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ARTICLE

Targeting polyethylene waxes: 9-(2-Cycloalkylphenylimino)-5,6,7,8-tetrahydrocycloheptapyridylnickel halides and their ethylene polymerization

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A series of 9-(2-cycloalkylphenylimino)-5,6,7,8-tetrahydrocycloheptapyridine derivatives (**L1** – **L3**) was synthesized, and reacted with nickel halides to form their corresponding nickel complexes (bromide: **Ni1** – **Ni3**; chloride: **Ni4** – **Ni6**). The nickel complexes and organic compounds were well characterized. The representative complex **Ni1** was determined by single crystal X-ray study, revealing a distorted trigonal bipyramidal geometry at nickel centre. Upon activation with either modified methylaluminoxane (MMAO) or diethylaluminiumchloride (Et₂AlCl), all nickel complexes showed high activities toward ethylene polymerization. The obtained polymers were confirmed to be polyethylene waxes with low molecular weights (in the range of 1.83 to 6.78 kg·mol⁻¹) and narrow polydispersity (PDI: 1.38 – 1.78); moreover, the obtained polyethylenes were highly branched ones. These polyethylene waxes are potential application as functional adducts, lubricants or pour-point depressants.

Introduction

The developments of organo-nickel compounds in its first hundred years was introduced within a historical significance by Wilke about three decades ago.¹ In addition to the catalytic performances towards hydrogenation and C-C coupling cyclization, ethylene insertion induced by nickel (nickel effect) was recognized as the pioneer work resulting to Ziegler catalysts for massive polyolefin industry.² In fact, nickel catalysts have made significant contribution in petrochemical industry; instead of olefin polymerization, ethylene oligomerization has been achieved by nickel complex pre-catalysts as a commercialized “SHOP” process for α -olefins as basic substances for fine chemicals.³ The discovery of α -diiminometal (Ni²⁺ or Pd²⁺) complex pre-catalysts toward ethylene polymerization resurrected the late-transition metal pre-catalysts towards olefin polymerization in 1995,⁴ and extensive investigations have been made and assumed for the useful catalytic system.⁵ The late-transition metal complex pre-catalysts have fixed necessary requirements of petrochemical companies to implement; besides catalytic activities, unique properties of newly obtained polyolefin materials would be an

important issue. Therefore the useful polymers with advanced properties are demanded in order to attract further investments for the potentially commercializing process. Within the nickel complex pre-catalysts exploited,^{5a-c} two models of the α -diiminonickel (**A**, Scheme 1)^{4,6,7} and 2-iminopyridylnickel (**B**, Scheme 1)⁸ complexes have been extensively investigated. The α -diimino ligands (model **A**) have been developed from either simple diketones^{4,6} or acenaphthylene-1,2-dione as well as its analogues,^{4,7} in which pre-catalysts using rigid ligands generally showed higher catalytic activities. To create the rigid ligands on the basis of the 2-iminopyridyl frame (model **B**), the pyridine-based frames fused with cyclic ketones have been designed and used to form 8-arylimino-5,6,7-trihydroquinolylnickel (**C**, Scheme 1)^{9,10} and 9-aryliminocycloheptapyridylnickel (**D**, Scheme 1) complexes;¹¹ and these new pre-catalysts (**C** and **D**) showed better performance in ethylene polymerization than their analogues of 2-iminopyridylnickel complexes (**B**).⁸ Moreover, using cycloalkyl-substituted anilines instead of anilines, 8-(2-cycloalkylphenylimino)-5,6,7-trihydroquinolylnickel pre-catalysts (model **C**)¹⁰ produced polyethylenes with lower molecular weights and narrow polydispersity than those by their analogues (**C**) without cycloalkyl-substituents,⁹ which are highly demanded in market as the polyethylene waxes. Until now, there are only a few examples of metal complexes developed from cycloalkyl-substituted anilines^{10,12} because of no cycloalkyl-substituted anilines commercially available; however, the conveniently synthetic procedure for cycloalkyl-substituted anilines has been developed and potentially scaled up for the industrial requirement. Subsequently, the reactions of 5,6,7,8-tetrahydrocycloheptapyridine-9-one with

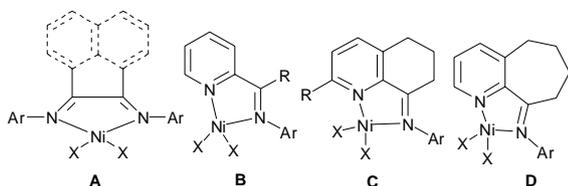
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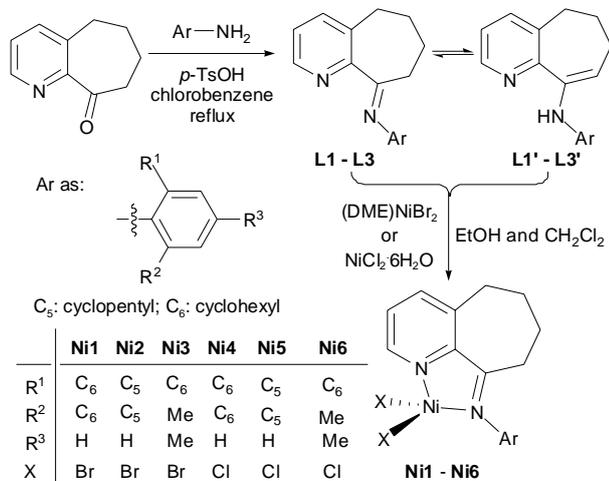
cycloalkylanilines were conducted to form a series of 9-(2-cycloalkylphenylimino)-5,6,7,8-tetrahydrocycloheptapyridine derivatives, which further reacted with nickel halides for the title complexes. Upon activation with either MMAO or Et₂AlCl, all nickel complexes performed high activities towards ethylene polymerization; more importantly, the obtained polyethylenes possessed lower molecular weights and narrower polydispersity.



