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2-(1-(2-Benzhydrylnaphthylimino)ethyl)pyridylnickel halides: synthesis, characterization, and ethylene polymerization behavior

On fine tuning the ligands, mono-nickel bromide complexes exhibited a distorted square pyramidal geometry, whilst their chloride analogs revealed a centrosymmetric dimeric structure possessing a distorted octahedral geometry at each metal. All nickel pre-catalysts afforded high activity toward ethylene polymerization yielding highly branched polyethylene with narrow PDI.

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2-(1-(2-Benzhydrylnaphthylimino)ethyl)-pyridylnickel halides: synthesis, characterization, and ethylene polymerization behavior†

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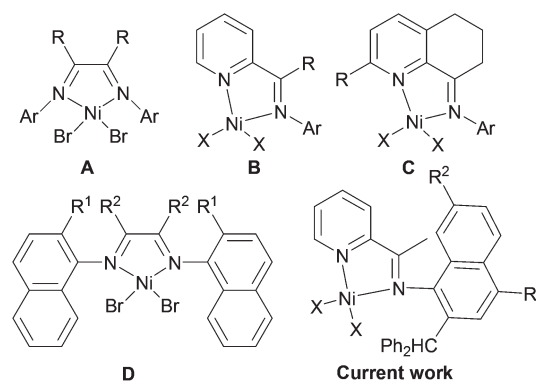
A series of 2-(1-(2-benzhydrylnaphthylimino)ethyl)pyridine derivatives (**L1–L3**) was synthesized and fully characterized. The organic compounds acted as bi-dentate ligands on reacting with nickel halides to afford two kinds of nickel complexes, either mononuclear bis-ligated L_2NiBr_2 (**Ni1–Ni3**) or chloro-bridged dinuclear $L_2Ni_2Cl_4$ (**Ni4–Ni6**) complexes. The nickel complexes were fully characterized, and the single crystal X-ray diffraction revealed for **Ni2**, a distorted square pyramidal geometry at nickel comprising four nitrogens of two ligands and one bromide; whereas for **Ni4**, a centrosymmetric dimer possessing a distorted octahedral geometry at nickel was formed by two nitrogens of one ligand, two bridging chlorides and one terminal chloride along with oxygen from methanol (solvent). When activated with diethyl-aluminium chloride (Et_2AlCl), all nickel complexes performed with high activities (up to 1.22×10^7 g (PE) mol^{-1} (Ni) h^{-1}) towards ethylene polymerization; the obtained polyethylene possessed high branching, low molecular weight and narrow polydispersity, suggestive of a single-site active species. The effect of the polymerization parameters, including the nature of the ligands/halides on the catalytic performance is discussed.

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Introduction

Studies of late-transition metal complexes, including those of iron, cobalt, nickel, and palladium, have seen a significant rise, particularly when applied to ethylene oligomerization and polymerization since the pioneering work on α -diiminometal (nickel or palladium) complexes (**A**, Scheme 1)¹ and bis(imino)pyridyl metal (iron or cobalt) complexes which appeared in the middle to late 1990s.² Interestingly, branched polyethylenes were obtained using nickel and palladium complex pre-catalysts,^{1,3} for which the proposed mechanism involving β -hydride elimination explained the formation of methyl branches. Other more attractive polyethylenes possessed longer branches (such as propyl, amyl and longer branches),⁴ and better properties



Scheme 1 Representative *N,N*-bidentate nickel complex pre-catalysts.

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†CCDC 955454 and 955455 for **Ni2** and **Ni4**·2CH₃OH. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt52234b

are anticipated from other branched products. This has stimulated both academics and industrialists to further study new nickel-based complex pre-catalysts. In particular, the modification of α -diimino derivatives was extensively investigated,⁵ and in addition, various related ligand sets were explored such as 2-iminopyridines (**B**, Scheme 1),⁶ 2-arylimino-5,6,7-trihydroquinolines (**C**, Scheme 1),⁷ as well as bicyclic compounds.⁸ Furthermore, tridentate ligand sets have also been developed such as those based on conjugated 1,10-phenanthroline



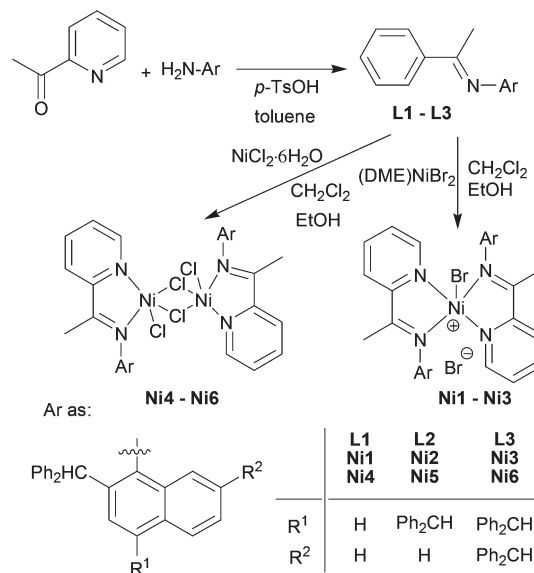
derivatives⁹ and quinoline derivatives¹⁰ as well as a number of non-conjugated derivatives.¹¹ This progress has been illustrated in a number of review articles.¹² Although the nickel catalytic system has been commercialized in the form of the SHOP process,¹³ the utilization of the newly developed nickel complex pre-catalysts is still problematic due to a number of critical issues concerning both the nature of the catalytic systems and the usefulness of the resulting products.

