analogous nickel precatalysts.[7,9] The T_m values are usually relative to the branches of polyethylenes: higher T_m value corresponds to lower branched of polyethylene. The T_m values of polyethylenes obtained at 50 and 60 °C (entries 8 and 9, Table 3) were observed as 101.0 and 79.2 °C, and two samples in deuterated 1,2-dichlorobenzene were measured by the ^{13}C NMR measurement. Interpreted according to the literature,[14] the polyethylene produced at 50 °C (Figure 6) possessed 46 branches per 1000 carbons including methyl (62.4%), ethyl (16.8%) and longer chains (20.8%), whilst the polyethylene obtained at 60 °C (Figure 7) had 59 branches per 1000 carbons, containing methyl (47.1%), ethyl (8.0%) and longer chains (44.9%). At higher polymerization temperature, it is higher potential to have chain termination and migration instead of chain propagation; and the higher possibility of longer branches would be observed due to more chain migration.[15] That was consistent to the palladium precatalysts forming polyethylenes with high branching at the higher temeprature.[13b] Generally the polyethylenes obtained in the current system possessed lower branches than these produced by the nickel analogous precatalysts.[7,9]

Extensively, the nickel chlorides (**Ni6–Ni10**) were investigated and showed high activities towards ethylene polymerization (entries 19–23, Table 3). The tendency of their catalytic performance was similar to that showed above by their bromide analogs. Comparing two sets of catalytic data by the bromide and chloride complexes, the bromide precatalysts generally performed higher activities than chloride precatalysts did, but chloride precatalysts produced polyethylenes with slightly higher molecular weights; these trends were in good agreement with observations by its analogs.[7,8]

Conclusion

A series of 1-(2,4-dibenzhydryl-6-chlorophenylimino)-2-aryliminoacenaphthylnickel halides was prepared and characterized as well as the single crystal X-ray diffraction of representative complexes. Upon activation with EASC at very low Al/Ni ratio (500), all nickel complex pre-catalysts exhibited high activities up to 1.09×10^7 g of PE (mol of Ni)$^{-1}$h^{-1} toward ethylene polymerization; importantly the optimum polymerization temperature was operated at 50 °C along with high activity maintained at 80 °C in the trial of **Ni1**, indicating the better thermal stability than their analogs. The bromide precatalysts showed higher activities than their chloride analogs did, but the chloride precatalysts produced polyethylenes with higher molecular weights. The branching degrees of polyethylenes were observed as several tens by ^{13}C NMR measurement, which were slightly lower than these obtained by their analogs.[7-9] Therefore the polyethylenes could be well tailored in controlling molecular weights and branching through finely tuning the substituents of ligands within 1,2-bis(arylimino)acenaphthylnickel complexes, which are potentially modified to be a practicable precatalysts for a commercial process in near future.

Experimental section

General procedure

All manipulations of air and/or moisture sensitive compounds were carried out under a nitrogen atmosphere using standard Schlenk techniques. All solvents were refluxed and purified under a nitrogen atmosphere before to use. Methylaluminoxane (MAO) (1.46 mol/L in toluene) and methylaluminoxane (MMAO) (1.93 mol/L in heptane, 3A) were purchased from Akzo Nobel Corp.. Dichloride ethylalumium ($AlEtCl_2$) (1.44 mol/L in toluene) and ethylaluminium sesquichloride ($Et_3Al_2Cl_3$, EASC, 0.87 mol/L in toluene) were purchased from Acros Chemical. High-purity ethylene was purchased from Beijing Yanshan Petrochemical Co. and used as received. Other reagents were purchased from Aldrich, Acros, or local suppliers. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DMX 400 MHz instrument at ambient temperature using TMS as an internal standard; δ values were given in ppm and J values in Hz. FT-IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer. Elemental analyses were carried out using a Flash EA 1112 microanalyzer. Molecular weights (M_w) and molecular weight distribution (MWD) of polyethylene were determined by a PL-GPC220 at 150 °C, with 1,2,4-trichlorobenzene as the solvent. The trace and melting points of polyethylene were measured from the second scanning run on Perkin-Elmer TA-Q2000 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 heating rate of 20 °C min^{-1}, and kept for 5 min at 150 °C to remove the thermal history and then cooled at a rate of 20 °C min^{-1} to –20 °C. ^{13}C NMR spectra of the polyethylene was recorded on a Bruker DMX 300 MHz instrument at 135 °C in deuterated 1,2-dichlorobenzene with TMS as an internal standard.