Scheme 1. Typical bidentate nickel complex pre-catalysts

Results and discussion

Synthesis and characterization. The condensation reactions of 5,6,7,8-tetrahydrocycloheptapyridine-9-one with a series of 2-cycloalkylanilines were conducted to form 9-(2-cycloalkylphenylimino)-5,6,7,8-tetrahydrocycloheptapyridine derivatives (**L1** – **L3**, including their corresponding enamine analogues **L1'** – **L3'**, Scheme 2) with yellowish compounds according to our reported procedure.^{9b,10} The mixture of two isomer ligands reacted with NiCl₂ or DME-NiBr₂ in the solvent of ethanol and dichloromethane at ambient temperature for 12 hours forming complexes (**Ni1** – **Ni6**) with reasonable to excellent yields (71–94%, Scheme 2). All organic compounds were identified by ¹H/¹³C NMR measurements, FT-IR spectroscopy as well as elemental analysis, and the corresponding nickel complexes were also characterized by FT-IR spectroscopy and elemental analysis. As reported in the previous work,^{9b,10} all the ligands contained two isomers, forming enamine (**L1'**) and Schiff-base (**L**) (Scheme 2) due to the migration of double bond from imino part to the cycloheptane. Furthermore, the representative complex **Ni1** was confirmed by the single-crystal X-ray diffraction.



Scheme 2. Synthetic procedures for 9-(2-cycloalkylphenylimino)-5,6,7,8-tetrahydrocycloheptapyridines and their nickel halides

Single-crystal X-ray diffraction studies

Single crystal of **Ni1** suitable for X-ray diffraction analysis could be obtained within two days by layering diethyl ether onto the mixed solution of dichloromethane and methanol at room temperature. The molecular structure of complex **Ni1** is shown in Fig. 1, accompanied by selected bond lengths and angles in Table 1.

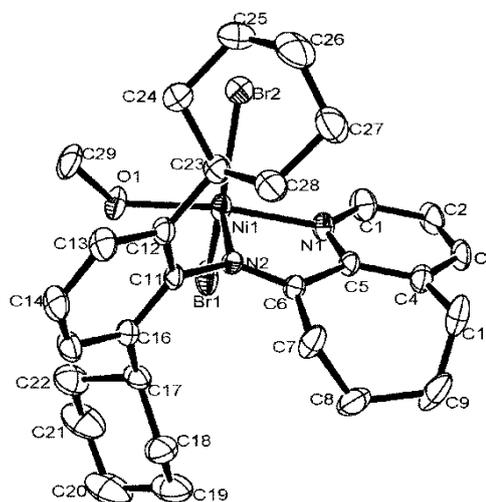


Fig. 1. ORTEP drawing of the molecular structure of **Ni1**·CH₃OH. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms were omitted for clarity.

Table 1. Selected bond lengths (Å) and angles (°) for **Ni1**·CH₃OH

Bond lengths (Å)		Bond angles(°)	
Ni1-N1	2.038(3)	O1-Ni1-N2	94.68(12)
Ni1-N2	2.027(3)	O1-Ni1-N1	170.80(13)
Ni1-O1	2.053(3)	N2-Ni1-N1	79.20(12)
Ni1-Br1	2.4705(9)	O1-Ni1-Br2	95.95(9)
Ni1-Br2	2.4117(9)	N2-Ni1-Br2	112.15(8)
N1-C1	1.327(5)	N1-Ni1-Br1	92.75(10)
N1-C5	1.338(5)	O1-Ni1-Br1	86.89(9)
N2-C6	1.279(4)	N2-Ni1-Br1	110.15(8)
N2-C11	1.449(4)	N1-Ni1-Br1	88.78(10)
		Br2-Ni1-Br1	137.18(3)

As shown in Fig. 1, the nickel atom exists as penta-coordinated with a *N,N*-bidentate ligand, two bromides and a assisted coordination of methanol molecule. Furthermore, the molecular structure of **Ni1** reveals a distorted trigonal bipyramidal geometry at nickel atom centre consistent to its analogous.^{13,14} The equatorial plane is made up of N1, N2 and O1 along with a 0.129 Å deviation of the nickel metal atom, and the axial plane is made up of three atoms (N2, Br1 and Br2). The length of the Ni–N_{imino} (Ni1–N2, 2.027(3) Å) is slightly shorter than the Ni–N_{pyridine} (Ni1–N1, 2.038(3) Å), suggesting the stronger electron donation from N_{imino} to nickel core, which is actually opposite to the observation in the previous work without cycloalkyl-substituents;¹¹ in another word, the Ni–N_{imino} bond is enhanced by coordinating between nickel and the rich-electronic N_{imino} atom due to the electron-donating cycloalkyl substituents. The dihedral angle between the plane of Ni1, N1 and N2 and phenyl plane (C1, C2, C3, C4, C5, C6, C7, C8, C9, C10, C11, C12, C13, C14, C15, C16, C17, C18, C19, C20, C21, C22, C23, C24, C25, C26, C27, C28, C29) is 12.3(1)°.

C5 and N1) is 1.90°. As shown in Table 1, the bond angles of O1-Ni1-N2 and N2-Ni1-N1 are at 94.67° and 79.20°, respectively.

Ethylene Polymerization

Based on our previous work,⁹ ethylene polymerization was carried out with nickel complex (**Ni2**) by using different co-catalysts (MAO, MMAO, Et₂AlCl, Me₂AlCl and EASC) to probe the suitable co-catalyst. Obviously, the co-catalysts Et₂AlCl (entry 3, Table 2) showed the highest activity towards ethylene polymerization among these alkylaluminium reagents. Meanwhile, MMAO (entry 2, Table 2) also obtained reasonable activity when appending diverse aluminoxane reagents. Hence, MMAO and Et₂AlCl, were selected for the further investigations.