To overcome some of these shortcomings (such as deactivation and production of polymers of low molecular weight at elevated reaction temperatures), we note that a number of iron complex pre-catalysts have been successfully modified with improved thermo-stability and have produced useful products,¹⁴ and now are considered promising catalytic systems for both ethylene oligomerization¹⁵ and polymerization.¹⁶ Ligands bearing bulky benzhydryl-substituents were recognized to exert a significant influence on improving the thermo-stabilities of their metal complexes and for producing polyethylene of narrow polydispersity.^{16,17} As a consequence, nickel complex pre-catalysts bearing benzhydryl-substituted ligands have also been explored, and better performances in terms of both thermo-stability and catalytic activities have been reported.¹⁸ In general, benzhydryl-substituents have been introduced through the use of benzhydryl-substituted anilines.^{16–18} Following on from this, the next challenge is to design benzhydryl-substituted 1-aminonaphthalene derivatives, and subsequently a new series of 2-iminopyridine derivatives. With this in mind, we have prepared new 2-iminopyridine derivatives, from which their nickel halide complexes were synthesized. These nickel complexes performed with high activities toward ethylene polymerization. During the preparation of this manuscript, 2-bulky-substituted 1-aminonaphthalene derivatives (**D**, Scheme 1) have been used for preparing α -diimino nickel complex pre-catalysts in ethylene polymerization.¹⁹ Herein, the synthesis and characterization of the 2-(1-(2-benzhydrylnaphthylimino)ethyl)pyridine derivatives and their nickel halides are reported as well as the catalytic performance of the nickel complexes in ethylene polymerization.

Results and discussion

Synthesis and characterization of 2-(1-(2-benzhydrylnaphthylimino)ethyl)pyridine derivatives (L1–L3) and their nickel complexes (Ni1–Ni6)

The 2-benzhydrylnaphthylamine, 2,4-dibenzhydrylnaphthylamine, and 2,4,7-tribenzhydrylnaphthylamine compounds were prepared in acceptable yields using modified synthetic procedures according to the literature.²⁰ The routine condensation reaction of 2-acetylpyridine with the above benzhydryl-substituted naphthylamine derivatives formed the respective 2-(1-(2-benzhydrylnaphthylimino)ethyl)pyridine derivatives (**L1–L3**) in moderate yields (Scheme 2). All organic compounds were characterized by ¹H/¹³C NMR and FT-IR spectroscopy, and were further confirmed by elemental analysis data.



Scheme 2 Synthetic procedure for the 2-(1-(2-benzhydrylnaphthylimino)ethyl)pyridines and their nickel complexes.

The 2-(1-(2-benzhydrylnaphthylimino)ethyl)pyridine derivatives (**L1–L3**) readily reacted with the nickel halides NiCl₂·6H₂O or (DME)NiBr₂ in a mixture of ethanol and dichloromethane to form the corresponding complexes (Scheme 2). From these stoichiometric reactions, the nickel bromide complexes were commonly isolated in low yield, whereas the nickel chloride complexes were obtained in high yields. The FT-IR spectroscopy indicated effective coordination of the cationic nickel with the ligands as evidenced by the $\nu_{C=N}$ stretching vibrations of the complexes **Ni1–Ni6** shifting to lower frequencies and with weaker intensities in the region 1619–1628 cm⁻¹ versus the free organic compounds in the region 1642–1643 cm⁻¹. Moreover, elemental analysis data were consistent with the bromide complexes having the formula L₂NiBr₂ (**Ni1–Ni3**) and the chloride complexes as LNiCl₂ (**Ni4–Ni6**). Given this, the reaction of (DME)NiBr₂ was conducted with two equivalents of 2-(1-(2-benzhydrylnaphthylimino)ethyl)pyridine derivatives to form the corresponding nickel bromide complexes L₂NiBr₂ (**Ni1–Ni3**) in much higher yield. To confirm their molecular structures, single crystals of the nickel complexes **Ni2** and **Ni4** were obtained and were subjected to single crystal X-ray crystallographic studies.

Single-crystal X-ray diffraction study

A single crystal of the nickel bromide complex **Ni2** suitable for X-ray diffraction analysis was obtained by slow diffusion of heptane into an ethanol solution at room temperature. The molecular structure is shown in Fig. 1, and the selected bond lengths and angles are tabulated in Table 1.

As shown in Fig. 1, complex **Ni2** possesses a distorted square-based pyramidal geometry at the nickel, comprising four nitrogen atoms (N1, N2, N3 and N4) of two ligands and one bromide (Br1), and another bromide (Br2) as a free-anion, which is similar to bis(2-((2,4-dibenzhydryl-



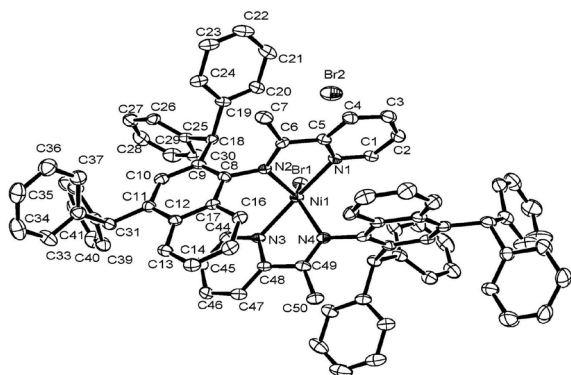


Fig. 1 ORTEP drawing of Ni2. Thermal ellipsoids are shown at 30% probability level. Hydrogen atoms have been omitted for clarity.

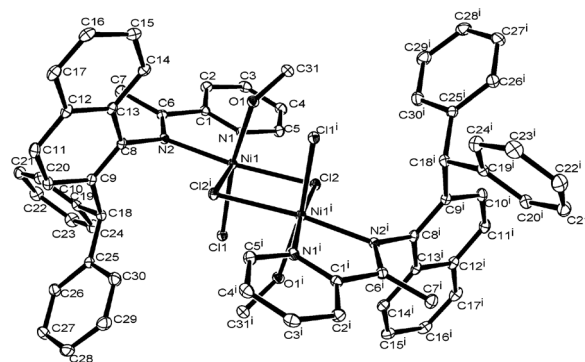


Fig. 2 ORTEP drawing of Ni4·2CH₃OH. Thermal ellipsoids are shown at 30% probability level. Hydrogen atoms have been omitted for clarity.

