PAPER

N-(5,6,7-Trihydroquinolin-8-ylidene)arylaminonickel dichlorides as highly active single-site pro-catalysts in ethylene polymerization[†]

Jiangang Yu,^a Yanning Zeng,^a Wei Huang,^a Xiang Hao^a and Wen-Hua Sun^{*a,b}

Received 31st March 2011, Accepted 8th June 2011 DOI: 10.1039/c1dt10541h

A series of N-(5,6,7-trihydroquinolin-8-ylidene)arylamine ligands was synthesized and fully characterized by NMR, IR spectroscopy and elemental analysis. Dimeric N-(5,6,7trihydroquinolin-8-ylidene)arylaminonickel dichlorides were prepared and examined by IR spectroscopy and elemental analysis, and the molecular structures of the representative nickel complexes were determined by the single crystal X-ray diffraction. On treatment with various alkylaluminiums, all the title complexes exhibited highly active, single-site active behavior for ethylene polymerization producing polyethylene (PE) waxes. The catalytic systems using the co-catalysts diethylaluminium chloride (Et₂AlCl) or methylaluminoxane (MAO) were investigated in detail, and the molecular weights and distributions of the PEs obtained were found to significantly rely on the nature of the different ligands present and reaction parameters such as the molar ratios of Al/Ni, reaction temperature and reaction time.

1. Introduction

The discovery of diiminonickel dichlorides as highly active procatalysts in ethylene polymerization resurrected nickel research in ethylene reactivity.¹ Subsequently, there has been a tremendous surge in publications of nickel pro-catalysts, which have recently been reviewed.² There is industrial demand for both olefins, which can be produced by ethylene oligomerization, and polyethylenes, which can be produced by ethylene polymerization. However the catalytic systems used to produce both olefins and polyethylenes would be useless in this context due to the fact that polyethylenes are produced as the by-product of ethylene oligomerization and olefins are produced as the by-product of ethylene polymerization. In fact, some amount of oligomers have been commonly observed during ethylene polymerization using nickel pro-catalysts,³ and ethylene oligomerization is often reported due to β -hydrogen elimination in nickel-induced ethylene reactivity.⁴ Driven by academic and commercial considerations, different models of nickel pro-catalysts have been verified using ligands such as bidentate NAN,3d,5 NAP,6 NAO,7 PAO,4f,8 and tridentate $N \wedge N \wedge N$, $^{9} N \wedge N \wedge O$, $^{3e,10} N \wedge P \wedge N$. 4g,11 Inspired by cationic olefin polymerization employing active 14e-species,¹² the nickel pro-catalysts^{3d,5} bearing N,N-bidentate ligands including 2iminopyridines have drawn more attention.13 However, it would be critical that nickel pro-catalysts should have single-site active species in order to produce polymers with a narrow molecular weight dispersion. In exploring new ligands from the fusedcycloalkanonylpyridines instead of 2-acetylpyridine, we have reported the nickel pro-catalysts bearing N-(2-substituted-5,6,7trihydroquinolin-8-ylidene) arylamines, which showed good activities towards ethylene oligomerization.¹⁴ Using 5,6,7-trihydroquinolin-8-one as the starting material, a series of N-(5,6,7trihydroquinolin-8-ylidene)arylamines and their nickel complexes were prepared. Surprisingly the newly synthesized nickel procatalysts showed high activities for ethylene polymerization without the observation of any oligomers. Moreover, the polyethylenes obtained were confirmed as waxes with narrow molecular weight distribution. Herein, the synthesis and characterization of N-(5,6,7-trihydroquinolin-8-ylidene)arylaminonickel dichlorides are reported in detail, as well as their catalytic behavior in the polymerization of ethylene.

2. Results and discussion

2.1 Synthesis and characterization

The condensation reaction of 5,6,7-trihydroquinolin-8-one with various anilines¹⁵ in toluene produces the corresponding *N*-(5,6,7-trihydroquinolin-8-ylidene)arylamine derivatives in good yields (Scheme 1). All organic compounds were characterized by FT-IR, ¹H NMR and ¹³C NMR spectra as well as by elemental analyses. However, the ¹H-NMR and FT-IR spectra for those products revealed the presence of two isomers due to the enolization of the

[&]quot;Key Laboratory of Engineering Plastics and Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, China. E-mail: whsun@iccas.ac.cn; Fax: +86 10 62618239; Tel: +86 10 62557955

^bState Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, China

[†] CCDC reference numbers 798841 and 798842 for crystallographic data of complexes Ni1 and Ni3 respectively. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10541h



Scheme 1 Synthetic procedure.

imine¹⁶ (Scheme 1). It was noteworthy that only the sp²-*N* (imine isomer) can easily coordinate with nickel dichloride. Therefore the stoichiometric reaction of the corresponding ligands with NiCl₂·6H₂O was performed in ethanol, the FT-IR showed that only *N*-(5,6,7-trihydroquinolin-8-ylidene)arylaminonickel dichloride was obtained (Scheme 1). According to their IR spectra, the C=N stretching frequencies of nickel complexes appeared at lower values (1580–1590 cm⁻¹) with weaker intensity than those of their free ligands, indicating the effective coordination between the imino-nitrogen and the nickel atom. Meanwhile, there is no signal around 3360 or 1570 cm⁻¹ (v_{N-H}) in the complexes indicating the isomerization of L1′–L5′ into L1–L5 happened during the coordination reaction with NiCl₂. In addition, the unambiguous structures of the complexes Ni1 and Ni3 in the solid state were further confirmed by single-crystal X-ray diffraction studies.