Syntheses and characterization

The syntheses of 1-(2,4-dibenzhydryl-6-chlorophenylimino)-2-aryliminoacenaphethylene derivatives and their nickel halide complexes were performed according to the literature procedure (scheme 2). The 2-(2,4-dibenzhydryl-6-chlorophenylimino) acenaphthylenone was firstly prepared by the stoichiometrial condensation of 2,4-dibenylmethyl-6-chloroaniline with acenaphthylene-1,2-dione, and then further reacted with common aniline derivatives to obtain unsymmetrical 1,2-diiminoacenaphthylene derivatives (**L1–L5**), which individually reacted with either (DME)$NiBr_2$ or $NiCl_2$ to form their bromide (**Ni1–Ni5**) or chloride complexes (**Ni6–Ni10**), respectively.

2-(2,4-Dibenzhydryl-6-chlorophenylimino)acenaphthylenone. A mixture of 2,4-diphenylmethyl-6-chloroaniline (18.38 g, 40 mmol), acenaphthylene-1,2-dione (7.28 g, 40 mmol) and a catalytic amount of *p*-toluenesulfonic acid (1.50 g) were mixed in 500 ml dichloromethane and 50 ml ethanol, and the mixture was stirred at room temperature over night. The solution was concentrated under vacuum, and its residue was further purified by alumina column chromatography (50/1 petroleum ether/ethyl acetate) to obtain the expected compound as the red powder in 9.73 g (39%). *Mp*: 126–128 °C. ^{1}H NMR (400MHz, $CDCl_3$, TMS): δ 8.07 (t, J = 7.4 Hz, 2H), 7.88 (d, J = 8.4 Hz, 1H), 7.75 (t, J = 7.6 Hz, 1H), 7.65–7.21 (m, 7H), 7.14–6.98 (m, 7H), 6.96 (d, J = 6.8 Hz, 3H), 6.78 (s, 1H), 6.75 (d, J = 4.0 Hz, 2H), 6.56 (d, J = 7.2 Hz, 1H), 6.47 (t, J = 7.6 Hz, 2H), 6.22 (t, J = 7.4 Hz, 1H), 5.61 (s, 1H), 5.49 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 144.5,143.3, 141.0, 135.8, 131.8, 130.3, 129.6, 129.3, 129.2, 128.4, 128.3, 128.1, 127.9, 127.7, 127.6, 127.5, 126.5, 126.3, 125.3, 123.0, 121.8.