Table 1 Selected bond lengths (Å) and angles (°) for Ni2 and Ni4·2CH₃OH

Ni2		Ni4·2CH ₃ OH	
Bond lengths (Å)			
Ni(1)–N(1)	2.056(4)	Ni(1)–N(1)	2.0410(15)
Ni(1)–N(2)	2.059(4)	Ni(1)–N(2)	2.1097(15)
Ni(1)–N(3)	2.058(4)	Ni(1)–Cl(1)	2.4162(6)
Ni(1)–N(4)	2.062(4)	Ni(1)–Cl(2)	2.4358(6)
Ni(1)–Br(1)	2.4012(10)	Ni(1)–O(1)	2.1635(14)
Bond angles (°)			
N(1)–Ni(1)–N(2)	79.04(16)	N(1)–Ni(1)–N(2)	79.21(6)
N(1)–Ni(1)–N(3)	165.93(16)	N(1)–Ni(1)–Cl(1)	93.71(5)
N(3)–Ni(1)–N(2)	92.67(15)	N(2)–Ni(1)–Cl(1)	97.95(5)
N(1)–Ni(1)–N(4)	92.62(16)	N(1)–Ni(1)–O(1)	89.20(6)
N(3)–Ni(1)–N(4)	78.48(16)	N(2)–Ni(1)–O(1)	91.20(6)
N(2)–Ni(1)–N(4)	105.15(15)	N(1)–Ni(1)–Cl(2)	96.24(5)
N(1)–Ni(1)–Br(1)	95.96(12)	N(2)–Ni(1)–Cl(2)	173.21(4)
N(3)–Ni(1)–Br(1)	98.11(11)	O(1)–Ni(1)–Cl(1)	170.76(4)
N(2)–Ni(1)–Br(1)	125.67(10)	O(1)–Ni(1)–Cl(2)	83.65(4)
N(4)–Ni(1)–Br(1)	129.17(11)	Cl(1)–Ni(1)–Cl(2)	87.31(2)

6-ethylphenylimino)ethyl)pyridyl) nickel dibromide.^{18e} In this structure, there is a five-membered heteronickel-cycle constructed from Ni1, N1, C5, C6 and N2, in which the C5 atom deviates by 1.222 Å from the co-plane of the atoms N1, N2 and Ni1, whilst the C6 atom deviates by 1.506 Å. The Ni1–N1 bond length is similar to the Ni1–N2 at 2.056(4) Å and 2.059(4) Å, respectively. The dihedral angle between the pyridyl and imino-naphthalene planes is 46.86°, which is consistent with the structures of the 2-iminopyridylnickel halide analogs reported previously.^{18e}

Single crystal of the nickel chloride complex Ni4 suitable for X-ray diffraction analysis was obtained by laying diethyl ether on to their dichloromethane–methanol (*v/v* = 1 : 1) solutions at room temperature. The nickel chloride complex Ni4 (Fig. 2) was found to be a centrosymmetric dimer with a slightly distorted octahedral geometry at the nickel center, in which the nickel is symmetrically bridged by the two chloride atoms (Cl2 and Cl2i), and the two nickel atoms, as evidenced by the intramolecular distance of 3.404 Å, which is slightly shorter than 3.475 Å observed in the analogous 2-iminopyridine–Ni(II) dimers,^{6a} but slightly longer than 3.363 Å found in 2-((2,4-dibenzhydryl-6-methylphenylimino)methyl)pyridylnickel

dichloride.^{18e} For the Ni–N bond lengths of different types, the length of the Ni–N_{pyridine} is slightly shorter than the Ni–N_{imino}, (Ni1–N1, 2.0410(15) and Ni1–N2, 2.1097(15)). The pyridyl and imino-naphthalene planes are near perpendicular with a dihedral angle of 85.55° consistent with the dihedral angles between the pyridyl and imino-phenyl for the reported 2-aryl-iminopyridylnickel analogues.^{6a,c,7,18c}

Catalytic behavior toward ethylene polymerization

The complex Ni2 was used to optimize the polymerization parameters. Various alkylaluminum reagents such as MAO, MMAO, and Et₂AlCl were explored as activators under 10 atm of ethylene pressure and all catalytic systems indicated high activities toward ethylene polymerization (Table 2). With potential industrial applications in mind, the cheaper and more readily available Et₂AlCl was used for further systematically exploring the catalysis.

Variations of the Al/Ni ratio from 300 to 450 (runs 1–5 in Table 3) were conducted at 30 °C, and the highest activity was observed at 9.89×10^6 g (PE) mol⁻¹ (Ni) h⁻¹ using the Al/Ni ratio of 400 (run 4 in Table 3). Catalytic activities increased with higher molar ratios of Al/Ni (runs 1–4 in Table 3), however, on further increasing the Al/Ni molar ratio to 450, a dramatic decrease of the catalytic activity 5.19×10^6 g (PE) mol⁻¹ (Ni) h⁻¹ (run 5 in Table 3) was observed. As indicated by the data and the curves of the GPC for the obtained polyethylene (Fig. 3), these catalytic systems exhibited single-site active species; the molecular weights of the obtained polyethylenes slightly decreased on increasing the molar ratio of Al/Ni,

Table 2 Ethylene polymerization by Ni2 using various co-catalysts^a

Run	Co-catalyst	Al/Ni	Yield/g	Activity ^b	<i>M_w</i> ^c /g mol ⁻¹	<i>M_n</i> ^c	<i>T_m</i> ^d /°C
1	MAO	1500	8.58	8.58	2653	2.19	89.0
2	MMAO	1500	10.9	10.9	2272	2.37	101.3
3	Et ₂ AlCl	400	9.89	9.89	1676	1.99	72.3

^a General conditions: 2 μmol of Ni; 30 min; 30 °C; 100 mL of toluene for 10 atm of ethylene. ^b 10⁶ g (PE) mol⁻¹ (Ni) h⁻¹. ^c Determined by GPC. ^d Determined by DSC.