Table 2. Selection of the Suitable Alkylaluminiums Based on **Ni2**^a

Entry	Co-cat.	Al/Ni	Yield(g)	Act. ^b	M_w^c (kg mol ⁻¹)	M_w/M_n^c	T_m^d (°C)
1	MAO	1000	0.06	0.04	4.51	1.49	71.2
2	MMAO	1000	1.08	0.72	4.88	1.66	68.3
3	Et ₂ AlCl	200	4.80	3.20	3.89	1.76	54.6
4	Me ₂ AlCl	200	trace	Trac e	--	--	--
5	EASC	200	trace	Trac e	--	--	--

^a Conditions: 3 μmol of **Ni2**; 30 min; 30 °C; 10 atm of ethylene; total volume 100 mL; ^b values in units of 10⁶ g (PE) mol(Ni)⁻¹ h⁻¹; ^c Determined by GPC; ^d Determined by DSC.

Ethylene polymerization in the presence of Et₂AlCl

Ethylene polymerizations were performed using Et₂AlCl as co-catalyst at elevated ethylene pressure (10 atm). The complex **Ni2** was used to screen the optimum conditions including the Al/Ni molar ratio, temperature and reaction time, and the corresponding results were tabulated in Table 3.

On changing the molar ratio of Al/Ni from 200 to 700 (entries 1 – 6, Table 3), the best activity was observed with the molar ratio of 400 at 4.97 × 10⁶ g(PE)·mol⁻¹(Ni)·h⁻¹ (entry 3, Table 3). With the increase of Al/Ni ratios (entries 1 – 6, Table 3), molecular weights of the obtained polyethylene exhibited the tendency of slightly decrease, which was attributed to the increase of the aluminum concentration led to more chain transfers.¹⁵ Impressively, the resulting polyethylenes possessed the narrow molecular weight distributions in the range of 1.46 to 1.76, illustrating the well-defined single-site catalysis.

Regarding to the thermo-stability, the ethylene polymerization was conducted under the reaction temperature setting from 20 to 50 °C (entries 3 and 7 – 9, Table 3). In all cases, the real temperature was commonly higher than the setting temperature due to the exothermal reaction of the ethylene polymerization. The maximum activity was obtained at 30 °C (entry 3, Table 3). The thermo-stability of this system was better than those detected by the 9-arylamino-5,6,7-trihydrocycloheptapyridylnickel complexes.¹¹ According to the GPC curves in Figure 2, the lower molecular weight of polyethylene was attained at higher temperature, that is

interpreted both deactivation of active species at elevated temperature and fast chain transfer at higher temperature.^{4,15} These phenomena were consistent with the observations of their analogs^{10,11}. All GPC curves of the resulting polyethylenes (Figure 2) show narrow polydispersity, which indicates the typical single-site behavior for the system.

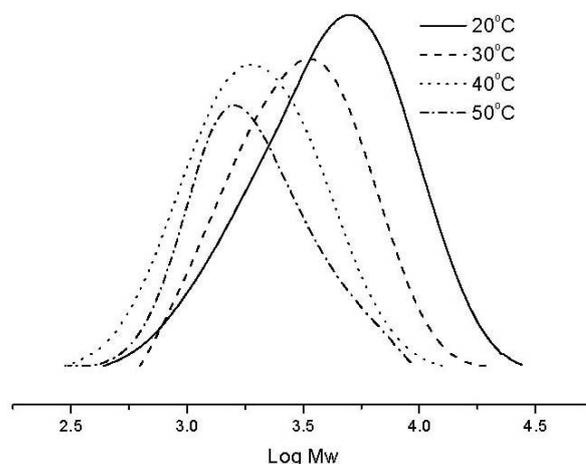


Fig. 2. The GPC curves of polyethylene obtained at different temperatures (entries 3, 7–9, Table 3)

In addition, the ethylene polymerization was investigated at different times. On prolonging the reaction time from 15 to 60 min (entries 3 and 10 – 12, Table 3), the obtained polyethylenes accumulated higher molecular weights. Interestingly, the higher activity of 4.97 × 10⁶ g(PE) mol(Ni)⁻¹ h⁻¹ (entry 3, Table 3) was showed at 30 min, meanwhile a lower polyethylene activity was obtained with 3.41 × 10⁶ g(PE) mol(Ni)⁻¹ h⁻¹ at 15 min (entry 10, Table 3), indicating the inducing time required in the current system. This phenomenon was also observed in the previous nickel precatalysts derived from cycloalkyl-substituted anilines;¹⁰ that means, the cycloalkyl-substituents occupied the space around nickel core and caused the slowly activating metal complex to form active species. The longer reaction times (entries 11 and 12, Table 3), the amounts of polyethylene obtained were increased, however, the catalytic activities were decreased along with prolonging polymerization time; that indicated the parts of active species being deactivated during the ethylene polymerization.

On the basis of above information, the optimum conditions (the Al/Ni ratio of 400 at 30 °C) were employed in exploring the catalytic behavior of other nickel analogs (**Ni1** and **Ni6**), and the best activity was achieved by **Ni3**/Et₂AlCl (up to 6.27 × 10⁶ g(PE)mol⁻¹(Ni)h⁻¹). Regarding the influence by anionic halides, their catalytic activities were in the order **Ni1** [Br, 2,6-di(cyclohexyl)] < **Ni4** [Cl, 2,6-di(cyclohexyl)], **Ni2** [Br, 2,6-di(cyclopentyl)] > **Ni5** [Cl, 2,6-di(cyclopentyl)] and **Ni3** [Br, 2-methyl-6-cyclohexyl] > **Ni6** [Cl, 2-methyl-6-cyclohexyl], indicating random results; however, the bromide positively affected catalytic performances for complexes containing less bulky substituents. For bromide complexes, their activities decreased in the order **Ni3** [2-methyl-6-cyclohexyl] > **Ni2** [2,6-di(cyclopentyl)] > **Ni1** [2,6-di(cyclohexyl)] > **Ni6** [2-methyl-6-cyclohexyl] > **Ni5** [2,6-di(cyclopentyl)] > **Ni4** [2,6-di(cyclohexyl)].

