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Synthesis and characterization of 2-(2-benzhydrylnaphthyliminomethyl) pyridylnickel halides: formation of branched polyethylene

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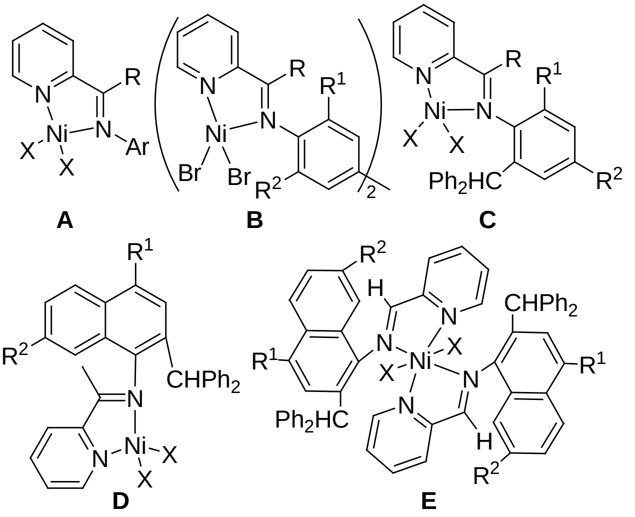
Abstract: A series of 2-(2-benzhydrylnaphthyliminomethyl)pyridine derivatives (**L1**–**L3**) was prepared and used to synthesize the corresponding bis-ligated nickel(II) halide complexes (**Ni1**–**Ni6**) in good yield. The molecular structures of representative complexes, namely the bromide **Ni3** and the chloride complex **Ni6**, were confirmed by single crystal X–ray diffraction, and revealed a distorted octahedral geometry at nickel. Upon activation with either methylaluminoxane (MAO) or modified methylaluminoxane (MMAO), all nickel complex pre-catalysts exhibited high activities (up to 2.02 × 10^7 g(PE)·mol^{-1}(Ni)·h^{-1}) towards ethylene polymerization, producing branched polyethylene of low molecular weight and narrow polydispersity. The influence of the reaction parameters and the nature of the ligands on the catalytic behavior of the title nickel complexes were investigated.

Introduction

Polyolefin materials are extensively used in our daily life and the annually consumption amounts to over 130 million tonnes. In order to produce advanced polyolefins using new catalytic systems, attention has switched to late-transition metal complex pre-catalysts in both the industrial and academic arenas.[1,2] Since the discovery of the α-diiminometal (Ni or Pd) complexes[3] and bis(imino)pyridylmetal (Fe or Co) complexes,[4] the characteristic features of the polyethylene obtained have been shown to rely on metal employed: highly linear polyethylene was generally produced from either iron or cobalt complex pre-catalysts,[1,2a] whereas branched polyethylene was commonly observed from catalytic systems based on nickel complex pre-catalysts.[1,2b] The polymerization mechanism operating within nickel systems is an illustration of how hydrogen-elimination facilitates chain-transfer to produce branched polymers.[5] Currently, industrial processes for accessing branched polyethylenes mostly rely on the copolymerization of ethylene with α-olefins. Nickel pre-catalysts are providing new approaches to highly branched polyethylene, and the resulting new polymers can potentially exhibit new properties and may yield a new family of advanced polyethylenes.[2b] Therefore, the syntheses of nickel complexes have extensively been conducted through designing new ligands with modification via the use of different substituents.[6] As an example, the 2-iminopyridylnickel complex pre-catalysts (**A**, Scheme 1) exhibited high activities towards ethylene polymerization or oligomerization,[7] whilst the methyl-bridged binuclear complex pre-catalysts (**B**, Scheme 1) performed ethylene oligomerization and polymerization.[8,9] Recently, progress has been made through the use of benzhydryl-substituted anilines,[10–12] and the 2-iminopyridylnickel complex model (**C**, Scheme 1) was revisited to reveal high activities solely for ethylene polymerization.[13]



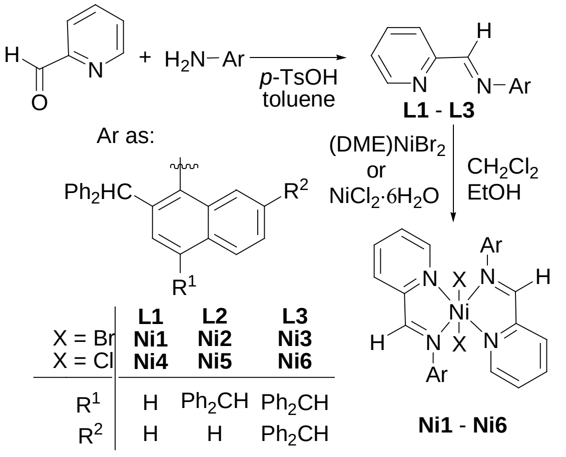
Scheme 1 Models of *N*,*N*-bidentate mono- and bi-metallic nickel complexes