2.2 Molecular structures

Crystals of complexes Ni1·CH₃OH and Ni3·CH₃OH suitable for single crystal X-ray analysis were grown by layering diethyl ether on methanol solutions at room temperature. Both complexes Ni1·CH₃OH and Ni3·CH₃OH crystallized as centrosymmetric dimers and their molecular structures show distorted octahedral geometry around each nickel center with the coordinative assistance of a methanol solvent molecule. The molecular structures of complexes Ni1·CH₃OH and Ni3·CH₃OH are shown in Fig. 1 and 2, and the selected bond lengths and angles are tabulated in Table 1.



Fig. 1 ORTEP drawing of complex Ni1 CH₃OH. Thermal ellipsoids are shown at 30% probability. Hydrogen atoms have been omitted for clarity.

As shown in Fig. 1, there is a five-membered heteronickel-cycle constructed by Ni, N1, C8, C9 and N2, in which the nickel atom

Table 1 Selected bond lengths and angles for $Ni1\cdot CH_{3}OH$ and $Ni3\cdot CH_{3}OH$

	Ni1·CH ₃ OH	Ni3·CH ₃ OH
Bond lengths (Å)		
Ni…Ni	3.409	3.369
Ni–N1	2.078(3)	2.062(3)
Ni–N2	2.108(3)	2.115(2)
Ni–O	2.133(3)	2.128(2)
Ni-Cl1	2.3911(10)	2.3940 (9)
Ni–Cl2	2.4368(10)	2.4221(10)
N1-C1	1.328(4)	1.327(4)
N1-C5	1.349(4)	1.355(4)
N2-C9	1.284(4)	1.278(4)
N2-C10	1.441(4)	1.441(4)
Bond angles (°)		
N1–Ni–N2	78.54(9)	78.60(10)
N1-Ni-O1	97.66(10)	94.42(10)
N2-Ni-O1	91.46(9)	90.06(10)
N1-Ni-Cl1	86.60(7)	88.53(8)
N2-Ni-Cl1	96.12(8)	98.08(7)
O1-Ni-Cl1	171.93(8)	171.75(7)
N1-Ni-Cl2	96.25(7)	96.57(7)
N2-Ni-Cl2	173.00(7)	172.26(7)
O1-Ni-Cl2	84.57(7)	84.26(7)
Cl1–Ni–Cl2	88.16(3)	87.76(4)

deviates by 0.418 Å from the co-plane of the four atoms N1, C8, C9 and N2 with two Ni–N bond lengths of Ni–N1 [2.079(3) Å] and Ni–N2 [2.109(3) Å]. The pyridyl and iminophenyl planes are nearly perpendicular with a dihedral angle of 88.83° . The intra-molecular Ni…Ni distance (3.409 Å) is slightly shorter than that (3.475 Å) within their iminopyridylnickel dimer.¹⁷ The axial chloride Cl1 forms stronger bonding with the nickel center [Ni–Cl1, 2.3910(10) Å] than does the horizontal bridging chloride Cl2 {Ni–Cl2 [2.4368(10) Å]}. The phenomenon is similar to that observed in the analogous iminopyridylnickel dimer, in which the Ni–Cl bond lengths were 2.3366(8) Å with the related terminal chloride and 2.2729(9) Å with the bridging chloride.¹⁷

Compared with the intra-molecular Ni \cdots Ni (3.409 Å) in Ni1, the interaction observed in Ni3, with Ni \cdots Ni length 3.369 Å, is a little shorter (Fig. 2). The nickel atom is more planar with the co-plane of N1, C8, C9 and N2 atoms with a deviated distance of 0.156 Å in Ni3, and a similar structural feature is observed with Ni–N bond distances of Ni–N1 [2.062(3) Å] and Ni–N2 [2.116(2) Å], and Ni–Cl bond lengths of Ni–Cl1 [2.3934(9) Å] and Ni–Cl2 [2.4221(10) Å]. The differences are caused by the various substituents on the iminophenyl group.



Fig. 2 ORTEP drawing of complex **Ni3**·CH₃OH. Thermal ellipsoids are shown at 30% probability. Hydrogen atoms have been omitted for clarity.

 Table 2
 Selection of the suitable alkylaluminiums based on Ni3^a

Entry	Cocat.	Al/Ni	Polymer g	Activity ^b	$M_{ m w}{}^c~ m kg~mol^{{\scriptscriptstyle -1}}$	$M_{\rm w}/M_{\rm n}{}^c$	$T_{\mathbf{m}}{}^{d}$ °C	Branches/1000C ^e
1	Et ₂ AlCl	200	3.90	5.20	3.2	1.7	92.7	12.52
2	Et ₃ Al ₂ Cl ₃	200	4.32	5.76	3.3	1.8	93.0	16.6
3	AlEt,	200	3.81	5.08	3.2	1.8	92.0	8.52
4	MAO	1000	4.42	5.89	4.5	1.9	100.1	5. 54
5	MMAO	1000	3.92	5.23	4.2	1.8	97.9	11.8

^{*a*} Reaction conditions: 1.5 μ mol of Ni; 20 °C; 30 min; 10 atm of ethylene; 100 mL total volume of toluene. ^{*b*} 10⁶ g(PE) mol(Ni)⁻¹ h⁻¹. ^{*c*} Determined by GPC. ^{*d*} Determined by DSC. ^{*e*} Determined by FT-IR¹⁸