Table 3. Ethylene Polymerization by Ni1–Ni6/Et₂AlCl^a

Entry	Cat.	Al/Ni	t (min)	T (°C)	Yield(g)	Act. ^b	M _w ^c (kg mol ⁻¹)	M _w /M _n ^c	T _m ^d /(°C)
1	Ni2	200	30	30	4.80	3.20	3.89	1.76	54.6
2	Ni2	300	30	30	5.45	3.63	3.87	1.69	56.3
3	Ni2	400	30	30	7.45	4.97	3.64	1.46	32.7
4	Ni2	500	30	30	6.08	4.05	3.63	1.67	35.1
5	Ni2	600	30	30	5.96	3.97	3.61	1.53	33.7
6	Ni2	700	30	30	4.43	2.95	3.58	1.64	52.7
7	Ni2	400	30	20	4.62	3.08	5.32	1.70	75.7
8	Ni2	400	30	40	2.02	1.35	2.37	1.49	17.4
9	Ni2	400	30	50	0.32	0.21	2.25	1.38	76.0
10	Ni2	400	15	30	3.62	4.83	3.41	1.60	32.3
11	Ni2	400	45	30	9.80	4.36	3.70	1.76	31.0
12	Ni2	400	60	30	11.03	3.68	3.77	1.78	35.5
13	Ni1	400	30	30	4.62	3.08	2.36	1.53	52.9
14	Ni3	400	30	30	9.41	6.27	1.91	1.65	53.0
15	Ni4	400	30	30	5.20	3.47	2.32	1.64	51.9
16	Ni5	400	30	30	7.14	4.76	3.21	1.53	33.4
17	Ni6	400	30	30	6.25	4.17	1.83	1.66	53.1
18 ^e	Ni2	400	30	30	1.82	1.21	2.93	1.52	18.9

^a Conditions: 3 μmol of Ni; 10 atm of ethylene; total volume 100 mL; ^b values in units of 10⁶ g(PE)·mol⁻¹(Ni)·h⁻¹; ^c Determined by GPC; ^d Determined by DSC. ^e 5 atm of ethylene.

di(cyclopentyl)] > Ni1 [2,6-di(cyclohexyl)] (entries 3, 13–14, Table 3), which is ascribed to the steric hindrance by the bulky substituents. Moreover, the polyethylene produced by Ni2 possessed higher molecular weight and narrower polydispersity, but lower T_m, indicating higher branching polyethylene obtained. For chloride complexes, the order of their activities is as Ni5 [2,6-di(cyclopentyl)] > Ni6 [2-methyl-6-cyclohexyl] > Ni4 [2,6-di(cyclohexyl)] (entries 15–17, Table 3), indicating the synergic influences of the substituents linked on phenyl bridged to N_{imino} and chloride in both steric and electronic manners. Similar to its bromide analogues, the precatalyst Ni5 produced the polyethylene having a higher molecular weight, narrower polydispersity and lower T_m.

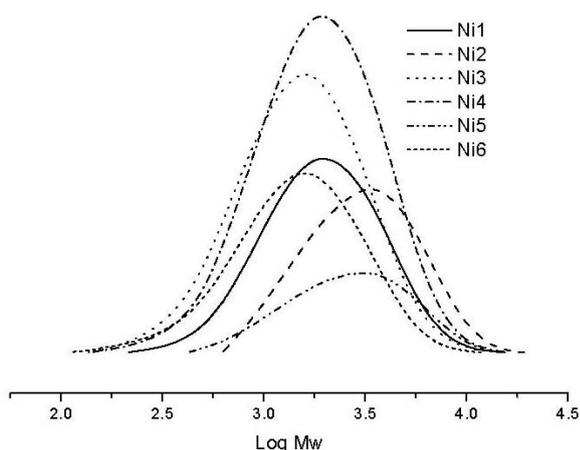


Fig. 3 The GPC curves of polyethylenes obtained by pre-catalysts (entries 3, 13–17, Table 3).

Comparing with 8-(2-cycloalkylphenylimino)-5,6,7-trihydroquinolynickel complexes,¹⁰ these catalytic systems exhibited much higher activities. By contrast to 9-arylamino-

5,6,7-trihydrocycloheptapyridynickel complexes,¹¹ these catalytic systems showed slightly narrower polydispersity, which probably due to the bulky substituents stabilizing the active species that made the narrower PDIs. It could also be confirmed by the GPC curves (Figure 3).

In general, both bromide and chloride nickel pre-catalysts produced polyethylene waxes with narrow polydispersity, low molecular weights and low melting points (T_m). The low melting points (T_m) of the obtained polyethylenes were general caused by high branching. For example, the polyethylenes obtained at 40 and 50 °C possessed the similar molecular weights and polydispersity (entries 8 and 9, Table 3), but lower T_m, for the polyethylene formed at 40 °C indicating higher branching. Therefore the ¹³C NMR measurement was conducted in deuterated tetrachloroethane for the polyethylene by Ni2/Et₂AlCl at 40 °C (entry 8, Table 3, Figure 4), indicating the branch number of 95 per 1000 carbons being interpreted according to the literature;¹⁶ and the main branches were methyl (55.1%), ethyl (17.6%), propyl (5.9%) as well as longer chains (21.4%).

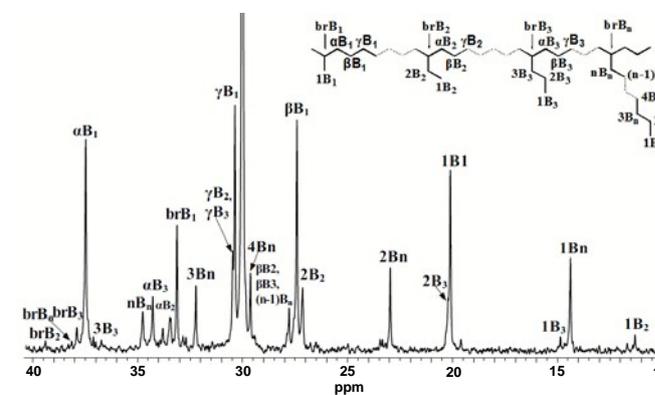


Fig. 4. ¹³C NMR spectrum of the polyethylene by Ni2/Et₂AlCl at 40 °C (entry 8, Table 3).