1-(2,4-Dibenzhydryl-6-chlorophenylimino)-2-(2,6-dimethyl phenylimino)acenaphthylene (L1). 2.49 g (4.0 mmol) 2-(2,4-Dibenzhydryl-6-chlorophenylimino) acenaphethylenone, 0.73 g (6.0 mmol) 2,6-dimethylaniline and a catalytic amount of 0.3 g *p*-toluenesulfonic acid were mixed and refluxed in 100 ml toluene for 2 h. The solution was concentrated under vacuum, then its residue was further purified by the alumina column chromatography (50/1 petroleum ether/ethyl acetate) to obtain the compound **L1** as the yellow powder, 0.46 g (16%). Mp: 138–140 °C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.78 (t, J = 8.4 Hz, 2H), 7.31 (t, J = 7.1 Hz, 5H), 7.23–7.08 (m, 16H), 6.89 (d, J = 7.2 Hz, 2H), 6.76 (s, 1H), 6.59 (d, J = 7.2 Hz, 1H), 6.53–6.46 (m, 3H), 6.27 (t, J = 7.2 Hz, 1H), 5.79 (s, 1H), 5.51 (s, 1H), 2.27 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 142.6, 141.3, 140.5, 140.4, 136.2, 130.5, 130.0, 129.7, 129.5, 129.[illegible], 129.1, 128.9, 128.8, 128.5, 128.3, 128.2, 128.0, 127.7, 127.[illegible], 126.6, 126.3, 125.5, 125.0, 124.9, 123.9, 123.2, 122.3, 122.2, 56.2, 52.8, 31.7, 22.8, 18.3, 17.9, 14.3. IR (KBr; cm^{-1}): 3025(w), 2957(w), 2920(w), 2361(s), 1738(m), 1669(s), 1643(m), 1595(s), 1552(m), 1494(s), 1444(s), 1234(m), 1206(m), 1078(m), 1036(m), 923(s), 888(m), 698(vs). Anal. Calcd. For $C_{52}H_{39}N_2Cl$ (727.33): C, 85.87; H, 5.40; N, 3.85. Found: C, 85.39; H, 5.80; N, 3.62.

1-(2,4-Dibenzhydryl-6-chlorophenylimino)-2-(2,6-diethyl phenylimino)acenaphethylene (L2). According to the synthetic procedure of **L1**, the compound **L2** was obtained from the reaction of 2-(2,4-dibenzhydryl-6-chlorophenylimino) acenaphthylenone (2.00 g, 3.20 mmol), 2,6-diethylaniline (0.72, 4.80 mmol) and *p*-toluenesulfonic acid (0.2 g), as the yellow powder in 0.26 g (11%). *Mp*: 180–182 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.77 (t, J = 8.8 Hz, 2H), 7.33–7.27(m, 5H), 7.24–7.12 (m, 13H), 7.00 (d, J = 6.8 Hz, 3H), 6.89 (d, J = 7.2 Hz, 2H), 6.77 (s, 1H), 6.57 (d, J = 6.8 Hz, 1H), 6.52–6.48 (m, 3H) , 6.28 (t, J = 7.2 Hz, 1H), 5.80 (s, 1H), 5.51 (s, 1H), 2.77–2.68 (m, 1H), 2.62–2.49 (m, 2H), 2.41–2.31 (m, 1H), 2.24 (t, J = 7.4 Hz, 3H), 1.06 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 164.1, 163.7, 161.0, 148.4, 143.6, 143.5, 142.6, 141.1, 140.2, 136.1, 130.7, 129.8, 129.6, 129.3, 129.1, 128.8, 128.6, 128.4, 128.0, 127.7, 127.6, 127.4, 126.5, 126.4, 126.2, 125.4, 124.1, 123.0, 122.5, 122.1, 56.1, 52.7, 24.8, 24.5, 14.4, 13.7. IR (KBr; cm^{-1}): 3023(w), 2965(w), 2361(s), 1677(s), 1651(m), 1597(s), 1549(m), 1493(s), 1439(s), 1257(m), 1193(m), 1080(m), 1032(m), 924(m), 891(m), 830(m), 697(vs). Anal. Calcd. For $C_{54}H_{43}N_2Cl$ (755.39): C, 85.86; H, 5.74; N, 3.71. Found: C, 85.74; H, 5.79; N, 3.68.