 Table 3
 Polymerization of ethylene in the presence of MAO^a

Entry	Procat.	T∕°C	Al/Ni	<i>t</i> /min	Polymer/g	Activity ^b	$M_{ m w}{}^c$ kg mol ⁻¹	$M_{\rm w}/M_{\rm n}{}^c$	$T_{\rm m}{}^d/{}^{\rm o}{\rm C}$	Branches/1000C ^e
1	Ni3	20	1000	30	4.42	5.89	4.5	1.9	100.1	5. 54
2	Ni3	20	1500	30	4.64	6.19	4.2	1.9	100.6	4.18
3	Ni3	20	2000	30	5.33	7.11	4.3	1.9	99.1	5.87
4	Ni3	20	2250	30	5.59	7.45	4.3	1.9	89.0	6.70
5	Ni3	20	2500	30	5.30	7.07	4.5	1.9	89.5	6.13
6	Ni3	20	3000	30	4.45	5.93	4.5	2.0	89.6	5.79
7	Ni3	40	2250	30	3.83	5.11	4.4	2.1	89.3	2.11
8	Ni3	60	2250	30	1.98	2.64	5.4	2.1	89.1	8.45
9	Ni3	80	2250	30	1.03	1.37	6.9	3.5	111.9	11.2
10	Ni3	20	2250	10	1.90	7.60	2.3	1.6	98.6	2.50
11	Ni3	20	2250	20	3.76	7.52	4.2	2.0	101.2	4.47
12	Ni3	20	2250	40	6.26	6.26	4.8	2.1	101.0	12.0
13	Ni3	20	2250	60	8.92	5.95	5.0	2.0	103.9	10.7
14	Ni3	20	2250	90	13.2	5.87	5.1	1.9	102.3	12.7
15	Ni3	20	2250	120	17.5	5.83	5.0	2.1	103.1	12.3
16	Ni1	20	2250	30	5.51	7.35	9.2	2.2	112.5	9.82
17	Ni2	20	2250	30	5.53	7.37	6.0	2.2	108.0	5.12
18	Ni4	20	2250	30	6.34	8.45	5.5	2.2	107.7	1.36
19	Ni5	20	2250	30	6.43	8.57	3.3	2.4	106.9	0.81

^{*a*} Reaction conditions: 1.5 µmol of Ni; 10 atm of ethylene; 100 mL total volume of toluene. ^{*b*} 10⁶ g(PE)·mol(Ni)⁻¹·h⁻¹. ^{*c*} Determined by GPC. ^{*d*} Determined by DSC. ^{*e*} Determined by FT-IR.¹⁸

2.3 Ethylene oligomerization

Ethylene polymerization catalyzed by these nickel complexes with various co-catalysts has been systematically investigated. The type of co-catalyst, the molar ratio of Al/Ni, temperature, reaction time and the nature of the complexes have been shown to have a large influence on the activities as well as the M_w and M_w/M_n of the polyethylenes produced.

2.3.1 Selection of suitable co-catalysts. Several alkylaluminiums (Et₂AlCl, Et₃Al₂Cl₃, AlEt₃, MAO, MMAO) were initially used to activate complex Ni3 for ethylene reactivity at room temperature (Table 2). Ni3/alkylaluminoxane (MAO) (entry 4 in Table 2) exhibited higher activity and produced polyethylene with higher molecular weight than did the Ni3 catalytic systems containing other alkylaluminiums; the catalytic system using a smaller molar ratio of common diethylaluminium chloride (Et₂AlCl) also showed good activity (entry 1 in Table 2). Therefore the cocatalysts MAO or Et₂AlCl were used in further investigations.

2.3.2 Ethylene polymerization in the presence of MAO. The influence of the reaction parameters, including the molar ratio of Al/Ni and reaction temperature, were investigated using Ni3/MAO. Increasing the Al/Ni from 1000 to 3000 (entries 1–6 in Table 3), the activities showed the best value with an optimum ratio of 2250 (entry 4 in Table 3). With the molar ratio of Al/Ni

(2250) fixed, the influence of reaction temperature was investigated (entries 4 and 7–9 in Table 3). Similar to the observations by other iminopyridyl late-transition pro-catalysts,¹³ the catalytic activities of **Ni3/MAO** sharply decreased as the temperature was elevated from 20 °C to 80 °C. Therefore the active species are partly unstable at higher temperature. Regarding the GPC curves of resultant PEs, wider molecular distributions were observed at elevated reaction temperature, and a clear bimodal feature of the GPC curves were obtained for polyethylenes produced at 80 °C (shown in Fig. 3).

To understand the lifetime of the active species, trials of **Ni3/MAO** were carried out over different reaction times (entries 4, 10–15 in Table 3) at 20 °C. In general, the catalytic activities slowly decreased with prolonged reaction time, indicating a relatively long lifetime of the active species. In addition, the M_w (2.3–5.1 kg mol⁻¹) and M_w/M_n (1.6–2.1) values of obtained for the PEs were slightly increased on extending the reaction time, however, the narrow molecular distributions indicated the single-site active species in the catalytic system.

On the basis of the above results, all other pro-catalysts Ni1, Ni2 and Ni4–Ni5 were examined for ethylene polymerization by employing the optimum conditions found for Ni3 (entries 4, 16–19 in Table 3). Accordingly the nickel pro-catalysts with bulky substituent (R') showed higher catalytic activity (entries 4, 16 and 17 in Table 3). Such a phenomenon probably illustrates the protection afforded to the active site by the sterically bulky



Fig. 3 GPC traces of polyethylene produced by **Ni3**/MAO catalytic system (entry 4, 7–9 in Table 3).

substituent (R').¹⁹ In addition, the *para*-methyl on the aryl groups within **Ni4** and **Ni5** positively affected the catalytic activities (entries 18 and 19 in Table 3), which was assumed to be due to the better solubility of the methylated metal complexes.²⁰

2.3.3 Ethylene polymerization in the presence of Et₂AlCl. Using the co-catalyst Et₂AlCl instead of MAO, the pro-catalyst Ni3 showed similar trends with regard to the reaction temperature, time and Al/Ni molar ratio (entries 1–14 in Table 4). In general, the molar ratio of Al/Ni could be reduced by using Et₂AlCl. The molecular weights of resultant PEs were reduced in the range of Kg mol⁻¹; however, the feature of narrow molecular distributions remained. The best catalytic performance was observed with the optimum condition of Al/Ni 500 at 20 °C (entry 3 in Table 4). Notably, the increase of the Al/Ni molar ratio led to lower molecular weight polymers (entries 1–5 in Table 4). Higher molar ratios of Al/Ni enhanced chain transfer from nickel species to aluminium and resulted in short-chain polymers,²¹ meanwhile the melting points (T_m) of the polyethylene significantly decreased,