Ethylene polymerization in the presence of MMAO

Different from the previous works^{10,11} the catalyst activated by MMAO showed higher polyethylene activity in the co-catalyst of aluminoxane reagents. The performances of the influence of reaction conditions on the ethylene polymerization with **Ni2**/MMAO (Table 4) were investigated in detail, and exhibited slightly different to **Ni2**/Et₂AlCl system regarding to the Al/Ni molar ratios and reaction temperatures.

Changing the Al/Ni molar ratios from 1000 to 2500 (entries 1 – 6, Table 4), the higher activity of 2.70×10^6 g(PE)·mol⁻¹(Ni)·h⁻¹ was observed with the Al/Ni ratio of 1750 (entry 3, Table 4). On further increasing the Al/Ni molar ratios (entries 4 – 6, Table 4), the catalytic system resulted slightly lower activities and produced the polyethylenes with negligible differences of their molecular weights and polydispersity, which possesses the similar behavior in the system **Ni1**/MAO

Table 4. Ethylene Polymerization by **Ni1–Ni6**/MMAO^a

Entry	Cat.	Al/Ni	t (min)	T (°C)	Yield(g)	Act. ^b	M _w ^c (kg mol ⁻¹)	M _w /M _n ^c	T _m ^d /(°C)
1	Ni2	1000	30	30	1.08	0.72	4.88	1.66	68.3
2	Ni2	1500	30	30	2.41	1.61	4.08	1.62	53.3
3	Ni2	1750	30	30	4.05	2.70	3.94	1.66	53.2
4	Ni2	2000	30	30	3.91	2.61	3.93	1.53	61.9
5	Ni2	2250	30	30	3.15	2.10	4.24	1.67	53.6
6	Ni2	2500	30	30	2.74	1.83	4.39	1.67	53.5
7	Ni2	1750	30	20	5.53	3.69	5.80	1.76	80.2
8	Ni2	1750	30	40	1.65	1.10	2.48	1.50	19.0
9	Ni2	1750	30	50	0.17	0.11	2.16	1.34	82.2
10	Ni2	1750	15	20	2.25	3.00	5.73	1.74	80.2
11	Ni2	1750	45	20	8.03	3.57	5.99	1.73	76.7
12	Ni2	1750	60	20	9.42	3.14	6.15	1.78	76.9
13	Ni1	1750	30	20	3.50	2.33	4.11	1.64	79.8
14	Ni3	1750	30	20	5.67	3.78	4.68	1.68	92.8
15	Ni4	1750	30	20	3.55	2.37	4.15	1.62	78.8
16	Ni5	1750	30	20	3.38	2.25	6.78	1.66	85.6
17	Ni6	1750	30	20	7.45	4.97	3.96	1.51	86.3
18 ^e	Ni2	1750	30	20	1.58	1.05	4.73	1.56	38.7

^a Conditions: 3 μmol of Ni; 10 atm of ethylene; total volume 100 mL; ^b values in units of 10⁶ g(PE)·mol⁻¹(Ni)·h⁻¹; ^c Determined by GPC; ^d Determined by DSC. ^e 5 atm of ethylene.

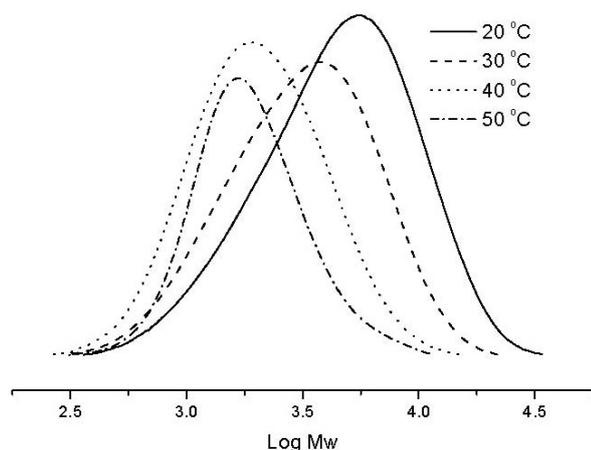


Fig. 5. The GPC curves of polyethylene obtained at different temperatures (entries 3, 7–9, Table 4)

of 8-(2-cycloalkylphenylimino)-5,6,7-trihydroquinolynickel complexes.¹⁰

Conducting the polymerization between 20 to 50 °C (entries 3 and 7 – 9, Table 4), unlike the **Ni2**/Et₂AlCl system, the best activity was achieved at 20 °C (entry 7, Table 4); higher reaction temperature applied, lower the activities were obtained, indicating the deactivation of active species at higher temperature, which may be decomposed due to generate Ni-hydride species.^{7c} The resultant polyethylenes showed gradually lower molecular weights with reaction temperature elevated (Fig. 5).

The trend for the lifetime of the pre-catalysts (entries 7 and 10 – 12, Table 4) was detected to be the same as the **Ni2**/Et₂AlCl system (entries 3 and 10 – 12, Table 3). Meanwhile, prolonging reaction time can also obtain the polyethylenes with higher molecular weights and narrow polydispersity.

Under the optimum conditions with an Al/Ni ratio of 1750 at 20 °C over 30 min (entry 7, Table 4), the other complexes were investigated for ethylene polymerization (entries 13 – 17, Table 4). In all cases, these nickel complex pre-catalysts exhibited high activities towards ethylene polymerization, producing polyethylenes with low molecular weights and narrow polydispersity. Moreover, these polyethylene samples possessed narrower polydispersity, indicating well-behaved single-site catalysis.