Subsequently, new benzhydryl-substituted naphthylamines were designed and were used to prepare 2-(1-(2-benzhydryl-naphthylimino)ethyl)pyridylnickel complexes (**D**, Scheme 1), which revealed high activities of up to 1.22×10^7 g(PE)·mol^{-1}(Ni)·h^{-1} towards ethylene polymerization.[14] Given this, the 2-(2-benzhydrylnaphthyliminomethyl)pyridine derivatives are also of interest, particularly in terms of their nickel complexes and the polymerization catalysis thereof. Interestingly, such 2-(2-benzhydrylnaphthyliminomethyl)pyridyl nickel halide complexes are bis-ligated complexes (**E**, Scheme 1), which according to literature would be expected to be inactive in catalysis polymerization.[15] However, the title nickel complexes were found to exhibit even higher activities toward ethylene polymerization than did their 2-(1-(2-benzhydrylnaphthylimino)ethyl)pyridyl-nickel analogues.[14] Herein, the synthesis and characterization of the 2-(2-benzhydrylnaphthyliminomethyl) pyridine derivatives and their nickel complexes are reported, and the catalytic performances of these nickel complexes, as well as the properties of the resulting polyethylene, are investigated.

Results and discussion

Synthesis and characterization

The series of 2-(2-benzhydrylnaphthyliminomethyl)pyridine derivatives (**L1–L3**, Scheme 2) was readily synthesized by the condensation reaction of picolinaldehyde with benzhydryl-substituted naphthylamines in moderate yields following the reported procedure.[14] All organic compounds were characterized by FT–IR, ^{1}H and ^{13}C NMR spectroscopy as well as by elemental analysis.



Scheme 2 Synthetic procedure for the organic and nickel complexes

Trials of the reaction of the 2-(2-benzhydrylnaphthyl-iminomethyl)pyridine in dichloromethane solution with different molar ratios of $NiCl_2\cdot 6H_2O$ or $(DME)NiBr_2$ in ethanol were conducted, and the bis-ligated nickel halide (chloride or bromide) complexes (**Ni1–Ni6**) were best isolated when using two equivalents of organic compound to nickel halide (Scheme 2). According to the FT–IR spectra, the C=N stretching vibrations in complexes **Ni1–Ni6** were shifted to lower frequencies in the region 1622–1634 cm^{-1} with weaker intensity compared to the peaks at 1642–1643 cm^{-1} for the free organic compounds, indicating the effective coordination between the imino-group and the cationic nickel center. Elemental analysis data was consistent with these nickel complexes having the formula L_2NiX_2 (X = Br, Cl). Crystal structures of a representative bromide (**Ni3**) and chloride (**Ni6**) complexes were determined.

Single-crystal X–ray diffraction studies

Single crystals of **Ni3** and **Ni6** suitable for X–ray diffraction analysis were obtained by laying diethyl ether onto their dichloromethane solutions at room temperature. Both complexes **Ni3** and **Ni6** are bis-ligated mononickel(II) complexes possessing a distorted octahedral geometry at the nickel center. The molecular structures of **Ni3** and **Ni6** are shown in Fig. 1 and 2, respectively, and their selected bond lengths and angels are tabulated in Table 1.

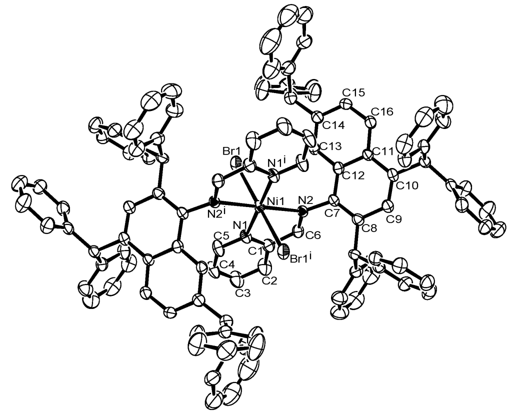


Fig. 1 ORTEP drawing of **Ni3**. Thermal ellipsoids are shown at 30 % probability level. Hydrogen atoms have been omitted for clarity.

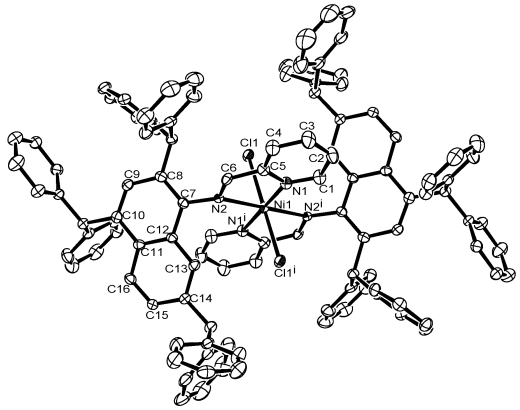


Fig. 2 ORTEP drawing of **Ni6**. Thermal ellipsoids are shown at 30 % probability level. Hydrogen atoms have been omitted for clarity.