1-(2,4-Dibenzhydryl-6-chlorophenylimino)-2-(2,6-diisopropyl-phenylimino)acenaphthylene (L3). Similarly compound **L3** was synthezised by the reaction of 2-(2,4-dibenzhydryl-6-chlorophenylimino)acenaphthylenone (1.20 g, 1.92 mmol), 2,6-diisopropylaniline (0.51 g, 2.89 mmol) and *p*-toluenesulfonic acid (0.2 g), as the yellow powder, 0.35 g (23%). *Mp*: 208–210 °C. ^{1}H NMR (400MHz, $CDCl_3$, TMS): δ 7.76 (t, J = 8.6 Hz, 2H), 7.33–7.28 (m, 7H), 7.24–7.11 (m, 12H), 7.00 (d, J = 6.8 Hz, 2H), 6.88 (d, J = 7.2 Hz, 2H), 6.77 (s, 1H), 6.54–6.45 (m, 4H), 6.27 (t, J = 7.4 Hz, 1H), 5.80 (s, 1H), 5.51 (s, 1H), 3.23–3.[illegible]6 (m, 1H), 3.97–2.91 (m, 1H), 1.33 (d, *J* = 6.8 Hz, 3H), 1.20 (d, *J* = 6.8 Hz, 3H), 1.13 (d, *J* = 6.8 Hz, 3H), 0.86 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 163.9, 161.5, 147.3, 143.7, 143.6, 142.7, 141.2, 140.3, 136.2, 135.7, 135.6, 130.5, 129.9, 129.7, 129.5, 129.4, 129.2, 128.9, 128.8, 128.5, 128.2, 127.8, 127.6, 127.5, 126.6, 126.3, 125.6, 124.6, 123.8, 123.4, 123.2, 123.1, 122.2, 56.2, 52.8, 28.7, 28.6, 23.8, 23.7, 23.6, 23.3. IR (KBr; cm^{-1}): 3058(w), 2965(m), 2361(m), 1680(m), 1653(m), 1597(m), 1549(m), 1493(s), 1439(s), 1324(w), 1253(m), 1187(m), 1079(m), 1033(m), 923(m), 890(m), 780(s), 698(vs). Anal. Calcd. For $C_{56}H_{47}N_2Cl$ (783.44): C, 85.85; H, 6.05; N, 3.58. Found: C, 85.53; H, 6.20; N, 3.56.

1-(2,4-Dibenzhydryl-6-chlorophenylimino)-2-(2,4,6-trimethyl-phenylimino)acenaphthylene (L4). Extensively compound **L4** was obtained from the reaction of 2-(2,4-dibenzhydryl-6-chlorophenylimino)acenaphthylenone (1.87 g, 3.00 mmol), 2,4,6-trimethylaniline (0.61 g, 4.50 mmol) and *p*-toluenesulfonic acid (0.2 g), as the yellow powder, 0.40 g (18%). *Mp*: 140–142 °C. ^{1}H NMR (400MHz, $CDCl_3$, TMS): δ 7.78 (t, *J* = 9.6 Hz, 2H), 7.34–7.29 (m, 5H), 7.24–7.12 (m, 10H), 7.01–6.97 (m, 5H), 6.89 (d, *J* = 7.6 Hz, 2H), 6.77 (s, 1H), 6.66 (d, *J* = 7.2 Hz, 1H), 6.53–6.47 (m, 3H), 6.27 (t, *J* = 7.2 Hz, 1H), 5.80 (s, 1H), 5.51 (s, 1H), 2.39 (s, 3H), 2.24 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 163.7, 161.2, 146.7, 145.4, 143.6, 143.5, 142.5, 141.1, 140.4, 140.2, 136.1, 133.0, 130.3, 129.6, 129.2, 129.1, 128.9, 127.9, 127.3, 126.2, 125.4, 124.6, 124.6, 123.0, 122.2, 122.1, 56.1, 53.4, 52.7, 31.6, 22.7, 20.9, 18.1, 17.1, 14.1. IR (KBr; cm^{-1}): 2959(w), 2923(w), 2361(s), 1669(m), 1644(m), 1597(m), 1550(w), 1443(s), 1233(m), 1075(m), 1033(m), 922(m), 889(w), 783(s), 698(vs). Anal. Calcd. For $C_{53}H_{41}N_2Cl$ (741.36): C, 85.86; H, 5.57; N, 3.78. Found: C, 85.40; H, 5.88; N, 3.63.