 Table 4
 Ethylene polymerization in the presence of Et₂AlCl^a

indicating higher numbers of branches. Examining the data and trends shown with Et_2AlCl , the active species are rather stable and retain single-site features on changing the reaction parameters of temperature and time. The molecular weights of the resultant PEs were slightly increased on elevating the reaction temperature and prolonging the reaction time. Due to the slightly lower activity observed at 10 min, the catalytic systems were assumed to exhibit an initial time for starting the polymerization catalysis. Similarly, the molecular weight distributions of the obtained PEs became wider and bimodal feature for the PEs formed above 60 °C (Fig. 4).



Fig. 4 GPC traces of polyethylene produced by $Ni3/AlEt_2Cl$ catalytic system (entries 3, 6–8 in Table 4).

The nature of the ligands affected the catalytic activities of the pro-catalysts (Nin)/Et₂AlCl (n = 1-5) (entries 3, 15–18 in Table 4), and showed the same tendency as for Nin/MAO. Again, the nickel pro-catalysts (Ni4 and Ni5) bearing an additional *para*-methyl substituent provided better catalytic activities, such as Ni5/Et₂AlCl reaching up to 1.24×10^7 g(PE) mol(Ni)⁻¹ h⁻¹ (entry 18 in Table 4). The representative PE by Ni5/Et₂AlCl (entry 18 in Table 4) was characterized by ¹³C NMR measurements,

Entry	Procat.	T∕°C	Al/Ni	t/min	Polymer/g	Activity ^b	$M_{\rm w}{}^c/{ m kg}{ m mol}^{-1}$	$M_{\rm w}/M_{\rm n}{}^c$	$T_{\rm m}{}^d/{}^{\rm o}{ m C}$	Branches/1000C ^e
1	Ni3	20	200	30	3.90	5.20	3.2	1.7	92.7	12.52
2	Ni3	20	400	30	3.91	5.21	3.2	1.9	74.1	25.8
3	Ni3	20	500	30	4.12	5.49	3.0	2.0	71.4	36.8
4	Ni3	20	600	30	4.01	5.35	2.8	1.8	71.6	32.7
5	Ni3	20	800	30	3.80	5.07	1.8	1.9	71.6	28.0
6	Ni3	40	500	30	3.88	5.17	2.8	1.8	71.4	31.7
7	Ni3	60	500	30	2.85	3.80	3.4	2.4	82.1	31.9
8	Ni3	80	500	30	2.53	3.37	8.4	4.3	96.2	31.1
9	Ni3	20	500	10	1.30	5.20	2.9	1.7	71.4	35.1
10	Ni3	20	500	20	2.70	5.40	3.1	1.7	73.4	35.4
11	Ni3	20	500	40	5.90	5.90	3.2	1.9	74.6	31.9
12	Ni3	20	500	60	8.12	5.41	3.2	1.9	74.6	30.5
13	Ni3	20	500	90	11.9	5.29	4.7	2.0	84.7	9.82
14	Ni3	20	500	120	14.2	4.73	5.4	1.9	91.2	10.6
15	Ni1	20	500	20	2.73	3 64	2.3	1.8	80.1	18.4
16	Ni2	20	500	20	3 90	5.20	3.9	2.1	87.5	9.81
17	Ni4	20	500	20	8 70	11.6	3.2	19	82.1	13.1
18	Ni5	20	500	20	9.30	12.4	3.4	2.0	84 2	22.1

^{*a*} Reaction conditions: 1.5 µmol of Ni; 10 atm of ethylene; 100 mL total volume of toluene. ^{*b*} 10⁶ g(PE)·mol(Ni)⁻¹·h⁻¹. ^{*c*} Determined by GPC. ^{*d*} Determined by DSC. ^{*e*} Determined by FT-IR¹⁸

and showed 39 branches/1000 carbons (Fig. 5) according to the interpretation reported by Galland *et al.*²² The highly branched PEs were obtained due to β - hydrogen migration, which happened on the active nickel species.^{2b,23}



Fig. 5 ¹³C-NMR spectrum of polyethylene (entry 18 in Table 4).

Compared with our previous work on N-(2-Cl (or Ph)-5,6,7-trihydroquinolin-8-ylidene)arylaminonickel dichlorides for ethylene oligomerization,¹⁴ the title N-(5,6,7-trihydroquinolin-8-vlidene)arylaminonickel pro-catalysts herein-for which there is one substituent less in the ligands-showed higher activity in ethylene polymerization.24 Both chloro- and phenylsubstituents generally have a significant difference due to their size and electronic influence.14 The electronic and steric natures of the substituents of the ligands changed the catalytic behaviors of their metal pro-catalysts, either affecting the microstructures of the polymers or producing oligomers instead of polymers.4b,4g,20a,25 It has been reported that procatalysts containing the electron-withdrawing substituents near to metal centers led to ethylene oligomerization, e.g. nickel procatalysts bearing the electron-withdrawing substituents on the para-position of N-aryl groups produced polymers with higher molecular weight and better activities, but pro-catalysts having the electron-withdrawing substituents on the ortho-positions of *N*-aryl groups resulted ethylene oligomerization.²⁶ That may be helpful in explaining why N-(2-Cl-5,6,7-trihydroquinolin-8ylidene)arylaminonickel pro-catalysts gave oligomers.¹⁴ In general, the steric bulkiness of the ligands were commonly considered a necessary feature for their nickel pro-catalysts to maintain high activity and form highly-ordered polyethylene.^{1a,27} However, there were examples of pro-catalysts containing bulky substituents inducing ethylene oligomerization,18a,28 and our observations also showed cases inconsistent with the effects associated with bulky ligands, 18a, 28b, 28d viz enhanced polymerization for the late-transition metal pro-catalysts.^{6a} Herein the current system not only gives an additional example but also indicates that the significant feature of fine-tuning the complex pro-catalyst fits the catalytic requirement for sole polymerization of ethylene. In addition, the resultant PEs are confirmed by their molecular weights, their formation as waxes and their narrow molecular weight distributions; narrow polydispersity waxes are material additives which are in demand.