Table 3 Ethylene polymerization by Ni₂-Et₂AlCl^a

Run	Al/Ni	T/°C	t/min	Yield/g	Activity ^b	M _w ^c /g mol ⁻¹	M _w /M _n ^c	T _m ^d /°C
1	300	30	30	Trace	Trace	nd	nd	nd
2	350	30	30	1.54	1.54	1833	2.13	80.8
3	375	30	30	8.59	8.59	1809	2.08	79.9
4	400	30	30	9.89	9.89	1676	1.99	72.3
5	450	30	30	5.19	5.19	1445	1.89	68.6
6	400	20	30	8.08	8.08	2529	2.15	88.2
7	400	40	30	4.22	4.22	1117	1.71	62.6
8	400	50	30	1.54	1.54	981	1.58	56.0
9	400	20	10	3.40	10.2	2270	2.05	85.5
10	400	20	20	6.57	9.86	2378	2.11	87.5
11	400	20	40	8.49	6.37	2898	2.49	90.1
12	400	20	60	9.37	4.69	3388	2.53	105.7

^a General conditions: 2 μmol of Ni; 100 mL of toluene. ^b 10⁶ g (PE) mol⁻¹ (Ni) h⁻¹. ^c Determined by GPC. ^d Determined by DSC.

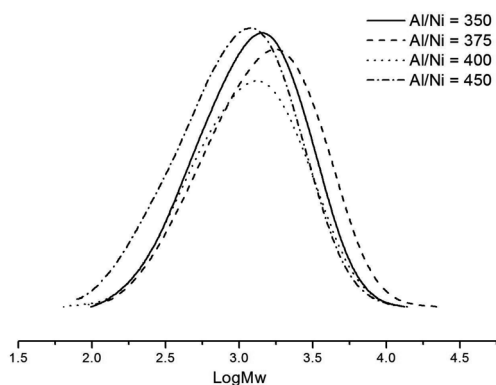


Fig. 3 GPC traces of polyethylenes by the Ni₂-Et₂AlCl system with various Al/Ni ratios (runs 2–5 in Table 3).

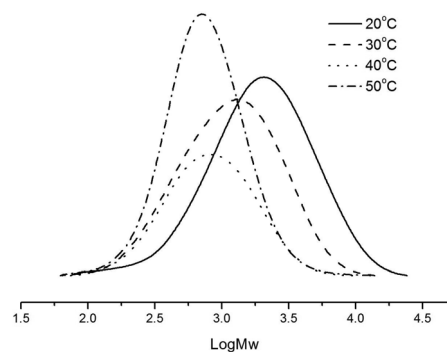


Fig. 4 GPC curves of polyethylenes by the Ni₂-Et₂AlCl system at different temperature (runs 4, 6–8 in Table 3).

indicative of more chain transfers from the nickel species to aluminium and chain termination.^{6f,21} The molecular weight/polydispersity values herein are at the limits of what can be determined accurately using such columns, and so we will limit our discussions to general trends.

To understand the influence of the reaction temperature, the ethylene polymerization was conducted over 30 min at the Al/Ni ratio of 400 and at 10 atm of ethylene using temperatures from 20 to 50 °C (runs 4 and 6–8 in Table 3). The data confirmed that the optimized temperature was 30 °C (run 4 in Table 3), and that the higher the reaction temperature, the lower the molecular weight of the obtained polyethylene (Fig. 4), which is consistent with observations on nickel pre-catalysts bearing α-diimino^{5a} or 2-iminopyridine ligands.¹⁸ This is likely to arise from faster chain termination *versus* chain propagation at the elevated temperature.^{12a}

With regard to the life time of the catalytic system, the ethylene polymerization by Ni₂-Et₂AlCl was quenched over different time periods, typically 10, 20, 30, 40 and 60 min (runs 6 and 9–12 in Table 3). On extending the reaction time, more polyethylene was obtained and with higher molecular weights, but the catalytic activities gradually decreased (Fig. 5). A similar catalytic behavior was observed for the nickel analogs bearing 2-iminopyridine.^{18a,e} After 30 min, the

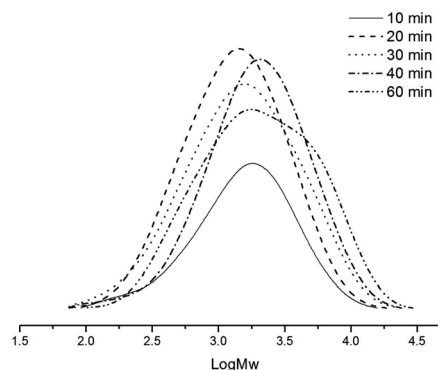


Fig. 5 GPC curves of polyethylenes by the Ni₂-Et₂AlCl system with different time (runs 6, 9–12 in Table 3).

catalytic system exhibited low activity towards polymerizing ethylene, but the isolation of polyethylene of increased molecular weight indicated that the catalytic species still remained active. In general, all the polyethylene products possessed narrow polydispersity in the range of 1.58–2.49, indicative of a single site active species.

The melting points of all resultant polyethylenes exhibited lower *T_m* values, not only reflecting the lower molecular weights but also indicating that branched polyethylene had formed. To understand the polyethylene obtained using



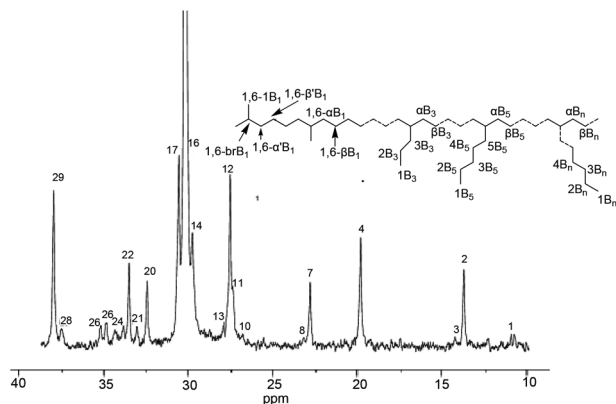


Fig. 6 ^{13}C NMR spectrum of the polyethylene by $\text{Ni2-Et}_2\text{AlCl}$ at $50\text{ }^\circ\text{C}$ (run 8 in Table 3).