1-(2,4-Dibenzhydryl-6-chlorophenylimino)-2-(2,6-diethyl-4-methylphenylimino)acenaphthylene (L5). The compound **L5** was similarly prepared by the reaction of 2-(2,4-dibenzhydryl-6-chlorophenylimino)acenaphthylenone (1.25 g, 2.00 mmol), 2,6-diethyl-4-methylaniline (0.49 g, 3.00 mmol) and *p*-tolunenesulfonic acid (0.2 g), as the orange powder in 0.37 g (24%). *Mp*: 134–136 °C. ^{1}H NMR (400MHz, $CDCl_3$, TMS): δ 7.76 (t, *J* = 9.0 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 5H), 7.24–7.11 (m, 11H), 7.04–7.00 (m, 4H), 6.89 (d, *J* = 7.6 Hz, 2H), 6.77 (s, 1H), 6.64 (d, *J* = 6.8 Hz, 1H), 6.52–6.47 (m, 3H), 6.28 (t, *J* = 7.2 Hz, 1H), 5.80 (s, 1H), 5.51 (s, 1H), 2.73–2.63 (m, 1H), 2.59–2.46 (m, 2H), 2.43 (s, 3H), 2.37–2.25 (m, 1H), 2.23 (t, *J* = 7.4 Hz, 3H), 1.06 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 163.8, 161.3, 145.8, 145.4, 143.6, 143.5, 142.6, 141.1, 140.4, 140.1, 136.1, 133.2, 130.6, 130.3, 129.8, 129.6, 129.3, 129.2, 128.7, 128.5, 128.4, 128.0, 127.7, 127.6, 127.3, 127.2, 127.0, 126.5, 126.2, 125.4, 123.0, 122.6, 122.1, 56.1, 52.7, 24.8, 24.5, 21.2, 14.6, 13.8. IR (KBr; cm^{-1}): 2966(w), 2361(m), 1678(m), 1651(m), 1598(m), 1549(s), 1493(s), 1443(s), 1257(m), 1153(w), 1079(m), 1031(m), 922(m), 891(m), 779(s), 738(s), 699(vs). Anal. Calcd. For $C_{55}H_{45}N_2Cl$ (769.41): C, 85.86; H, 5.90; N, 3.64. Found: 85.75; H, 5.85; N, 3.65.

1-(2,4-Dibenzhydryl-6-chlorophenylimino)-2-(2,6-dimethyl phenylimino)acenaphthylylnickel dibromide (**Ni1**). Compound **L1** (0.22 g, 0.30 mmol) and (DME)$NiBr_2$ (0.083 g, 0.27 mmol) were mixed in 10 ml dichloromethane, and stirred at room temperature for 24 h. The solution was concentrated and then 20 ml diethyl ether was added to precipitate resulting complex which was further washed by diethyl ether and given red nickel complex **Ni1**, 0.22 g (86%). IR (KBr; cm^{-1}): 2974(w), 2865(w), 2361(s), 1652(m), 1625(s), 1581(s),1491(m), 1442(s), 1295(s), 1193(w), 1138(w), 1105(s), 1033(m), 920(w), 890(w), 832(m), 776(s), 697(vs). Anal. Calcd. for $C_{52}H_{39}N_2ClBr_2Ni$ (945.83): C, 66.03; H, 4.16; N, 2.96. Found: C, 65.88; H, 4.33; N, 3.05.

1-(2,4-Dibenzhydryl-6-chlorophenylimino)-2-(2,6-diethyl phenylimino)acenaphethylylnickel dibromide (**Ni2**). Using compound **L2** instead of **L1** in the same procedure in synthesizing **Ni1**, complex **Ni2** was obtained as the brown powder in 0.10 g (88%). IR (KBr; cm^{-1}): 2972(m), 2931(w), 2869(w), 2361(m), 1654(m), 1626(s), 1586(s), 1491(m), 1446(s), 1291(m), 1261(m), 1183(m), 1109(s), 1075(m), 1029(m), 769(s), 741(s), 702(vs). Anal. Calcd. For $C_{54}H_{43}N_2ClBr_2Ni$ (973.89): C, 66.60; H, 4.45; N, 2.88. Found: C, 66.22; H, 4.79; N, 2.79.