The extensive research of further ligands derivatives is still ongoing in our group.

3. Conclusion

N-(5,6,7-Trihydroquinolin-8-ylidene)arylaminonickel(II) complexes were synthesized and fully characterized. Upon treatment with either MAO or Et₂AlCl, the nickel pro-catalysts worked as single-site catalysts for ethylene polymerization, forming polyethylene waxes with an activity of up to 10⁷ g(PE) mol(Ni)⁻¹ h⁻¹. The molecular weights and distributions of the polyethylene waxes could be controlled by modifying the nature of the different ligands and reaction conditions. The resultant polyethylenes were shown to be highly branched polymers; the β-hydrogen migration happened on the active species and, moreover, chain transfers from nickel species to aluminium could also take place.

4. Experimental

4.1 General considerations

All manipulations of air and/or moisture sensitive compounds were carried out under a nitrogen atmosphere using standard Schlenk techniques. Toluene was refluxed over sodiumbenzophenone and distilled under nitrogen prior to use. Methylaluminoxane (MAO, 1.46 M solution in toluene) and modified methylaluminoxane (MMAO, 1.93 M in heptane, 3Å) were purchased from Akzo Nobel Corp. Diethylaluminium chloride (Et₂AlCl, 0.79 M in toluene), triethylaluminium (AlEt₃, 0.74 M in toluene) and ethylaluminium sesquinochroride (Et₃Al₂Cl₃, EASC, 0.87 M in toluene) was purchased from Acros Chemicals. Highpurity 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 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 microanalyzer. Molecular weights and molecular (M_w) weight distribution (M_w/M_n) of polyethylenes were determined by a PL-GPC220 at 120 °C, with 1,2,4-trichlorobenzene as the solvent. DSC trace and melting points of polyethylenes were obtained from the second scanning run on Perkin-Elmer DSC-7 at a heating rate of 10 °C min⁻¹.

4.2 Syntheses and characterization

2,6-Dimethyl-*N***-(5,6,7-trihydroquinolin-8-ylidene)phenylamine** (L1) and *N***-(2,6-dimethylphenyl)-5,6-dihydroquinolin-8-amine** (L1'). A solution of 5,6,7-trihydroquinolin-8-one (0.59 g, 4 mmol), 2,6-dimethylaniline (0.50 g, 4.1 mmol), and a catalytic amount of *p*-toluenesulfonic acid in toluene (50 mL) was refluxed for 3.5 h. The solvent was evaporated at reduced pressure, then the mixture was purified by column chromatography [alumina, petroleum ether–ethyl acetate = 7:1 v/v] to get the desired compound (yellow oil, L1:L1' = 87:13, 0.66 g, 66% yield). ¹H NMR (400 MHz, CDCl₃, TMS): δ 8.72 (d, *J* = 4.0 Hz, 1H, L1-Py *H*); 8.41 (d, *J* = 4.6 Hz, L1'-Py *H*); 7.56 (d, *J* = 7.6 Hz, 1H, L1-Py *H*); 7.43 (d, *J* = 7.4 Hz, L1'-Py *H*), 7.29 (m, 1H, L1-Py *H*); 7.11 (m, L1'-Py *H*); 7.02 (d, J = 7.5 Hz, 2H, L1-Ar *H*); 6.94 (m, L1'-Ar *H*); 6.90 (t, J = 7.5 Hz, 1H, L1-Ar *H*); 6.58 (s, L1'-N*H*); 4.51 (t, L1'-C*H*) 2.94 (t, J = 6.0 Hz, 2H, L1-C*H*₂); 2.83 (t, L1'-C*H*₂); 2.35 (t, J = 6.2 Hz, 2H, L1-C*H*₂); 2.27 (s, L1'-2 × C*H*₃); 2.23 (t, L1'-C*H*₂); 2.04 (s, 6H, L1-2 × C*H*₃); 1.93 (m, 2H, L1-C*H*₂). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 164.6, 150.1, 149.0, 137.3, 137.1, 128.3, 125.3, 122.7, 122.1, 30.6, 29.6, 22.4, 18.4, 18.3. FT-IR (KBr, cm⁻¹): 3357 (v_{N-H}), 3038, 2928, 2828, 1925, 1641 ($v_{C=N}$), 1569 (v_{N-H}), 1476, 1435, 1279, 1195, 1099, 1041, 794, 796, 673. Anal. calcd for C₁₇H₁₈N₂ (250): C, 81.56; H, 7.25; N, 11.19. Found: C, 81.87; H, 7.30; N, 10.81