Table1 Selected bond lengths (Å) and angles (°) for **Ni3** and **Ni6**

Ni3		**Ni6**	
	Bond lengths (Å)		
Ni(1)–N(1)	2.068(3)	Ni(1)–N(1)	2.086(3)
Ni(1)–N(2)	2.257(3)	Ni(1)–N(2)	2.234(3)
Ni(1)–N(1^i)	2.068(3)	Ni(1)–N(1^i)	2.086(3)
Ni(1)–N(2^i)	2.257(3)	Ni(1)–N(2^i)	2.234(3)
Ni(1)–Br(1)	2.5415(6)	Ni(1)–Cl(1)	2.4024(9)
	Bond angles (°)		
N(1)–Ni(1)–N(2)	78.08(10)	N(1)–Ni(1)–N(2)	78.13(10)
N(1)–Ni(1)–N(1^i)	180.00(17)	N(1)–Ni(1)–N(1^i)	180.00(18)
N(1^i)–Ni(1)–N(2)	101.92(15)	N(1^i)–Ni(1)–N(2)	101.87(10)
N(1)–Ni(1)–N(2^i)	101.92(15)	N(1)–Ni(1)–N(2^i)	101.87(10)
N(1^i)–Ni(1)–N(2^i)	78.08(10)	N(1^i)–Ni(1)–N(2^i)	78.13(10)
N(2)–Ni(1)–N(2^i)	180.0(3)	N(2)–Ni(1)–N(2^i)	180.00(13)
N(1)–Ni(1)–Br(1)	87.98(8)	N(1)–Ni(1)–Cl(1)	91.33(8)
N(1^i)–Ni(1)–Br(1)	92.02(8)	N(1^i)–Ni(1)– Cl (1)	88.67(8)
N(2)–Ni(1)–Br(1)	96.26(7)	N(2)–Ni(1)– Cl (1)	83.32(7)
N(2^i)–Ni(1)–Br(1)	83.74(7)	N(2^i)–Ni(1)– Cl (1)	96.68(7)

As shown in Fig. 1, the nickel center is coordinated by four nitrogens (N1, N2, N1^i and N2^i) of the two chelate ligands and two bromides (Br1 and Br1^i), which is similar to the aniline-based bis(iminopyridyl)nickel dibromide.[13,16] There is a five-membered hetero-nickel plane with N1, Ni1, N2, C1 and C6 atoms, and the bond length of Ni1–N1$_{pyridine}$ 2.068 (3) Å is shorter than that of Ni1–N2$_{imino}$ 2.257 (3) Å, reflecting the stronger bonding between the N$_{imino}$ and cationic nickel center. The dihedral angle between the pyridyl and imino-naphthyl planes is 59.87 °, which is similar to that within the nickel analogues bearing (1-aryliminoethyl)pyridines.[13] A closely similar structure was observed for the chloride analogue **Ni6** (Fig. 2 and Table 1).

Catalytic Behavior toward Ethylene Polymerization

Various co-catalysts such as MAO, MMAO and Et_2AlCl were used to activate the nickel pre-catalyst **Ni2** for ethylene polymerization (runs 1–3 in Table 2), which indicated that higher catalytic activities in ethylene polymerization were achievable when employing either MAO or MMAO.

Table 2 Ethylene polymerization by **Ni2** using various co-catalysts [a]

Run	Co-catalyst	Al/Ni	Yield/g	Activity [b]	M_w/gmol^{-1} [c]	M_w/M_n [c]	T_m/ºC [d]
1	MAO	1000	11.3	11.3	2817	2.45	109.3
2	MMAO	1000	4.88	4.88	2251	2.24	111.7
3	Et_2AlCl	300	3.14	3.14	1425	1.88	101.2

[a] General conditions: 2 μmol of Ni; 30 min; 30 ºC; 100 mL of toluene for 10 atm of ethylene. [b] 10^6 g(PE)·mol^{-1}(Ni)·h^{-1}. [c] Determined by GPC. [d] Determined by DSC.

Ethylene polymerization in the presence of MAO

In the presence of the co-catalyst MAO, complex **Ni2** was evaluated to optimize the polymerization conditions including the molar ratio of Al/Ni and the reaction temperature, and the results are collected in Table 3, which also includes some of the properties of the obtained polyethylene.

Table 3 Ethylene polymerization by **Ni1–Ni6**/MAO [a]

Run	Pre-cat.	Al/Ni	T/ ºC	Yield/g	Activity [b]	M_w [c] /gmol^{-1}	M_w/M_n [c]	T_m [d]/ºC
1	**Ni2**	750	30	1.10	1.10	3093	2.54	122.4
2	**Ni2**	1000	30	11.3	11.3	2817	2.45	109.3
3	**Ni2**	1250	30	11.5	11.5	2434	2.34	107.5
4	**Ni2**	1500	30	14.5	14.5	1718	2.23	103.4
5	**Ni2**	1750	30	10.5	10.5	1700	2.06	87.0
6	**Ni2**	2000	30	13.4	13.4	1722	2.12	104.4
7	**Ni2**	2250	30	11.5	11.5	1850	2.16	105.8
8	**Ni2**	1500	20	5.26	5.26	5939	2.82	124.1
9	**Ni2**	1500	40	10.5	10.5	1642	1.95	101.5
10	**Ni2**	1500	50	6.27	6.27	942	1.71	67.3
11	**Ni2**	1500	60	4.14	4.14	716	1.68	58.5
12	**Ni1**	1500	30	17.5	17.5	1300	2.06	77.9
13	**Ni3**	1500	30	20.2	20.2	618	2.03	65.9
14	**Ni4**	1500	30	9.13	9.13	2701	2.17	118.7
15	**Ni5**	1500	30	10.7	10.7	2566	2.25	84.9
16	**Ni6**	1500	30	12.0	12.0	1112	1.89	84.8

[a] General conditions: 2 μmol of Ni; 30 min; 100 mL of toluene. [b] 10^6 g(PE)·mol^{-1}(Ni)·h^{-1}. [c] Determined by GPC. [d] Determined by DSC.