Table 4 Percentage of branching for the polyethylene (run 8 in Table 3)²²

Peak no.	Chem. shifts/ ppm	Integral exp.	Branch content	Percentage over total branching	
1	11.22	0.13	N_m	0.76	26.00%
1	11.38	0.08	$N_{m(1,4)}$	0	0.00%
2	14.08	1	$N_{m(1,5)}$	0	0.00%
3	14.58	0.14	$N_{m(1,6)}$	0.17	5.82%
4	19.98	1.76	N_e	0.17	5.82%
7	22.87	0.84	N_p	0.37	12.67%
8	23.24	0.14	N_b	0.07	2.40%
10	26.72	0.28	N_a	0.41	14.04%
11	27.3	0.74	N_l	0.97	33.22%
12	27.44	2.51	$N_{l(1,4)}$	0	0.00%
13	27.81	0.34	$\delta\delta\text{CH}_2$	23.54	
14	29.6	2.4	[E]	11.77	
16	30	24.51	[R]	2.92	100.00%
17	30.38	3.56	Total branching = 199		
20	32.19	0.97	Branches/1000C		
21	32.79	0.41			
22	33.23	1.1	Methyl branches	31.82%	
24	34.05	0.44	Ethyl branches	5.82%	
26	34.52	0.43	Propyl branches	12.67%	
26	34.85	0.38	Butyl branches	2.40%	
28	37.06	0.37	Amyl branches	14.04%	
29	37.54	2.24	Long branches	33.22%	

$\text{Ni2-Et}_2\text{AlCl}$ (run 8 in Table 3) at $50\text{ }^\circ\text{C}$, ^{13}C NMR spectroscopic measurements (Fig. 6) were conducted which indicated the presence of 199 branches/1000 carbons as measured according to the literature.²²

The signals were assigned and are listed in Table 4, which indicated that the main branches were methyl (32%), propyl (13%) and long chains (33%) as well as amyl chains (14%).

In comparison, the polyethylene obtained using the $\text{Ni2-Et}_2\text{AlCl}$ (run 6 in Table 3) at $20\text{ }^\circ\text{C}$ was also measured by ^{13}C NMR spectroscopy (Fig. 7), which indicated 91 branches/1000 carbons; the main branches were methyl (46%) and long chains (37%) as well as amyl chains (11%). Highly branched PEs are commonly obtained using nickel catalytic systems^{5d,23} due to β -hydride migrations.

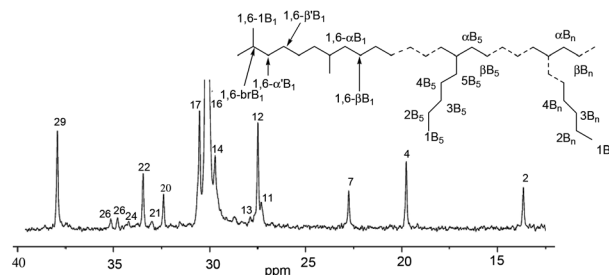


Fig. 7 ^{13}C NMR spectrum of the polyethylene by $\text{Ni2-Et}_2\text{AlCl}$ at $20\text{ }^\circ\text{C}$ (run 6 in Table 3).

Table 5 Ethylene polymerization by $\text{Ni1-Ni6/Et}_2\text{AlCl}^a$

Run	Pre-catalyst	Yield/ g	Activity ^b	M_w^c / g mol^{-1}	M_w/M_n^c	T_m^d / $^\circ\text{C}$
1	Ni1	12.2	12.2	1309	2.11	59.2
2	Ni2	9.89	9.89	1676	1.99	72.3
3	Ni3	8.18	8.18	515	1.78	56.7
4	Ni4	4.73	4.73	864	1.98	44.2
5	Ni5	4.44	4.44	978	2.02	55.9
6	Ni6	2.27	2.27	541	1.45	47.0

^a General conditions: $2\text{ }\mu\text{mol}$ of Ni; $\text{Al/Ni} = 400/1$; 30 min; $30\text{ }^\circ\text{C}$; 100 mL toluene; 10 atm of ethylene. ^b $10^6\text{ g (PE) mol}^{-1} (\text{Ni})\text{ h}^{-1}$. ^c Determined by GPC. ^d Determined by DSC.

To understand the influence of the ligands and halides present on the catalytic behavior of these nickel complex pre-catalysts, the complexes **Ni1-Ni6** were investigated under optimum conditions (Al/Ni molar ratio of 400:1 at $30\text{ }^\circ\text{C}$) under 10 atm of ethylene, and the catalytic results are tabulated in Table 5. Previous bis-ligated complexes were reported to be relatively inactive for olefin polymerization due to detrimental olefin insertions.²⁴ However, the current bis-ligated nickel bromide pre-catalysts exhibited higher activities than did the corresponding chloride analogs. Besides the better solubility of the bromide complexes, the bis-ligated nickel bromide pre-catalysts probably transformed into mono-ligated complexes during catalysis.²⁵ Overall, catalytic activities of these nickel complex pre-catalysts gradually decreased when more benzhydryl-substituted groups were incorporated (Fig. 8): **Ni1** > **Ni2** > **Ni3** and **Ni4** > **Ni5** > **Ni6**, illustrating that the bulky groups retard the insertion of ethylene.

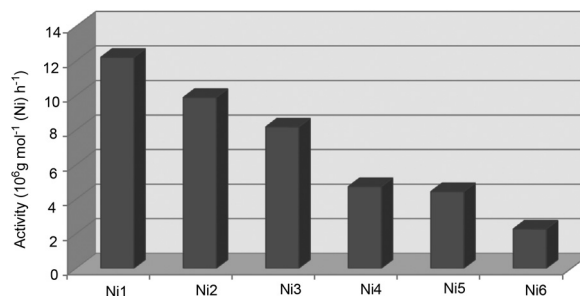


Fig. 8 The catalytic performances by $\text{Ni1-Ni6/Et}_2\text{AlCl}$ (Table 5).