2,6-Diethyl-N-(5,6,7-trihydroquinolin-8-ylidene)phenylamine (L2) and N-(2,6-diethylphenyl)-5,6-dihydroquinolin-8-amine (L2'). Using the same procedure as for the synthesis of L1, we got L2 and L2' (yellow oil, L2: L2' = 86: 14, 0.69 g, 62% yield). ¹H NMR (400 MHz, CDCl₃): δ 8.72 (d, J = 4.4 Hz, 1H, L2-Py H); 8.41 (d, *J* = 4.5 Hz, L2'-Py *H*); 7.56 (d, *J* = 7.4 Hz, 1H, L2-Py *H*); 7.43 (d, J = 7.6 Hz, L2'-Py H); 7.28 (m, 1H, L2-Py H); 7.14 (d, L2'-Py H); 7.08 (d, J = 7.6 Hz, 2H, L2-Ar H); 7.00 (m, 1H, L2-Ar H and L2'-Ar H); 6.62 (s, L2'-NH); 4.49 (t, L2'-CH); 2.93 (t, J = 6.1 Hz, 2H, **L2-** CH_2); 2.81 (t, **L2'-** CH_2); 2.45 (t, J = 7.4 Hz, 2H, **L2-** CH_2); 2.43 (m, $L2'-2 \times CH_2$); 2.35 (m, 4H, $L2-2 \times CH_2$); 2.25 (m, $L2'-CH_2$); 1.91 (m, 2H, L2-CH₂); 1.20 (t, L2'-2 × CH₃); 1.14 (t, J = 7.5 Hz, 6H, L2-2 × CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 164.4, 150.5, 149.9, 148.9, 137.0, 134.7, 131.0, 125.5, 124.9, 122.9.6, 30.8, 29.5, 24.4, 22.3, 13.9. FT-IR (KBr, cm⁻¹): 3363 (*v*_{N-H}),3034, 2963, 2932, $2870, 2831, 1940, 1639 (v_{C=N}), 1563 (v_{N-H}), 1462, 1422, 1277, 1191,$ 1101, 819, 675. Anal. calcd for C₁₇H₁₈N₂ (278): C, 81.97; H, 7.97; N, 10.06. Found: C, 82.11; H, 7.60; N, 9.76.

2,6-Bis(1-methylethyl)-N-(5,6,7-trihydroquinolin-8-ylidene)phenylamine (L3) and N-(2,6-diisopropylphenyl)-5,6-dihydroquinolin-8-amine (L3'). Using the same procedure as for the synthesis of L1, we got L3 and L3' (yellow oil, L3: L3' = 85: 15, 0.81 g, 66% yield). ¹H NMR (400 MHz, CDCl₃): δ 8.73 (d, J = 4.1 Hz, 1H, L3-Py H); 8.39 (d, J = 4.3 Hz, L3'-Py H); 7.57 (d, J = 7.7 Hz, 1H, L3-Py H); 7.41 (d, J = 7.8 Hz, L3'-Py H); 7.30 (t, J =4.5 Hz, 1H, L3-Py *H*); 7.20 (m, L3'-Py *H*); 7.14 (d, *J* = 7.5 Hz, 2H, **L3**-Ar *H*); 7.07 (t, J = 6.7 Hz, 1H, **L3**-Ar *H*); 7.00 (m, **L3'**-Ar *H*); 6.55 (s, L3'-NH); 4.48 (t, L3'-CH); 3.23 (m, L3'-CH₂); 2.95 (t, J = 6.0 Hz, 2H, L3-CH₂); 2.85 (m, 2H, L3-2 × CH); 2.85 (m, L3'-2 × CH); 2.43 (t, J = 6.1 Hz, 2H, L3-CH₂); 2.25 (m, L3'-CH₂); 1.93 (m, 2H, L3-C H_2); 1.18 (m, L3'-4 × C H_3); 1.15 (m, 12H, L3-4 × CH_3). ¹³C NMR (100 MHz, CDCl₃): δ 164.7, 148.9, 146.7, 137.5, 137.1, 136.2, 125.0, 123.5, 123.0, 122.9, 31.0, 21.6, 28.1, 23.6, 22.3. FT-IR (KBr, cm⁻¹): 3376 (v_{N-H}),3047, 2960, 2866, 2829, 1929.3, 1864, 1640 ($v_{C=N}$), 1571 (v_{N-H}), 1571, 1476, 1426, 1329, 1254, 1194, 1104, 1050, 1016, 796, 771, 674. Anal. calcd for C₂₁H₂₆N₂ (306): C, 82.31; H, 8.55; N, 9.14. Found: C, 82.57; H, 8.23; N, 9.06.

2,4,6-Trimethyl-*N***-**(**5,6,7-trihydroquinolin-8-ylidene**)**phenylamine (L4) and** *N***-mesityl-5,6-dihydroquinolin-8-amine (L4').** Using the same procedure as for the synthesis of **L1**, we got **L4** and **L4'** (yellow oil, **L4**: **L4'** = 91 : 9, 0.86 g, 81.3% yield). ¹H NMR (400 MHz, CDCl₃): δ 8.72 (d, *J* = 4.1 Hz, 1H, **L4-**Py *H*); 8.41 (d, *J* = 4.6 Hz, **L4'**-Py *H*); 7.56 (d, *J* = 7.7 Hz, 1H, **L4-**Py *H*); 7.43 (d, *J* = 7.4 Hz, **L4'**-Py *H*); 7.10 (m, **L4'**-Py *H*); 7.29 (m, 1H, **L4**-Py *H*); 6.92 (s, **L4'**-Ar *H*); 6.85 (s, 2H, **L4**-Ar *H*); 6.48 (s, **L4'**-N*H*); 4.50 (t, **L4'**-C*H*₂) 2.93 (t, *J* = 6.0 Hz, 2H, **L4**-C*H*₂); 2.82 (t, **L4'**-*CH*₂); 2.36 (t, *J* = 6.1 Hz, 2H, **L4**-*CH*₂); 2.29 (s, **L4'**-*CH*₃); 2.27 (s, 3H, **L4**-*CH*₃); 2.23 (s, 6H, **L4'**-2 × *CH*₃); 2.20 (m, **L4'**-*CH*₂); 2.01 (s, 6H, **L4**-2 × *CH*₃); 1.93 (m, 2H, **L4**-*CH*₂). ¹³C NMR (100 MHz, CDCl3): δ 164.7, 150.1, 149.0, 146.8, 137.2, 137.0, 131.7, 128.9, 128.4, 125.1, 124.8, 30.5, 29.5, 22.4, 20.8, 18.3, 18.1. FT-IR (KBr, cm⁻¹): 3368 ($v_{\text{N-H}}$), 3001, 2916, 2841, 2728, 1942, 1902, 1861, 1636 ($v_{\text{C=N}}$), 1566 ($v_{\text{N-H}}$), 1566, 1480, 1410, 1268, 1098, 1021, 846, 793, 668. Anal. calcd for C₁₈H₂₀N₂ (264): C, 81.78; H, 7.63; N, 10.60. Found: C, 82.03; H, 7.42; N, 10.32.