At 30 °C and 10 atm of ethylene, the Al/Ni ratio was changed from 750 to 2250 (runs 1–7, Table 3), and the highest activity was observed with the Al/Ni ratio 1500 (run 4, Table 3) at 1.45 × 10^7 g(PE)·mol^{-1}(Ni)·h^{-1}. In general, the molecular weights of the resultant polyethylene slightly decreased on increasing the Al/Ni ratio (runs 1–5, Table 3), which was ascribed to faster chain transfer on increasing the Al concentration.[12b] However, the catalytic system with the Al/Ni ratio of 2000 (run 6, Table 3) revealed a higher activity than did the system with the Al/Ni ratio of 1750 (run 5, Table 3). Therefore there are two maximum activities for such catalytic systems at different Al/Ni ~~ratio~~ ratios of 1500 and 2000. ~~of MAO, indicating potentially two kinds of active species.~~ As seen in the GPC curve (Fig. 3), all catalytic systems generally exhibited single-site catalysis with narrow polydispersity for all the obtained polyethylene.

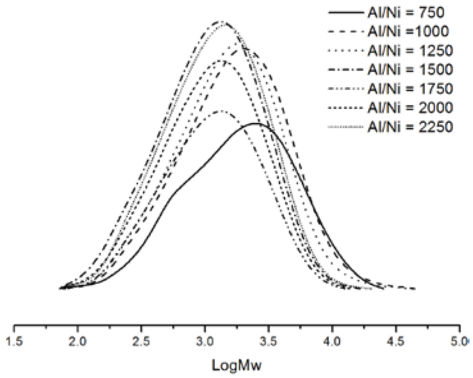


Fig. 3 GPC traces for the polyethylene by **Ni2/**MAO system with various Al/Ni ratios (runs 1–7 in Table 3).

On fixing the Al/Ni molar ratio at 1500, the reaction temperature was changed from 20 to 60 °C (runs 4, and 8–11, Table 3); the highest activity observed, namely 1.45 × 10^7 g (PE)·mol^{-1}(Ni)·h^{-1}, was at 30 °C (run 4 in Table 3). The GPC data indicated that higher molecular weight polyethylene was obtained at lower temperatures, and the GPC curves are shown in Fig. 4. These phenomena were consistent to previous observations for 2-iminopyridylnickel pre-catalysts,[6,10,13,14] and are ascribed to increased chain-transfer and termination at higher temperature. As well as the GPC measurements, the melting points of resultant polyethylenes were measured by differential scanning calorimetry (DSC). The T_m values of the polyethylene dramatically decreased on elevating the reaction temperature (runs 4, and 8–11, Table 3), and are slightly higher than those of their analogs bearing 2-(1-(2-benzhydrylnaphthylimino)ethyl) pyridines, probably reflecting less branches in the current systems.

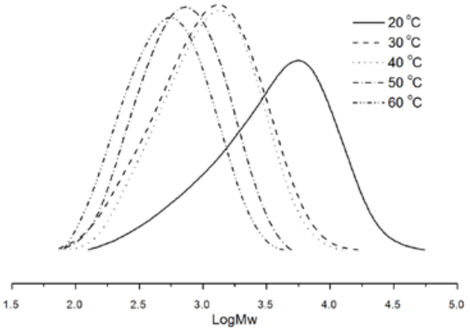


Fig. 4 GPC curves for the polyethylene obtained using the **Ni2**/ MAO system at different temperatures (runs 4, 8–11 in Table 3)

On the basis of above results, the optimum conditions with an Al/Ni ratio of 1500 at 30 °C were utilized to explore the catalytic behavior of all the other nickel pre-catalysts **Ni1** and **Ni3–Ni6** (runs 12–16, Table 3). All nickel pre-catalysts exhibited high activities towards ethylene polymerization, which differs from reported bis-ligated nickel pre-catalysts which usually possess low catalytic activities.[15] In addition, the two halides are located in *trans* positions, which is not favorably for coordination insertion; the transformation of these bis-ligated nickel species into mono-ligated active species is assumed to occur during the ethylene polymerization.[17] It is noteworthy that the nickel pre-catalysts (**Ni3** and **Ni6**) bearing more benzhydryl substituents exhibited relatively higher activities than did their analogues, which is different to the catalytic performances by the analogues ligated by 2-(1-(2-benzhydrylnaphthylimino)ethyl) pyridines in the presence of Et_2AlCl.[14]

The ^{13}C NMR spectrum for the polyethylene obtained from the **Ni2**/MAO at 60 °C (run 11 in Table 3) is shown in Fig. 5. Interpreted according to the literature,[18] there are 182 branches per 1000 carbons, and the signals are presented in Table 4, which indicates that the main branches include methyl (26.88 %), some long chains (35.18 %) and amyl chains (17.00 %), which is consistent to the observations for the analogue system comprising the 2-(1-(2-benzhydrylnaphthylimino)ethyl)pyridylnickel halide complexes.[14]