Conclusion

2-((2-Benzhydrylnaphthylimino)ethyl)pyridine derivatives and their nickel complexes were synthesized and fully characterized. The anionic halides caused a different coordination and a different structural geometry at nickel, *viz* distorted square pyramidal at nickel for the bromides *versus* a centrosymmetric dimer with distorted octahedral nickel for the chlorides. All nickel complexes exhibited high activities (up to 1.22×10^7 g (PE) mol⁻¹ (Ni) h⁻¹) for ethylene polymerization. The obtained polyethylene was found to be of low molecular weight waxes with narrow PDI and high branching. Such nickel complex pre-catalysts are of potential industrial interest for the production of polyethylene waxes and lubricants.

Experimental section

General consideration

All manipulations involving air- and moisture-sensitive compounds were performed using standard Schlenk techniques under a nitrogen atmosphere. Toluene was refluxed over sodium and distilled under nitrogen prior to use. Methylaluminumoxane (MAO, 1.46 M solution in toluene) and modified methylaluminumoxane (MMAO, 1.93 M in heptane) were purchased from Akzo Nobel Corp. Diethylaluminium chloride (Et₂AlCl, 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 using 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 using 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 at the rate of 20 °C min⁻¹ and kept for 2 min at 140 °C to remove the thermal history and then cooled at the rate of 20 °C min⁻¹ to -40 °C. ¹³C NMR spectra of the polyethylenes were recorded using a Bruker DMX 300 MHz instrument at 135 °C in deuterated 1,2-dichlorobenzene with TMS as an internal standard.

Synthesis of various bulky naphthylamines

A variety of benzhydryl-substituted naphthylamines were successfully synthesized according to modified literature procedures.²⁰ 2-Benzhydrylnaphenamine was obtained as a red solid, Mp: 136–137 °C. ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.84–7.80 (m, 2H, Ar-H), 7.49–7.47 (m, 2H, Ar-H), 7.39–7.22 (m, 11H, Ar-H), 6.96 (d, 1H, *J* = 8.4 Hz, Ar-H), 5.79 (s, 1H, -CHPh₂), 3.98 (s, 2H, -NH₂). ¹³C NMR (100 MHz, CDCl₃, TMS):

142.8, 139.2, 133.3, 129.7, 128.7, 128.6, 128.1, 126.8, 125.5, 125.1, 123.7, 122.8, 120.5, 118.2, 52.5. FT-IR (KBr, disk, cm⁻¹): 3382, 3057, 3023, 1620, 1597, 1563, 1511, 1491, 1396, 1243, 1075, 1027, 917, 858, 801, 747, 697. Anal. Calcd for C₂₃H₁₉N (309.15): C, 89.28; H, 6.19; N, 4.53%; found: C, 88.89; H, 6.26; N, 4.38%.

2,4-Dibenzhydrylnaphthylamine was obtained as a red solid, Mp: 145–146 °C. ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.84–7.80 (m, 2H, Ar-H), 7.49–7.47 (m, 2H, Ar-H), 7.39–7.22 (m, 11H, Ar-H), 6.96 (d, 1H, *J* = 8.4 Hz, Ar-H), 5.79 (s, 1H, -CHPh₂), 3.98 (s, 2H, -NH₂). ¹³C NMR (100 MHz, CDCl₃, TMS): 144.2, 142.6, 137.9, 131.5, 130.6, 129.7, 129.5, 129.4, 128.6, 128.3, 126.6, 126.1, 125.7, 125.1, 124.8, 124.3, 122.2, 121.1, 52.9, 52.5. FT-IR (KBr, disk, cm⁻¹): 3397, 3057, 3024, 1624, 1598, 1513, 1490, 1448, 1379, 1322, 1249, 1178, 1075, 1028, 917, 815, 743, 695. Anal. Calcd for C₃₆H₂₉N (475.23): C, 90.91; H, 6.15; N, 2.94%; found: C, 90.65; H, 6.13; N, 3.19%.

2,4,7-Tribenzhydrylnaphthylamine was obtained as a light yellow solid, Mp: 161–162 °C. ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.86 (d, 1H, *J* = 8.8, Ar-H), 7.47 (s, 1H, Ar-H), 7.31–7.11 (m, 23H, Ar-H), 7.01–6.96 (m, 8H, Ar-H), 6.35 (s, 1H, Ar-H), 6.06 (s, 1H, -CHPh₂), 5.69 (s, 1H, -CHPh₂), 5.57 (s, 1H, -CHPh₂), 3.90 (s, 2H, -NH₂). ¹³C NMR (100 MHz, CDCl₃, TMS): 144.1, 143.7, 142.5, 140.2, 137.9, 130.3, 130.1, 129.6, 129.5, 129.4, 129.3, 128.5, 128.4, 128.2, 127.8, 126.6, 126.5, 126.0, 125.0, 124.0, 122.4, 121.1, 57.2, 52.9, 52.5. FT-IR (KBr, disk, cm⁻¹): 3412, 3353, 3057, 3024, 1627, 1598, 1563, 1514, 1492, 1447, 1378, 1251, 1179, 1151, 1075, 1029, 918, 824, 784, 747, 697. Anal. Calcd for C₄₉H₃₉N (641.31): C, 91.69; H, 6.12; N, 2.18%; found: C, 91.38; H, 6.28; N, 2.09%.