2,6-Diethyl-4-ethyl-N-(5,6,7-trihydroquinolin-8-ylidene)phenylamine (L5) and N-(2,6-diethyl-4-methylphenyl)-5,6-dihydroquinolin-8-amine (L5'). Using the same procedure as for the synthesis of L1, we got L5 and L5' (yellow oil, L5:L5' = 89:11, 0.86 g, 74.1% yield). ¹H NMR (400 MHz, CDCl₃): δ 8.72 (d, J = 4.4 Hz, 1H, L5-Py *H*); 8.41 (d, *J* = 4.3 Hz, L5'-Py *H*); 7.56 (d, *J* = 7.4 Hz, 1H, L5-Py H); 7.43 (d, J = 7.2 Hz, L5'-Py H); 7.30 (m, 1H, L5-Py H); 7.10 (m, L5'-Py H); 6.89 (s, 2H, L5-Ar H); 6.95 (s, L5'-Ar H); 6.52 (s, L5'-NH); 4.49 (t, L5'-CH₂); 2.93 (t, J = 6.0 Hz, 2H, L5-CH₂); 2.81 (t, L5'-CH₂); 2.58 (m, L5'-2 × CH₂); 2.40 (m, 4H, L5-2 × CH₂); 2.33 (m, L5'-CH₃); 2.32(s, 3H, L5-CH₃); 2.25 (m, **L5'**- CH₂); 1.91 (m, 2H, **L5**-CH₂); 1.13 (t, J = 7.5 Hz, 6H, **L5**-2 × CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 164.7, 150.2, 149.0, 145.7, 137.3, 137.2, 137.0, 132.0, 131.0, 127.1, 126.3, 124.8, 30.7, 29.6, 24.7, 24.4, 22.3, 21.2, 14.0. FT-IR (KBr, cm⁻¹): 3362 (v_{N-H}), 2964, 2930, 2873, 2828, 1743, 1640 ($v_{C=N}$), 1571 (v_{N-H}), 1531, 1426, 1326, 1293, 1270, 1195, 1098, 859, 193, 677. Anal. calcd for C₂₀H₂₄N₂ (292): C, 82.15; H, 8.27; N, 9.58. Found: C, 82.32; H, 8.14; N, 9.46.

Synthesis of nickel complexes

General procedure: A solution of NiCl₂·6H₂O (2 mmol) in ethanol was added dropwise to the corresponding ligand (2 mmol) in ethanol. The mixture was stirred at room temperature overnight, then the precipitate was collected by filtration and washed with diethyl ether (3×5 mL), then dried under vacuum. All of the complexes were prepared in high yield in this manner.

2,6-Dimethyl-*N***-(5,6,7-trihydroquinolin-8-ylidene)phenylaminonickel(II) dichloride (Ni1).** (Blue, 0.58 g, 76% yield): FT-IR (KBr, disk, cm⁻¹): 3067, 2949, 1624, 1583 ($v_{C=N}$), 1461, 1336, 1217, 1197, 1131, 1107, 789, 656. Anal. calcd for C₁₇H₁₈Cl₂N₂Ni (380): C, 53.74; H, 4.78; N, 7.37. Found: C, 53.42; H, 4.42; N, 7.03.

2,6-Diethyl-*N***-(5,6,7-trihydroquinolin-8-ylidene)phenylaminonickel(II) dichloride (Ni2).** (Blue, 0.64 g, 78% yield): FT-IR (KBr, disk, cm⁻¹): 3068, 2963, 2932, 2873, 1623, 1585 ($v_{C=N}$), 1487, 1334, 1287, 1217, 1192, 1131, 1046, 927, 859, 779, 661. Anal. calcd for C₁₉H₂₂Cl₂N₂Ni (408): C, 55.93; H, 5.44; N, 6.87. Found: C, 55.61; H, 5.15; N, 6.53.

2,6-Bis(1-methylethyl)-*N*-(**5,6,7-trihydroquinolin-8-ylidene)phenylaminonickel(II) dichloride (Ni3).** (Yellow, 0.71 g, 82% yield): FT-IR (KBr, disk, cm⁻¹): 3064, 2946, 2865, 2363, 1626, 1586 ($v_{C=N}$), 1459, 1330, 1217, 1136, 1050, 807, 779, 735, 661. Anal. calcd for C₂₁H₂₆Cl₂N₂Ni (436): C, 57.84, H, 6.01; N, 6.42. Found: C, 57.57; H, 5.64; N, 6.09.

2,4,6-Trimethyl-*N***-(5,6,7-trihydroquinolin-8-ylidene)phenylami**nonickel(II) dichloride (Ni4). (Yellow, 0.57 g, 72% yield): FT-IR (KBr, disk, cm⁻¹): 3055, 2920, 1626, 1585 ($v_{C=N}$), 1456, 1332, 1285, 1213, 1131, 924, 854, 789, 661. Anal. calcd for C₁₈H₂₀Cl₂N₂Ni (394): C, 54.88, H, 5.12; N, 7.11. Found: C, 55.09; H, 5.51; N, 7.27.