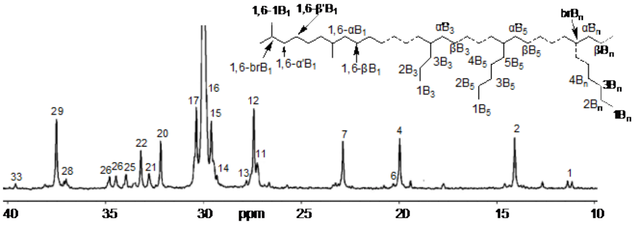


Fig. 5 ^{13}C NMR spectrum of the polyethylene by **Ni2**/ MAO at 60 °C (run 11 in Table 3)

Table 4 Percentage of branches for the polyethylene (run 11 in Table 3)[18]

Peak no.	Chem. Shifts /ppm	Integral exp.	Branch content		Percentage over total branching
1	11.16	0.68	Nm	3.12	1
1	11.39	0.73	Nm(1,4)	0	1
2	14.09	6.41	Nm(1,5)	0	2
4	19.97	5.86	Nm(1,6)	0.5	4
6	20.29	0.55	Ne	0.147	6
7	22.87	5.18	Np	1.71	7
11	27.26	3.93	Nb	0.965	11
12	27.44	10.24	Na	2.29	12
13	27.81	1	Nl	4.74	13
14	29.32	1.16	Nl(1,4)	0	14
15	29.6	11.13	δδCH2	121.17	15
16	30	125.91	[E]	60.585	16
17	30.37	11.8	[R]	13.472	17
20	32.2	4.74	Total branching = 182 Branches/1000C		
21	32.79	2.29			
22	33.2	4.12			
25	33.96	1.93	Methyl branches		26.88 %
26	34.48	1.78	Ethyl branches		1.09 %
26	34.81	1.55	Propyl branches		12.69 %
28	37.03	1.71	Butyl branches		7.16 %
29	37.52	8.12	Amyl branches		17.00 %
33	39.61	0.44	Long branches		35.18 %

Ethylene polymerization in the presence of MMAO

In a similar manner, the pre-catalyst **Ni2** in the presence of MMAO was explored (runs 1–9, Table 5), and the highest activity of 8.99 × 10^6 g(PE)·mol^{-1}(Ni)·h^{-1} was obtained with the Al/Ni ratio of 1750 at 30 °C (run 4 in Table 5). On comparison with the system using MAO, the system with MMAO is less thermally stable, whilst the resultant polyethylene exhibited relatively lower molecular weights and narrower PDIs, but slightly higher melting points suggestive of less branching.

Table 5 Ethylene polymerization by **Ni1–Ni6**/ MMAO [a]

Run	Pre-cat.	Al/Ni	T/ °C	t/ min	Yield/ g	Act.[b]	M_w[c]/ gmol^{-1}	M_w/M_n[c]	T_m[d]/ °C
1	**Ni2**	1000	30	30	4.88	4.88	2251	2.24	111.7
2	**Ni2**	1250	30	30	6.71	6.71	2054	2.19	110.6
3	**Ni2**	1500	30	30	7.30	7.30	1797	2.16	108.1
4	**Ni2**	1750	30	30	8.99	8.99	1659	2.12	106.8
5	**Ni2**	2000	30	30	5.71	5.71	1487	2.08	105.0
6	**Ni2**	1750	20	30	4.68	4.68	3867	2.73	118.1
7	**Ni2**	1750	40	30	6.49	6.49	1234	1.80	100.6
8	**Ni2**	1750	50	30	2.05	2.05	1157	2.19	77.2
9	**Ni2**	1750	60	30	0.83	0.83	1075	1.78	66.0
10	**Ni2**	1750	30	10	4.00	12.0	1017	1.92	113.1
11	**Ni2**	1750	30	20	6.26	9.39	1413	1.96	113.9
12	**Ni2**	1750	30	40	9.57	7.18	1984	2.17	114.1
13	**Ni1**	1750	30	30	10.2	10.2	1623	2.19	105.3
14	**Ni3**	1750	30	30	10.9	10.9	959	1.91	83.9
15	**Ni4**	1750	30	30	6.32	6.32	2144	2.27	109.5
16	**Ni5**	1750	30	30	7.36	7.36	2099	2.16	111.3
17	**Ni6**	1750	30	30	7.84	7.84	1073	1.84	88.6

[a] General conditions: 2 μmol of Ni; 100 mL of toluene for 10 atm of ethylene. [b] 10^6 g(PE)·mol^{-1}(Ni)·h^{-1}. [c] Determined by GPC. [d] Determined by DSC.