Compared with **Ni**/Et₂AlCl systems, the catalytic systems with MMAO generally showed slightly lower activities, but produced polyethylenes having higher molecular weights and higher T_m values; the most of the resultant polyethylenes possessed molecular weights around 5.0 kg·mol⁻¹, which were higher than those obtained by **Ni**/Et₂AlCl systems and their analogues.^{10,11} In addition, the lowest T_m value was observed to the polyethylene obtained at 40 °C (entry 8, Table 4), being consistent to the observation with **Ni**/Et₂AlCl system. Though

the higher T_m value to polyethylene obtained by **Ni3**/MMAO (entry 14, Table 4), the ^{13}C NMR spectrum of the polyethylene shown in Figure 6 indicated the branch number of 53 per 1000 carbons, in which the main branches were methyl (84.4%), ethyl (5.3%) and long chains (10.3%).¹⁶

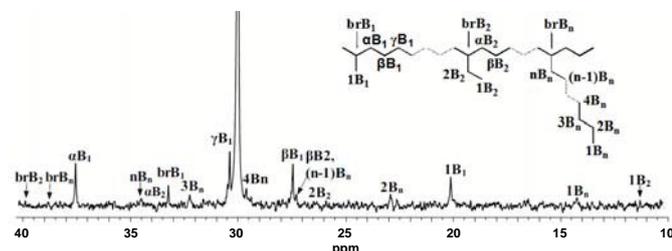


Fig. 6 ^{13}C NMR spectrum of the polyethylene by **Ni3**/MMAO (entry 14, Table 4).

Conclusion

9-(2-cycloalkylphenylimino)-5,6,7,8-tetrahydrocycloheptapyridinickel complexes (**Ni1** – **Ni6**) were successfully synthesized and characterized. The influences of these pre-catalysts and various reaction conditions have been extensively investigated towards ethylene polymerization. The complex **Ni1**, confirmed by single crystal X-ray, showed distorted trigonal bipyramidal geometry around nickel center. Upon activation by either MMAO or Et_2AlCl , all nickel complexes exhibited the well-behaved single-site catalysis with high activities (up to $6.27 \times 10^6 \text{ g(PE)·mol(Ni)}^{-1}\cdot\text{h}^{-1}$). The resultant polyethylenes possessed highly branched with low molecular weights and narrow molecular weight distributions, which were the unique property of polyethylene waxes as additive of lubricants and pour-point depressants. Therefore these typical polyethylenes are potentially useful and worthily considered for the industrial application.

Experimental

General considerations. All manipulations involving air- and moisture-sensitive compounds were performed 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), modified methylaluminoxane (MMAO, 1.93 M in heptane), ethylaluminum sesquichloride (EASC, 0.87M in toluene) and dimethylaluminium chloride (Me_2AlCl , 1.0 M solution in toluene) were purchased from Akzo Nobel Corp. Diethylaluminium chloride (Et_2AlCl , 1.17 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. ^{13}C NMR spectra of the polyethylenes were recorded using a Bruker DMX 400 MHz instrument at ambient temperature in deuterated 1,1,2,2-tetrachloroethane with TMS as an internal standard.

Synthesis of organic compounds

9-(2,6-Dicyclohexylphenylimino)-5,6,7,8-tetrahydrocycloheptapyridine (L1) and 9-(2,6-dicyclohexylphenylamino)-5,6,7-trihydrocycloheptapyridine (L1'). 5,6,7,8-tetrahydrocycloheptapyridin-9-one (0.37 g, 2.5 mmol) and 2,6-dicyclohexyl aniline (0.51 g, 2 mmol) were stirred with a catalytic amount of *p*-toluenesulfonic acid dissolved in 100 mL chlorobenzene. The solution was refluxed for 4 hours. Then the solvent was evaporated at reduced pressure, the mixture was isolated by silica gel column chromatography ($V_{\text{petroleum ether}} : V_{\text{ethyl acetate}} = 25 : 1$) to get the target product (yellow powder L1 : L1' = 91 : 9, 0.32 g, 40% yield). ^1H NMR (400 MHz, CDCl_3 , TMS): δ 8.64(d, $J = 3.6\text{Hz}$, 1H, L1-Py-H), 8.54(d, $J = 3.6\text{Hz}$, L1'-Py-H), 7.55(s, L1'-Py-H), 7.51(d, $J = 7.6\text{Hz}$, 1H, L1-Py-H), 7.26(t, $J = 3.8\text{Hz}$, 1H, L1-Py-H), 7.24(s, L1'-Py-H), 7.19-7.15(m, L1'-Ar-H), 7.13(d, $J = 7.2\text{Hz}$, 2H, L1-Ar-H), 7.07(d, $J = 6.4\text{Hz}$, 1H, L1-Ar-H), 7.04(s, L1'-Ar-H), 6.24(s, L1'-NH), 4.57(t, $J = 6.8\text{Hz}$, L1-CH), 3.01(t, $J = 8.0\text{Hz}$, L1-CH₂), 2.89(t, $J = 6.2\text{Hz}$, 2H, L1-CH₂), 2.69(t, $J = 6.8\text{Hz}$, L1'-CH₂), 2.59(t, $J = 12\text{Hz}$, 2H, L1-CH₂), 2.31(t, $J = 6.2\text{Hz}$, 2H, L1-CH₂ and L1'-CH₂), 2.04-2.00(m, L1'-CH₂), 1.96(d, $J = 11.6\text{Hz}$, 2H, L1-CH₂), 1.69-1.55(m, 10H, L1-CH₂ and L1'-CH₂), 1.40-1.15(m, 10H, L1-CH₂ and L1'-CH₂). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 172.8, 157.2, 148.5, 146.1, 136.6, 134.8, 134.2, 123.8, 123.7, 123.3, 38.8, 34.2, 33.2, 31.9, 31.5, 27.3, 27.0, 26.4, 25.9, 23.1. FT-IR (KBr, cm^{-1}): 2923, 2849, 1632, 1568, 1442, 1301, 1257, 1225, 1175, 1096, 1019, 965, 889, 853, 799, 779. Anal. calcd for $\text{C}_{28}\text{H}_{36}\text{N}_2$ (400): C, 83.95; H, 9.06; N, 6.99 Found: C, 83.63; H, 8.89; N, 7.21%.