1-(2,4-Dibenzhydryl-6-chlorophenylimino)-2-(2,6-diisopropyl phenylimino)acenaphthylylnickel dibromide (**Ni3**). Similarly the complex **Ni3** was isolated as the red powder in 0.13 g (96%). IR (KBr; cm^{-1}): 2970(m), 2871(w), 2362(s), 1652(m), 1624(m), 1583(m), 1560(w), 1491(m), 1443(s), 1415(m), 1383(m), 1295(m), 1108(s), 1075(m), 1052(m), 919(w), 773(m), 698(vs). Anal. Calcd. For $C_{56}H_{47}N_2ClBr_2Ni$ (1001.94): C, 67.13; H, 4.73; N, 2.80. Found: C, 66.76; H, 4.75; N, 2.78.

1-(2,4-Dibenzhydryl-6-chlorophenylimino)-2-(2,4,6-trimethyl phenylimino)acenaphthylylnickel dibromide (**Ni4**). Extensively complex **Ni4** was obtained as the brown powder in 0.12 g (69%). IR (KBr; cm^{-1}): 2977(m), 2362(s), 1650(m), 1624(s),1593(s), 1494(s), 1442(s), 1295(m), 1231(m), 1156(w), 1075(m), 1032(m), 919(m), 772(s), 697(vs). Anal. Calcd. For $C_{53}H_{41}N_2ClBr_2Ni$ (959.86): C, 66.32; H, 4.31; N, 2.92. Found: C, 66.07; H, 4.39; N, 2.92.

1-(2,4-Dibenzhydryl-6-chlorophenylimino)-2-(2,6-diethyl-4-methylphenylimino)acenaphethylylnickel dibromide (**Ni5**). Extensively complex **Ni5** was obtained as the red powder in 0.15 g (84%). IR (KBr; cm^{-1}): 2964(m), 2929(m), 2361(s), 1656(m), 1625(s), 1585(s), 1560(m), 1493(s), 1446(s), 1414(s), 1292(m), 1075(m), 1030(s), 957(w), 923(w), 858(m), 827(m), 773(s), 696(vs). Anal. Calcd. For $C_{55}H_{45}N_2ClBr_2Ni$ (987.91): C, 66.87; H, 4.59; N, 2.84. Found: C, 66.43; H, 4.52; N, 2.85.

1-(2,4-Dibenzhydryl-6-chlorophenylimino)-2-(2,6-dimethyl phenylimino)acenaphthylylnickel dichloride (**Ni6**). Employing the same procedure for **Ni1**, using the equimolar $NiCl_2{\cdot}6H_2O$ instead of its analog (DME)$NiBr_2$, complex **Ni6** was obtained as the yellow powder in 0.11 g (74%). IR (KBr; cm^{-1}): 3057(w), 3025(w), 1661(w), 1628(m), 1588(s), 1494(s), 1444(s), 1291(m), 1262(w), 1191(w), 1080(m), 1031(m), 921(w), 888(w), 831(m), 773(s), 739(s), 697(vs). Anal. Calcd. for $C_{52}H_{39}N_2Cl_3Ni$ (856.93): C, 72.88; H, 4.59; N, 3.27. Found: C, 72.72; H, 4.35; N, 3.55.

1-(2,4-Dibenzhydryl-6-chlorophenylimino)-2-(2,6-diethyl phenylimino)acenaphthylylnickel dichloride (**Ni7**). Using the similar synthetic procedure of complex **Ni6**, but compound **L2** was used instead of **L1**, complex **Ni7** was isolated as the yellow powder in 0.11 g (74%). IR (KBr; cm^{-1}): 3058(w), 3026(w), 2964(w), 1665(m), 1633(m), 1588(s), 1559(w), 1494(m), 1445(s), 1415(m), 1291(m), 1264(m), 1186(m), 1079(m), 1033(m), 829(m), 775(s), 743(s), 698(vs). Anal. Calcd. For $C_{54}H_{43}N_2Cl_3Ni$ (884.99): C, 73.29; H, 4.90; N, 3.17. Found: C, 73.07; H, 5.00; N, 2.89.