Regarding the lifetime of the active species, the polymerization was conducted over different periods from 10 to 40 min (runs 4, and 10–12, Table 5). On prolonging the reaction time, the catalytic activities slightly decreased, whilst the obtained polyethylene revealed higher molecular weight and wider polydispersity (Fig. 6). These results are consistent to the observations for the reported nickel analogues bearing the 2-iminopyridine ligand system.[10, 13-14]

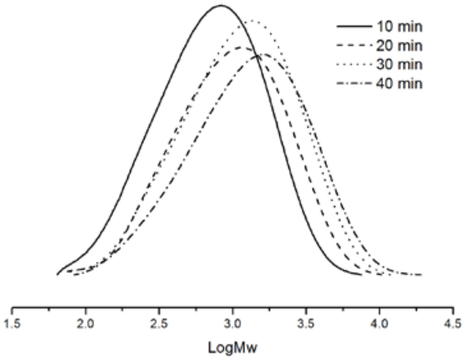


Fig. 6 GPC curves of polyethylene obtained using the **Ni2**/ MMAO system over different times (runs 4, 10–12 in Table 5)

All the other nickel pre-catalysts were investigated in the presence of MMAO, and were found to perform with good activities in ethylene polymerization under the optimum conditions of Al/Ni molar ratio 1750 at 30 °C (runs 13–17, Table 5). Regarding to the influences of reaction parameters and the nature of ligands, the tendency of catalytic performance of the **Ni**/MMAO systems is highly similar to the observation of the **Ni**/MAO; however, the system with MMAO exhibited slightly lower activity and produced lower molecular weight polyethylene than did the system using MAO.

Conclusion

The series of 2-(2-benzhydrylnaphthyliminomethyl)pyridine derivatives and their nickel halide complexes were synthesized and fully characterized, and single crystal X–ray diffraction revealed the complexes **Ni3** and **Ni6** to contain bis-ligated mononickel with a distorted octahedral geometry at the metal. All the nickel complex pre-catalysts, activated by either MAO or MMAO, exhibited high activities (up to 2.02 × 10^7 g(PE)·mol^{-1}(Ni)·h^{-1}) towards ethylene polymerization, and produced polyethylene of lower molecular weight and narrow molecular polydispersity. This is a rare example of bis-ligated nickel halides performing with high activities towards ethylene polymerization, especially given that the two halides are *trans*. The nickel complexes bearing 2-(aryliminomethyl)pyridines showed slightly higher activity than their analogues bearing 2-(1-(arylimino)ethyl)pyridine derivatives.[14]

Experimental Section

General consideration. All manipulations involving air- and moisture-sensitive compounds were carried out under a nitrogen atmosphere using standard Schlenk techniques. Toluene was refluxed over sodium and distilled under nitrogen prior to use. Methylaluminoxane (MAO, 1.46 M solution in toluene) and modified methylaluminoxane (MMAO, 1.93 M in heptane) were purchased from Akzo Nobel Corp. Diethylaluminium chloride (Et_2AlCl, 0.5 M in toluene) was purchased from Acros Chemicals. High-purity ethylene was purchased from Beijing Yansan 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; 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 4.0 mg was heated to 140 °C a rate of 20 °C /min and kept for 2 min at 140 °C to remove the thermal history and then cooled at a rate of 20 °C /min to -40 °C. ^{13}C 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.

Synthesis of ligands

2-(2-Benzhydrylnaphthyliminomethyl)pyridine (L1). A solution of picolinaldehyde (0.221 g, 2.06 mmol), 2-benzhydrylnaphthylamine (0.670 g, 2.17 mmol) and a catalytic amount of *p*-toluenesulfonic acid (0.079 g, 0.41 mmol) in toluene (80 mL) was refluxed for 8 h. The solvent was evaporated under reduced pressure, and then the residue was purified by column chromatography on basic alumina with the eluent of petroleum ether–ethyl acetate (v : v = 20 : 1) to afford a yellow solid in 76 % isolated yield. Mp: 108–109 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.71 (d, 1H, J = 4.8 Hz, Py–H), 8.19 (d, 1H, J = 8.0 Hz, Py–H), 8.05 (s, 1H, –CH=N), 7.87–7.82 (m, 2H, Py–H), 7.76 (d, 1H, J = 8.4 Hz, Ar–H), 7.59 (d, 1H, J = 8.4 Hz, Ar–H), 7.48–7.37 (m, 3H, Ar–H), 7.24–7.09 (m, 11H, Ar–H), 5.84 (s, 1H, –$CHPh_2$). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): 165.7, 154.2 (–CH=N), 149.9, 146.9, 143.9, 136.8, 133.1, 129.8, 128.7, 128.4, 128.0, 127.6, 126.4, 126.1, 125.9, 125.7, 125.6, 124.1, 123.5, 122.0, 51.8 (–$CHPh_2$). FT–IR (KBr, disk, cm^{-1}): 3052, 3024, 1642 ($\nu_{C=N}$), 1576, 1466, 1302, 1275, 1098, 810, 748, 736, 698. Anal. Calcd for $C_{29}H_{22}N_2$ (398.18): C, 87.41; H, 5.56; N, 7.03 %; Found: C, 87.26; H, 5.79; N, 6.93 %.