9-(2,6-Dicyclopentylphenylimino)-5,6,7,8-tetrahydrocycloheptapyridine (L2) and 9-(2,6-Dicyclopentylphenylamino)-5,6,7-trihydrocycloheptapyridine (L2'). This compound was synthesized in the same procedure as described for L1. L2 and L2' were obtained (yellow oil, L2 : L2' = 91 : 9, 0.60 g, 80% yield). ^1H NMR (400 MHz, CDCl_3 , TMS): δ 8.64(d, $J = 3.6\text{Hz}$, 1H, L1-Py-H), 8.53(d, $J = 3.6\text{Hz}$, L1'-Py-H), 7.56(d, $J = 7.2\text{Hz}$, 1H, L1-Py-H), 7.51(d, $J = 7.2\text{Hz}$, L1'-Py-H), 7.26(t, $J = 6.2\text{Hz}$, 1H, L1-Py-H and L1'-Py-H), 7.20(s, L1-Ar-H), 7.15(d, $J = 7.6\text{Hz}$, 2H, L1-Ar-H), 7.05(t, $J = 7.6\text{Hz}$, 1H, L1-Ar-H), 6.96-6.89(m, L1-Ar-H), 6.21(s, L1'-NH), 4.61(t, $J = 6.8\text{Hz}$, L1-CH), 3.05(t, $J = 8.8\text{Hz}$, 2H, L1-CH₂ and L1'-CH₂), 2.84(t, $J = 6.4\text{Hz}$, 2H, L1-CH₂), 2.66(t, $J = 6.4\text{Hz}$, L1'-CH₂), 2.33(t, $J = 6.0\text{Hz}$, 2H, L1-CH₂ and L1'-CH₂), 2.15-2.12(m, 2H, L1-CH₂ and L1'-CH₂), 1.91-1.88 (m, L1'-CH₂), 1.82-1.73(m, 8H, L1-CH₂), 1.65-1.61(m, 8H, L1-CH₂), 1.59-1.57(m, L1-CH₂). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 172.8, 156.8, 148.4, 147.5, 136.9, 134.5, 133.9, 123.9, 123.7, 123.4, 39.8, 34.8, 34.3, 31.8.

31.2, 26.1, 25.8, 25.6, 22.4. FT-IR (KBr, cm^{-1}): 2946, 2864, 1635, 1568, 1447, 1297, 1185, 1094, 766. Anal. calcd for $\text{C}_{26}\text{H}_{32}\text{N}_2$ (372): C, 83.82; H, 8.66; N, 7.52 Found: C, 83.64; H, 8.75; N, 7.65%.

9-(2,4-Dimethyl-6-cyclohexylphenylimino)-5,6,7,8-tetrahydrocycloheptapyridine (L3) and 9-(2,4-Dimethyl-6-cyclohexylphenylamino)-5,6,7-trihydrocyclohepta-pyridine (L3'). This compound was synthesized in the same procedure as described for L1. L3 and L3' were obtained (yellow oil, L3: L3' = 93 : 7, 0.41 g, 59 % yield). ^1H NMR (400 MHz, CDCl_3 , TMS): δ 8.64(d, $J = 3.6\text{Hz}$, 1H, L1-Py-H), 8.53(d, $J = 3.6\text{Hz}$, L1'-Py-H), 7.51(d, $J = 7.6\text{Hz}$, 1H, L1-Py-H), 7.34(d, $J = 6.8\text{Hz}$, L1'-Py-H), 7.26(t, $J = 3.6\text{Hz}$, 1H, L1-Py-H), 7.24(s, L1'-Py-H), 7.04(s, L1'-Ar-H), 6.97(s, L1'-Ar-H), 6.93(s, 1H, L1-Ar-H), 6.86(s, 1H, L1-Ar-H), 6.07(s, L1'-NH), 4.55(t, $J = 6.8\text{Hz}$, L1'-CH), 2.89-2.84(m, 2H, L1'-CH₂), 2.69-2.65 (m, L1'-CH₂), 2.30(s, 3H, L1'-CH₃), 2.28(s, L1'-CH₃), 2.13(s, 3H, L1'-CH₃), 2.11(s, L1'-CH₃), 1.92-1.50(m, 12H, L1'-CH₂ and L1'-CH₂), 1.38-1.26(m, 4H, L1'-CH₂ and L1'-CH₂). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 173.1, 157.4, 148.3, 144.7, 136.8, 135.0, 134.3, 132.1, 128.5, 124.6, 124.5, 123.8, 38.6, 34.0, 33.6, 31.6, 31.5, 27.2, 26.9, 26.3, 25.8, 23.2, 21.0, 18.2. FT-IR (KBr, cm^{-1}): 2945, 2864, 1635, 1567, 1447, 12297, 1185, 1094, 766. Anal. calcd for $\text{C}_{24}\text{H}_{30}\text{N}_2$ (346): C, 83.19; H, 8.73; N, 8.08 Found: C, 83.38; H, 8.69; N, 8.12%.

Synthesis of nickel complexes

General procedure: $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ or $\text{DME} \cdot \text{NiBr}_2$ (0.4 mmol) was dissolved in 5 mL ethanol and added dropwise to the corresponding ligand (0.4 mmol) which dissolve in 10 mL dichloromethane. The mixture was stirred at room temperature 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, and dried under vacuum.

9-(2,6-Dicyclohexylphenylimino)-5,6,7,8-tetrahydrocycloheptapyridylnickel bromide (Ni1). (Yellow, 0.23 g, 94% yield) FT-IR (KBr, cm^{-1}): 3318, 2925, 2850, 1606, 1574, 1445, 1342, 1265, 1085, 1045, 881, 775. Anal. calcd for $\text{C}_{28}\text{H}_{36}\text{Br}_2\text{N}_2\text{Ni}$ (616): C, 54.32; H, 5.86; N, 4.52 Found: C, 54.65; H, 6.34; N, 4.45%.

9-(2,6-Dicyclopentylphenylimino)-5,6,7,8-tetrahydrocycloheptapyridylnickel bromide (Ni2). (Yellow, 0.18 g, 76% yield) FT-IR (KBr, cm^{-1}): 3315, 2946, 2863, 2361, 1609, 1576, 1449, 1339, 769. Anal. calcd for $\text{C}_{26}\text{H}_{32}\text{Br}_2\text{N}_2\text{Ni}$ (588): C, 52.83; H, 5.46; N, 4.74 Found: C, 52.35; H, 5.64; N, 4.66%.