1-(2,4-Dibenzhydryl-6-chlorophenylimino)-2-(2,6-diisopropyl phenylimino)acenaphthylylnickel dichloride (**Ni8**). Similarly complex **Ni8** was obtained as the yellow powder in 0.07 g (43%). IR (KBr; cm^{-1}): 3058(w), 3026(w), 2967(m), 1660(m), 1624(m), 1591(s), 1491(m), 1445(s), 1416(w), 1291(m), 1259(m), 1182(m), 1080(m), 1033(s), 831(m), 779(s), 744(s), 702(vs). Anal. Calcd. For $C_{56}H_{47}N_2Cl_3Ni$ (913.04): C, 73.67; H, 5.19; N, 3.07. Found: C, 73.27; H, 5.14; N, 2.79.

1-(2,4-Dibenzhydryl-6-chlorophenylimino)-2-(2,4,6-trimethyl phenylimino)acenaphthylylnickel dichloride (**Ni9**). Extensively complex **Ni9** was isolated as the yellow powder in 0.08 g (71%). IR (KBr; cm^{-1}): 3058(w), 3025(w), 2972(s), 1661(m), 1630(m), 1591(s), 1558(w), 1494(m), 1444(s), 1416(m), 1290(m), 1155(m), 1113(m), 1033(m), 832(m), 774(s), 737(s), 699(vs). Anal. Calcd. For $C_{53}H_{41}N_2Cl_3Ni$ (870.96): C, 73.09; H, 4.74; N, 3.22. Found: C, 72.76; H, 4.75; N, 2.88.

1-(2,4-Dibenzhydryl-6-chlorophenylimino)-2-(2,6-diethyl-4-methylphenylimino)acenaphthylylnickel dichloride (**Ni10**). Extensively complex **Ni10** was obtained as the yellow powder in 0.08 g (49%). IR (KBr; cm^{-1}): 3061(w), 3025(w), 2971(m), 1666(m), 1634(m), 1594(s), 1492(m), 1447(s), 1414(m), 1291(m), 1259(m), 1113(m), 1077(m), 1034(s), 773(s), 741(s), 702(vs). Anal. Calcd. For $C_{55}H_{45}N_2Cl_3Ni$ (899.01): C, 73.48; H, 5.05; N, 3.12. Found: C, 73.01; H, 5.06; N, 3.19.

X-Ray crystallographic study

Single crystals of the nickel complexes **Ni2** and **Ni5** were obtained by slow diffusion of diethyl ether into dichloromethane solution at room temperature. Single-crystal X-ray diffraction studies for them were carried out on a Rigaku Saturn 724$^+$ CCD with graphite-monochromatic Mo-Kα radiation (λ = 0.71073 Å) at 173(2) K, the 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 structure was solved by direct methods and refined by full-matrix least squares on F^2. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package.[16] Details of the crystal data and structure refinements for **Ni2** and **Ni5** are shown in Table 4.

Ethylene polymerization

Ethylene polymerization at 1 atm ethylene pressure. The polymerization at 1 atm ethylene pressure was carried out in Schlenk techniques. The complex **Ni1** was added, and the require amount of co-catalyst (EASC) was added by a syringe, the solvent is toluene. Then the solution was stirred with 1 atm ethylene atmosphere at 50 °C. After 30 min, the solution was quenched with 10% hydrochloric acid in ethanol. The polymer was washed with ethanol, then dried in vacuum at 60 °C and weighed.