2-(2,4-dibenzhydrylnaphthyliminomethyl)pyridine (L2). Using the same procedure as for the synthesis of **L1**, **L2** was prepared as a yellow solid in 72 % yield. Mp: 147–148 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.70 (d, 1H, J = 4.8 Hz, Py–H), 8.20 (d, 1H, J = 8.0 Hz, Py–H), 8.09 (s, 1H, –CH=N), 7.96 (d, 1H, J = 8.4 Hz, Py–H), 7.86–7.79 (m, 2H, Py–H and Ar–H), 7.42–6.90 (m, 23H, Ar–H), 6.68 (s, 1H, Ar–H), 6.17 (s, 1H, –$CHPh_2$), 5.71 (s, 1H, –$CHPh_2$),. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): 165.6, 154.2 (–CH=N), 149.9, 145.7, 143.8, 143.7, 136.8, 135.7, 131.2, 130.3, 129.6, 129.5, 129.4, 128.6, 128.4, 128.2, 127.5, 126.3, 126.2, 126.1, 125.5, 124.3, 124.2, 121.9, 53.0 (–$CHPh_2$), 51.7 (–$CHPh_2$). FT–IR (KBr, disk, cm^{-1}): 3053, 3024, 1643 ($\nu_{C=N}$), 1578, 1491, 1440, 1384, 1342, 1252, 1155, 1075, 1030, 991, 948, 915, 753, 736, 698. Anal. Calcd for $C_{42}H_{32}N_2$ (564.26) C, 89.33; H, 5.71; N, 4.96 %; Found: C, 89.09; H, 5.74; N, 4.90 %.

2-(2,4,7-tribenzhydrylnaphthyliminomethyl)pyridine (L3). Using the same procedure as for the synthesis of **L1**, **L3** was prepared as a yellow solid in 64 % yield. Mp: 110–111 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.68 (d, 1H, J = 4.4 Hz, Py–H), 8.00 (d, 1H, J = 7.6 Hz, Py–H), 7.95 (s, 1H, –CH=N), 7.87 (d, 1H, J = 8.8 Hz, Py–H), 7.78 (t, 1H, J = 7.6 Hz, Py–H), 7.40–6.88 (m, 33H, Ar–H), 6.64 (s, 1H, Ar–H), 6.12 (s, 1H, –$CHPh_2$), 5.65 (s, 1H, –$CHPh_2$), 5.57 (s, 1H, –$CHPh_2$),. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): 165.6, 154.1 (–CH=N), 149.7, 145.6, 143.9, 143.8, 143.7, 140.9, 136.8, 136.6, 135.6, 130.2, 130.0, 129.6, 129.5, 129.4, 128.6, 128.4, 128.3, 128.2, 128.1, 127.7, 126.3, 126.2, 125.4, 124.5, 124.3, 121.9, 56.9 (–$CHPh_2$), 53.0 (–$CHPh_2$), 51.7 (–$CHPh_2$). FT–IR (KBr, disk, cm^{-1}): 3056, 3024, 1642 ($\nu_{C=N}$), 1597, 1493, 1446, 1375, 1336, 1182, 1074, 1032, 920, 779, 746, 700. Anal. Calcd for $C_{55}H_{42}N_2$ (730.33) C, 90.38; H, 5.79; N, 3.83 %; Found: C, 89.90; H, 5.89; N, 3.70 %.

Synthesis of nickel Complexes

General procedure. $NiCl_2·6H_2O$ (0.25 mmol) or (DME)$NiBr_2$ (0.25 mmol) was dissolved in 5 mL ethanol and added to the solution of the ligands (0.5 mmol) in 5 mL CH_2Cl_2. The mixture was stirred for 12 h, and then diethyl ether was poured into the mixture to precipitate the complex. The precipitant was collected by filtration, washed with diethyl ether (3 × 5 mL), and dried under vacuum at 60 °C.

Bis(2-(2-benzhydrylnaphthyliminomethyl)pyridyl)nickel bromide (Ni1~~)(~~, yellow, 92 % yield): FT–IR (KBr, disk, cm^{-1}): 3060, 3024, 1622 ($\nu_{C=N}$), 1596, 1493, 1446, 1375, 1322, 1261, 1076, 1027, 782, 741, 700. Anal. Calcd for $C_{58}H_{44}Br_2N_4Ni$ (1012.13): C, 68.60; H, 4.37; N, 5.52 %. Found: C, 68.36; H, 4.48; N, 5.46 %.

Bis(2-(2,4-dibenzhydrylnaphthyliminomethyl)pyridyl)nickel bromide (Ni2~~)(~~, yellow, 95 % yield): FT–IR (KBr, disk, cm^{-1}): 3059, 3024, 1633 ($\nu_{C=N}$), 1597, 1571, 1493, 1446, 1355, 1307, 1224, 1156, 1107, 1072, 1029, 945, 764, 742, 700. Anal. Calcd for $C_{84}H_{64}Br_2N_4Ni$ (1344.29): C, 74.85; H, 4.79; N, 4.16 %. Found: C, 74.59; H, 4.96; N, 4.02 %.

Bis(2-(2,4,7-tribenzhydrylnaphthyliminomethyl)pyridyl)nickel bromide (Ni3~~)(~~, yellow, 84 % yield): FT–IR (KBr, disk, cm^{-1}): 3060, 3025, 1628 ($\nu_{C=N}$), 1597, 1493, 1447, 1376, 1325, 1264, 1076, 1028, 782, 748, 698. Anal. Calcd for $C_{110}H_{84}Br_2N_4Ni$ (1676.44): C, 78.62; H, 5.04; N, 3.33 %. Found: C, 78.36; H, 5.28; N, 3.26 %.