9-(2,4-Dimethyl-6-cyclohexylphenylimino)-5,6,7,8-tetrahydrocycloheptapyridyl nickel bromide (Ni3). (Yellow, 0.17 g, 76% yield) FT-IR (KBr, cm^{-1}): 2926, 2850, 2361, 1604, 1568, 1447, 1274, 1205, 1119, 848, 819. Anal. calcd for $\text{C}_{24}\text{H}_{30}\text{Br}_2\text{N}_2\text{Ni}$ (562): C, 51.02; H, 5.35; N, 4.96 Found: C, 50.88; H, 5.47; N, 4.92%.

9-(2,6-Dicyclohexylphenylimino)-5,6,7,8-tetrahydrocycloheptapyridylnickel chloride (Ni4). (Yellow, 0.15 g, 71% yield) FT-IR (KBr, cm^{-1}): 3327, 2924, 2851, 2361, 1608, 1575, 1446, 1345, 1269, 1048, 883, 775. Anal. calcd for $\text{C}_{28}\text{H}_{36}\text{Cl}_2\text{N}_2\text{Ni}$ (528): C, 63.43; H, 6.84; N, 5.28 Found: C, 62.95; H, 7.31; N, 5.21%.

9-(2,6-Dicyclopentylphenylimino)-5,6,7,8-tetrahydrocycloheptapyridylnickel chloride (Ni5). (Yellow, 0.18 g, 90% yield) FT-IR (KBr, cm^{-1}): 3307, 2947, 2865, 2361, 1610, 1576, 1449,

1339, 770. Anal. calcd for $\text{C}_{26}\text{H}_{32}\text{Cl}_2\text{N}_2\text{Ni}$ (500): C, 62.19; H, 6.42; N, 5.58 Found: C, 61.71; H, 6.56; N, 5.21%.

9-(2,4-Dimethyl-6-cyclohexylphenylimino)-5,6,7,8-tetrahydrocycloheptapyridyl nickel chloride (Ni6). (Yellow, 0.17 g, 87% yield) FT-IR (KBr, cm^{-1}): 2928, 2852, 2361, 1606, 1571, 1443, 1208, 850, 826. Anal. calcd for $\text{C}_{24}\text{H}_{30}\text{Cl}_2\text{N}_2\text{Ni}$ (474): C, 60.54; H, 6.35; N, 5.88 Found: C, 60.41; H, 6.57; N, 5.93%.

X-ray crystallographic study

Table 5 Crystal data and structure refinement for $\text{Ni1} \cdot \text{CH}_3\text{OH}$

	$\text{Ni1} \cdot \text{CH}_3\text{OH}$
Crystal colour	Colourless
Empirical formula	$\text{C}_{29}\text{H}_{40}\text{Br}_2\text{N}_2\text{NiO}$
Formula weight	651.16
Temperature (K)	446(2)
Wavelength (\AA)	0.71073
Crystal system	Triclinic
Space group	P1
a (\AA)	10.561(2)
b (\AA)	10.773(2)
c (\AA)	14.329(3)
α ($^\circ$)	79.82(3)
β ($^\circ$)	88.35(3)
γ ($^\circ$)	63.18(3)
Volume (\AA^3)	1429.6(5)
Z	2
D calcd (mg m^{-3})	1.513
μ (mm^{-1})	3.498
F (000)	668
Crystal size (mm)	$0.57 \times 0.37 \times 0.10$
θ range ($^\circ$)	2.15–27.51
Limiting indices	-13 < h < 13, -13 < k < 13, -18 < l < 18
No. of rflns collected	13984
No. of unique rflns	6369
R_{int}	0.0682
Completeness to θ (%)	97 ($\theta = 27.51$)
Goodness-of-fit on F^2	1.046
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0556 wR2 = 0.1474
R indices (all data)	R1 = 0.0621 wR2 = 0.1549
Largest diff. Peak and hole ($\text{e} \text{\AA}^{-3}$)	0.722 and -1.409

A single crystal of the nickel complex $\text{Ni1} \cdot \text{CH}_3\text{OH}$ suitable for X-ray diffraction was obtained by layering diethyl ether onto the mixed solution of dichloromethane and methanol at room temperature. X-ray studies were carried out using a Rigaku Saturn724+CCD diffractometer with $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 173(2) K, 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 fullmatrix 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.¹⁷ Details of the X-ray structure determinations and refinements are provided in Table 5.

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. And the autoclave was evacuated by a vacuum pump and back-filled three times with N₂ and once with ethylene. When the required temperature was reached, 30 mL toluene (freshly distilled) was added under ethylene atmosphere, and another 20 mL toluene which dissolved the nickel pre-catalyst was injected. The required amount of co-catalyst (MMAO or Et₂AlCl) 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 desired ethylene pressure 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 vacuum until of constant weight.

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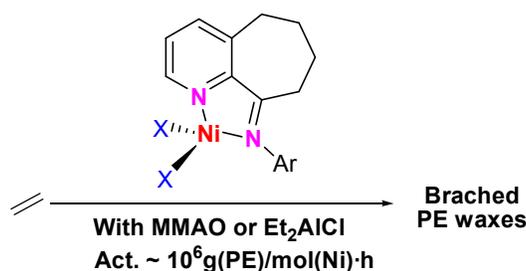
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Graphical Abstract

for

Targeting polyethylene waxes: 9-(2-Cycloalkylphenylimino)-5,6,7,8-tetrahydrocycloheptapyridyl nickel halides and their ethylene polymerization

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The 9-(2-Cycloalkylphenylimino)-5,6,7,8-tetrahydrocycloheptapyridylnickel halides exhibited high activities toward ethylene polymerization, producing branched polyethylene waxes under activation with either modified methylaluminoxane (MMAO) or diethylaluminiumchloride (Et₂AlCl).