Synthesis of ligands

2-((2-Benzhydrylnaphthylimino)ethyl)pyridine (L1). A mixture of 2-acetylpyridine (0.459 g, 3.79 mmol), 2-benzhydrylnaphthylamine (1.23 g, 3.98 mmol) and a catalytic amount of *p*-toluenesulfonic acid (0.144 g, 0.76 mmol) in toluene (80 mL) was refluxed for 8 h. After solvent evaporation at reduced pressure, 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 71% isolated yield. Mp: 114–115 °C. ¹H NMR (400 MHz, CDCl₃, TMS): δH 8.68 (d, 1H, *J* = 4.4 Hz, Py-H), 8.47 (d, 1H, *J* = 8.0 Hz, Py-H), 7.87–7.82 (m, 2H, Py-H), 7.51–7.07 (m, 16H, Ar-H), 5.72 (s, 1H, -CHPh₂), 1.55 (s, 3H, -CH₃). ¹³C NMR (100 MHz, CDCl₃, TMS): 170.4, 156.2, 148.8, 145.4, 144.0, 142.7, 136.6, 133.0, 129.9, 129.6, 128.5, 128.3, 128.2, 127.5, 126.3, 125.9, 125.1, 123.2, 123.0, 121.6, 52.2, 17.4. FT-IR (KBr, disk, cm⁻¹): 3051, 3003, 1643 ($\nu_{C=N}$), 1565, 1464, 1302, 1275, 1098, 810, 748, 725, 696. Anal. Calcd for C₃₀H₂₄N₂ (412.19): C, 87.35; H, 5.86; N, 6.79%; found: C, 87.06; H, 6.11; N, 6.59%.

2-((2,4-Dibenzhydrylnaphthylimino)ethyl)pyridine (L2). In a manner similar to that described for L1, L2 was prepared as a chartreuse solid in 61% yield. Mp: 111–112 °C. ¹H NMR (400 MHz, CDCl₃, TMS): δ 8.67 (d, 1H, *J* = 4.0 Hz, Py-H), 8.45 (d, 1H, *J* = 8.0 Hz, Py-H), 7.96 (d, 1H, *J* = 8.4 Hz, Py-H), 7.85 (t, 1H, *J* = 7.4 Hz, Py-H), 7.43–6.88 (m, 24H, Ar-H), 6.67 (s, 1H,



Ar-H), 6.18 (s, 1H, -CHPh₂), 5.58 (s, 1H, -CHPh₂), 1.59 (s, 3H, -CH₃). ¹³C NMR (100 MHz, CDCl₃, TMS): 170.5, 156.2, 148.8, 144.2, 144.0, 143.8, 142.7, 136.6, 134.6, 131.2, 130.1, 129.7, 129.6, 129.2, 128.3, 128.1, 127.0, 126.3, 126.2, 125.9, 125.4, 125.1, 123.8, 121.6, 53.0, 52.2, 17.6. FT-IR (KBr, disk, cm⁻¹): 3058, 3024, 1643 (ν_{C=N}), 1566, 1448, 1363, 1301, 1242, 1099, 1029, 787, 737, 696. Anal. Calcd for C₄₃H₃₄N₂ (578.27): C, 89.24; H, 5.92; N, 4.84%; found: C, 88.60; H, 6.24; N, 4.73%.

2-((2,4,7-Tribenzhydrylnaphthylimino)ethyl)pyridine (L3).

In a manner similar to that described for L1, L3 was prepared as a yellow solid in 72% yield. Mp: 106–107 °C. ¹H NMR (400 MHz, CDCl₃, TMS): δ 8.67 (d, 1H, *J* = 4.8 Hz, Py-H), 8.26 (d, 1H, *J* = 8.0 Hz, Py-H), 7.88 (d, 1H, *J* = 8.8 Hz, Py-H), 7.81 (t, 1H, *J* = 7.6 Hz, Py-H), 7.43–6.86 (m, 33H, Ar-H), 6.65 (s, 1H, Ar-H), 6.14 (s, 1H, -CHPh₂), 5.55 (s, 1H, -CHPh₂), 5.54 (s, 1H, -CHPh₂), 1.42 (s, 3H, -CH₃). ¹³C NMR (100 MHz, CDCl₃, TMS): 170.5, 156.2, 148.5, 144.0, 143.9, 143.8, 143.6, 142.9, 141.0, 136.5, 134.6, 129.9, 129.7, 129.6, 129.2, 128.4, 128.3, 128.1, 127.8, 126.4, 126.3, 126.2, 126.1, 125.0, 124.6, 124.3, 124.2, 121.6, 56.8, 53.0, 52.2, 17.7. FT-IR (KBr, disk, cm⁻¹): 3057, 3024, 1642 (ν_{C=N}), 1596, 1492, 1447, 1362, 1101, 1075, 1030, 785, 743, 697. Anal. Calcd for C₅₆H₄₄N₂ (744.35): C, 90.29; H, 5.95; N, 3.76%; found: C, 89.95; H, 6.03; N, 3.70%.

Synthesis of nickel complexes

Bis(2-((2-benzhydrylnaphthylimino)ethyl)pyridyl)nickel bromide (Ni1). (DME)NiBr₂ (0.25 mmol) and the ligand L1 (0.5 mmol) were dissolved in a mixture of 10 mL ethanol-CH₂Cl₂ (v/v = 1 : 1). The mixture was stirred for 12 h, and then diethyl ether was added to the mixture to precipitate the complex. The precipitant was collected by filtration, washed with diethyl ether (3 × 5 mL), and dried in vacuum to obtain a yellow powder in 84% yield. FT-IR (KBr, disk, cm⁻¹): 3058, 3026, 1619 (ν_{C=N}), 1594, 1493, 1446, 1373, 1318, 1261, 1119, 813, 776, 750, 700. Anal. Calcd for C₆₀H₄₈Br₂N₄Ni (1040.16): C, 69.06; H, 4.64; N, 5.37%. Found: C, 68.95; H, 4.82; N, 5.16%.

Bis(2-((2,4-dibenzhydrylnaphthylimino)ethyl)pyridyl)nickel bromide (Ni2). In a manner similar to that described for Ni1, Ni2 was prepared as a yellow powder in 88% yield. FT-IR (KBr, disk, cm⁻¹): 3060, 3024, 1622 (ν_{C=N}), 1596, 1493, 1446, 1375, 1322, 1261, 1076, 1027, 782, 741, 700. Anal. Calcd for C₈₆H₆₈Br₂N₄Ni (1372.32): C, 75.07; H, 4.98; N, 4.07%. Found: C, 74.91; H, 4.75; N, 4.16%.