Bis(2-(2-benzhydrylnaphthyliminomethyl)pyridyl)nickel chloride (Ni4~~)(~~, yellow, 91 % yield): FT–IR (KBr, disk, cm^{-1}): 3061, 2973, 1633 ($\nu_{C=N}$), 1596, 1573, 1504, 1382, 1304, 1227, 1155, 1108, 1067, 1043, 810, 780, 751, 705. Anal. Calcd for $C_{58}H_{44}Cl_2N_4Ni$ (924.23): C, 75.18; H, 4.79; N, 6.05 %. Found: C, 75.02; H, 4.86; N, 5.98 %.

Bis(2-(2,4-dibenzhydrylnaphthyliminomethyl)pyridyl)nickel chloride (Ni5~~)(~~, yellow, 83 % yield): FT–IR (KBr, disk, cm^{-1}): 3060, 3023, 1634 ($\nu_{C=N}$), 1598, 1573, 1491, 1447, 1377, 1308, 1224, 1157, 1108, 1074, 948, 765, 743, 700. Anal. Calcd for $C_{84}H_{64}Cl_2N_4Ni$ (1256.39): C, 80.13; H, 5.12; N, 4.45 %. Found: C, 79.98; H,5.26; N, 4.38 %.

Bis(2-(2,4,7-tribenzhydrylnaphthyliminomethyl)pyridyl)nickel chloride (Ni6~~)(~~, yellow, 84 % yield): FT–IR (KBr, disk, cm^{-1}): 3058, 3025, 1629 ($\nu_{C=N}$), 1597, 1492, 1448, 1353, 1306, 1156, 1111, 1076, 1028, 894, 742, 701. Anal. Calcd for $C_{110}H_{84}Cl_2N_4Ni$ (1588.54): C, 83.02; H, 5.32; N, 3.52 %. Found: C, 82.98; H, 5.48; N, 3.46 %.

X-ray crystallographic studies

Single crystals of **Ni3** and **Ni6** suitable for X–ray diffraction analyses were obtained by slow diffusion of diethyl ether onto the respective dichloromethane solution at room temperature. X–ray studies were carried out on a Rigaku Saturn 724$^+$ CCD with graphite-monochromatic Mo-Kα radiation (λ = 0.71073 Å) at 173(2) K (**Ni3**) and 100(2) K (**Ni6**), 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 hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL–97 package.[19] Within structure refinement of **Ni3** and **Ni6**, there were free solvent molecules which have no influence on the geometry of the main compounds. Therefore, the SQUEEZE option of the crystallographic program PLATON[20] was used to remove these free solvents from the structure. Details of the X–ray structure determinations and refinements are provided in Table 6.

General procedure for ethylene polymerization

A 250 mL stainless steel autoclave equipped with a mechanical stirrer and a temperature controller was used to perform ethylene polymerization. The autoclave was evacuated by a vacuum pump and back-filled twice with N_2 and once with ethylene. When the desired reaction temperature was reached, 30 mL toluene was added under ethylene atmosphere, and the nickel pre-catalyst in 20 mL toluene was injected. The required amount of co-catalysts (MAO, MMAO or Et_2AlCl) and additional toluene (maintaining total volume as 100 mL in reactor) were added by syringe. The reaction mixture was intensively stirred for the desired time under 10 atm of ethylene and maintained at this level by constant feeding of ethylene. The reaction was quenched by addition of acidic ethanol. The precipitated polymer was washed with ethanol several times and dried *in vacuo*.

Table 6 Crystal data and structure refinement for **Ni3** and **Ni6**

identification code	**Ni3**	**Ni6**
Crystal color	red	red
Empirical formula	$C_{110}H_{84}Br_2N_4Ni$	$C_{110}H_{84}Cl_2N_4Ni$
Formula weight	1680.34	1591.42
Temperature/K	173 (2)	100 (2)
Wavelength/Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/c	P2(1)/n
a/Å	17.508(3)	17.393(4)
b/Å	15.393(3)	15.219(3)
c/Å	24.027(8)	18.207(4)
Alpha/°	90	90
Beta/°	130.853(18)	95.81(3)
Gamma/°	90	90
Volume/Å^3	4898(2)	4794.6(17)
Z	2	2
D_{calcd}/(g·cm^{-3})	1.139	1.102
μ/mm^{-1}	1.060	0.305
F(000)	1740	1668
Crystal size/mm	0.81×0.61×0.27	0.33×0.26×0.14
θ range (ºC)	1.54–24.99	1.54–27.46
Limiting indices	$-15 \le h \le 20$ $-18 \le k \le 18$ $-28 \le l \le 22$	$-22 \le h \le 22$ $-19 \le k \le 19$ $-23 \le l \le 23$
No. of rflns collected	30479	36390
No. unique rflns	8618	10927
R(int)	0.0544	0.1017
No. of params	529	530
Completeness to θ	99.9 %	99.6 %
Goodness of fit on F^2	1.072	1.061
Final *R* indices [$I > 2\sum(I)$]	$R_1 = 0.0563$ $wR_2 = 0.1724$	$R_1 = 0.0810$ $wR_2 = 0.2164$
R indices (all data)	$R_1 = 0.0641$ $wR_2 = 0.1822$	$R_1 = 0.1051$ $wR_2 = 0.2300$
Largest diff. peak, and hole/(e.Å^{-3})	0.564 and -0.690	0.512 and -0.878

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Notes and references

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†Appendix A. Supplementary material: CCDC 971667 and 971668 contain the supplementary crystallographic data for **Ni3** and **Ni6**. 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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