Ethylene polymerization at 10/5 atm ethylene pressure. The polymerization at high ethylene pressure was carried out in stainless steel autoclave (0.25 L) equipped with an ethylene pressure control system, a mechanical stirrer and a temperature controller. At the required reaction temperature, 30 ml toluene (freshly distilled) was injected into the autoclave, then 50 ml toluene which dissolved the complex (2.0 μmol), the require amount of co-catalyst (MAO, MMAO, $AlEtCl_2$,EASC), the another 20 ml toluene were injected by syringe successively. The autoclave was immediately pressurized to high ethylene pressure and the stir started. After the required reaction time, the ethylene was released; the polymer was washed by ethanol, and then dried in vacuum at 60 °C and weighed.

Table 4. Crystal data and structure refinements for **Ni2** and **Ni5**

	Ni2	Ni5
Empirical formula	$C_{54}H_{43}N_2ClBr_2Ni·CH_2Cl_2$	$C_{55}H_{45}N_2ClBr_2Ni$
Formula weight	1058.81	987.91
Temperature/K	291(2)	173(2)
Wavelength/ Å	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic
Space group	P–1	P2(1)2(1)2(1)
a/ Å	12.0590(13)	16.470(3)
b/ Å	15.8340(14)	16.715(3)
c/ Å	26.7560(15)	16.782(3)
Alpha/°	88.590(2)	90
Beta/°	83.230(3)	90
Gamma/°	72.860(2)	90
Volume/ $Å^3$	4847.6(7)	4620.0(16)
Z	4	4
Dcalcd/($g·cm^{-3}$)	1.451	1.420
μ/mm^{-1}	2.253	2.247
F(000)	2152	2016
Crystal size/mm	0.37 × 0.14 × 0.08	0.44 × 0.43 × 0.26
θ Range (º)	1.35–27.00	1.74–27.48
Limiting indices	–15 ≤ h ≤ 15	–21 ≤ h ≤ 21
	–20 ≤ k ≤ 20	–21 ≤ k ≤ 21
	–34 ≤ l ≤ 34	–21 ≤ l ≤ 20
No. of rflns collected	66187	31595
No. unique rflns	21117	10563
R(int)	0.0128	0.0765
No. of params	1139	553
Completeness to θ	99.7 %	99.7 %
Goodness of fit on F^2	1.057	1.092
Final R indices [I >2∑(I)]	R1 = 0.0527	R1 = 0.0526
	wR2 = 0.0967	wR2 = 0.1146
R indices (all data)	R1 = 0.0757	R1 = 0.0574
	wR2 = 0.1001	wR2 = 0.1174
Largest diff. peak, and hole/($e\ Å^{-3}$)	0.679 and –0.473	0.475 and –0.751

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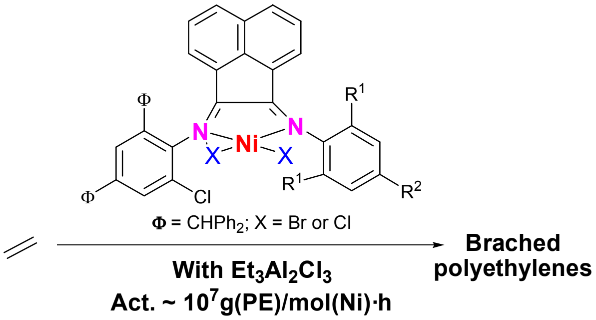
Graphical Abstract

for

Enhancing thermo-stability to ethylene polymerization: Ssynthesis, characterization and the catalytic behavior of 1-(2,4-dibenzhydryl-6-chlorophenylimino)-2-aryliminoacenaphthylnickel halides

Linlin Fan, Erlin Yue, Shizhen Du, Cun-Yue Guo, Xiang Hao, and Wen-Hua Sun



The title complexes had better thermo-stability and produced less branched PE in comparison to their analogs.

The 1-(2,4-dibenzhydryl-6-chlorophenylimino)-2-aryliminoacenaphthylnickel halides exhibited high activities up to 1.09 $\times 10^7$ g of PE (mol of Ni)$^{-1}$h^{-1} in ethylene polymerization with better thermo-stability under activation with ethylaluminium sesquichloride.