Bis(2-((2,4,7-tribenzhydrylnaphthylimino)ethyl)pyridyl)nickel bromide (Ni3). In a manner similar to that described for Ni1, Ni3 was prepared as a yellow powder in 84% yield. FT-IR (KBr, disk, cm⁻¹): 3058, 3025, 1624 (ν_{C=N}), 1596, 1494, 1446, 1369, 1319, 1257, 1076, 1029, 837, 742, 699. Anal. Calcd for C₁₁₂H₈₈Br₂N₄Ni (1704.47): C, 78.74; H, 5.19; N, 3.28%. Found: C, 78.48; H, 5.14; N, 3.28%.

2-((2-Benzhydrylnaphthylimino)ethyl)pyridylnickel chloride (Ni4). NiCl₂·6H₂O (0.5 mmol) and the ligand L1 (0.5 mmol) were dissolved in a mixture of 10 mL ethanol-CH₂Cl₂ (v/v = 1 : 1). The mixture was stirred for 12 h, and then diethyl ether was added to the mixture to precipitate the complex. The precipitant was collected by filtration, washed with diethyl ether

(3 × 5 mL), and dried in vacuum to obtain a yellow powder in 96% yield. FT-IR (KBr, disk, cm⁻¹): 3057, 2972, 2902, 1625 (ν_{C=N}), 1596, 1493, 1446, 1374, 1318, 1259, 1161, 1074, 1046, 814, 787, 752, 727, 703. Anal. Calcd for C₃₀H₂₄Cl₂N₂Ni (540.07): C, 66.46; H, 4.46; N, 5.17%. Found: C, 66.28; H, 4.48; N, 4.88%.

2-((2,4-Dibenzhydrylnaphthylimino)ethyl)pyridylnickel chloride (Ni5). In a manner similar to that described for Ni4, Ni5 was prepared as a yellow powder in 92% yield. FT-IR (KBr, disk, cm⁻¹): 3061, 3025, 1624 (ν_{C=N}), 1598, 1493, 1446, 1370, 1321, 1256, 1164, 1125, 1029, 821, 743, 701. Anal. Calcd for C₄₃H₃₄Cl₂N₂Ni (706.15): C, 72.91; H, 4.84; N, 3.95%. Found: C, 72.80; H, 5.02; N, 3.99%.

2-((2,4,7-Tribenzhydrylnaphthylimino)ethyl)pyridylnickel chloride (Ni6). In a manner similar to that described for Ni4, Ni6 was prepared as a yellow powder in 82% yield. FT-IR (KBr, disk, cm⁻¹): 3058, 3025, 1628 (ν_{C=N}), 1597, 1493, 1447, 1368, 1319, 1256, 1076, 1029, 838, 743, 698. Anal. Calcd for C₅₆H₄₄Cl₂N₂Ni (872.22): C, 76.91; H, 5.07; N, 3.20%. Found: C, 76.68; H, 5.30; N, 3.00%.

X-ray crystallographic studies

A single crystal of Ni2 suitable for X-ray diffraction analyses was obtained by laying heptane on ethanol solution at room temperature. A single crystal of the nickel chloride complex Ni4 suitable for X-ray diffraction analysis was obtained by laying diethyl ether on their dichloromethane-methanol (v/v = 1 : 1) solutions at room temperature. X-ray studies were carried out using a Rigaku Saturn724+CCD diffractometer with MoKα radiation (λ = 0.71073 Å) at 173(2) K (Ni2) and 100 K (Ni4), 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 F². All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package.²⁶ During structure refinement of Ni2 and Ni4·2CH₃OH, there were free solvent molecules which have no influence on the geometry of the main compounds. Therefore, the SQUEEZE option of the crystallographic program PLATON²⁷ 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

Ethylene polymerizations were carried out in a 250 mL stainless steel autoclave equipped with a mechanical stirrer and a temperature controller. The autoclave was evacuated by a vacuum pump and back-filled three times with N₂ 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 Et₂AlCl) and additional toluene (maintaining total volume at 100 mL in the reactor) were added by syringe. The reaction mixture was intensively stirred for the desired time under 10 atm of ethylene



Table 6 Crystal data and structure refinement for Ni₂ and Ni₄·2CH₃OH

Identification code	Ni ₂	Ni ₄ ·2CH ₃ OH
Crystal color	Brown	Yellow
Empirical formula	C ₈₆ H ₆₈ Br ₂ N ₄ Ni	C ₆₂ H ₅₆ Cl ₄ N ₄ Ni ₂ O ₂
Formula weight	1375.97	1148.33
Temperature/K	173 (2)	100 (2)
Wavelength/Å	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	P1	P2(1)/c
a/Å	11.391(2)	15.786(3)
b/Å	18.201(4)	10.024(2)
c/Å	18.612(4)	18.193(4)
Alpha/°	91.61(3)	90
Beta/°	104.33(3)	98.30(3)
Gamma/°	95.61(3)	90
Volume/Å ³	3715.4(13)	2848.6(10)
Z	2	2
D _{calcd} (g cm ⁻³)	1.230	1.339
μ/mm ⁻¹	1.382	0.895
F(000)	1420	1192
Crystal size/mm	0.175 × 0.122 × 0.056	0.248 × 0.127 × 0.109
θ range (°C)	1.13–27.43	2.41–27.48
Limiting indices	−14 ≤ h ≤ 14 −23 ≤ k ≤ 23 −22 ≤ l ≤ 24	−20 ≤ h ≤ 20 −12 ≤ k ≤ 13 −23 ≤ l ≤ 23
No. of rflns collected	33 431	18 670
No. unique rflns	16 797	6483
R(int)	0.0624	0.0326
No. of params	838	336
Completeness to θ	99.1%	99.5%
Goodness of fit on F ²	1.024	1.129
Final R indices [I > 2Σ(I)]	R ₁ = 0.0825 wR ₂ = 0.2210	R ₁ = 0.0368 wR ₂ = 0.0866
R indices (all data)	R ₁ = 0.1150 wR ₂ = 0.2529	R ₁ = 0.0399 wR ₂ = 0.0885
Largest diff. peak, and hole (e Å ⁻³)	0.728 and −0.783	0.479 and −0.284

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*.

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