2,6-Diethyl-4-methyl-*N***-(5,6,7-trihydroquinolin-8-ylidene)phenylaminonickel(II) dichloride (Ni5).** (Yellow, 0.63 g, 75% yield): FT-IR (KBr, disk, cm⁻¹): 3051, 2930, 2872, 1623, 1583 ($v_{C=N}$), 1460, 1336, 1287, 1212, 1130, 1045, 923, 859, 796, 663. Anal. calcd for C₂₀H₂₄Cl₂N₂Ni (422): C, 56.92, H, 5.73; N, 6.64. Found: C, 56.53; H, 5.45; N, 6.25.

4.3 X-Ray crystallographic studies

Single crystals of Ni1·CH₃OH, Ni3·CH₃OH suitable for X-ray diffraction analysis were obtained by layering diethyl ether on their methanol solution at room temperature, and the single-crystal X-ray diffraction studies for them were carried out on a Rigaku Saturn724+ CCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) 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 full-matrix least squares on F^2 . All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXTL-97 package.²⁹ Details of the X-ray structure determinations and refinements are provided in Table 5.

Table 5 Crystal data and structure refinement for Ni1·CH_3OH, and Ni3·CH_3OH

	Ni1·CH ₃ OH	Ni3·CH ₃ OH
Empirical formula	$C_{36}H_{44}Cl_4N_4Ni_2O_2$	C44H60Cl4N4Ni2O2
Fw	823.97	936.18
T/K	173(2)	173(2)
λ/Å	0.71073	0.71073
Cryst. syst.	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	11.372(2)	14.658(3)
b/Å	9.794(2)	10.414(2)
c/Å	16.445(3)	14.753(3)
α (°)	90	90
β(°)	94.82(3)	95.14(3)
γ (°)	90	90
$V(Å^3)$	1825.1(6)	2243.0(8)
Z	2	2
D_{caled} (g cm ⁻³)	1.496	1.386
μ/mm^{-1}	1.363	1.118
F(000)	856	984
Cryst. size/mm	$0.21 \times 0.17 \times 0.13$	$0.28 \times 0.20 \times 0.10$
θ range (°)	2.75-27.48	2.79-27.50
Limiting indices	$-14 \le h \le 14$	$-14 \le h \le 19$
8	$-12 \le k \le 12$	$-12 \le k \le 13$
	$-21 \le l \le 21$	$-19 \le l \le 19$
No. of rflns collected	21761	19512
No. unique rflns [R(int)]	4179 (0.0517)	5145 (0.0459)
Completeness to θ (%)	99.8%	99.7%
Abs corr.	Numerical	Numerical
Data/restraints/params	4181/0/221	5145/1/265
Goodness of fit on F^2	1 166	1 135
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0497$	$R_1 = 0.0552$
[- 20(1)]	$wR_2 = 0.1091$	$wR_2 = 0.1121$
R indices (all data)	$R_1 = 0.0521$	$R_1 = 0.0615$
it maters (an dutu)	$wR_2 = 0.1109$	$wR_2 = 0.1153$
Largest diff peak and hole/e $Å^{-3}$	0.615 and -0.609	0.548 and -0.375

4.4 General procedure for ethylene polymerization

A 300 mL stainless steel autoclave, equipped with a mechanical stirrer and a temperature controller, was employed for the reaction. Firstly, 50 mL toluene (freshly distilled) was injected to the autoclave which was filled with ethylene in advance. When the temperature was stabilized at the required temperature, another 30 mL toluene (with the catalyst pre-dissolved in it), the required amount of cocatalyst (MAO, MMAO, EASC, AlEt₃, Et₂AlCl) and the residual toluene were successively added by syringe. The reaction mixture was intensively stirred for the desired time under the corresponding pressure of ethylene throughout the entire experiment. The reaction was quenched by addition of acidic ethanol. The precipitated polymer was washed with ethanol several times and dried *in vacuo*.

Acknowledgements

This work is supported by MOST 863 program No. 2009AA033601.

Notes and references

- (a) L. K. Johnson, C. M. Killian and M. Brookhart, J. Am. Chem. Soc., 1995, 117, 6414; (b) M. D. Leatherman, S. A. Svejda, L. K. Johnson and M. Brookhart, J. Am. Chem. Soc., 2003, 125, 3068.
- G. J. P. Britovsek, V. C. Gibson and D. F. Wass, *Angew. Chem., Int. Ed.*, 1999, **38**, 428; (b) S. D. Ittel, L. K. Johnson and M. Brookhart, *Chem. Rev.*, 2000, **100**, 1169; (c) S. Mecking, *Coord. Chem. Rev.*, 2000, **203**, 325; (d) V. C. Gibson and S. K. Spitzmesser, *Chem. Rev.*, 2003, **103**, 283; (e) W.-H. Sun, D. Zhang, S. Zhang, S. Jie and J. Hou, *Kinet. Catal.*, 2006, **47**, 278; (f) M. Zhang, T. Xiao and W-H. Sun, *Acta Polym. Sin.*, 2009, **009**, 600; (g) D. H. Camacho and Z. Guan, *Chem. Commun.*, 2010, **46**, 7879; (h) B. M. Boardman and G. C. Bazan, *Acc. Chem. Res.*, 2009, **42**, 1597.
- 3 (a) I. Albers, E. Álvarez, J. Cámpora, C. M. Maya, P. Palma, L. J. Sánchez and E. Passaglia, J. Organomet. Chem., 2004, 689, 833; (b) J. M. Benito, E. de Jesús, F. J. de la Mata, J. C. Flores and R. Gómez, Chem. Commun., 2005, 5217; (c) S. Jie, D. Zhang, T. Zhang, W.-H. Sun, J. Chen, Q. Ren, D. Liu, G. Zheng and W. Chen, J. Organomet. Chem., 2005, 690, 1739; (d) J. M. Benito, E. de Jesús, F. J. de la Mata, J. C. Flores, R. Gómez and P. Gómez-Sal, Organometallics, 2006, 25, 3876.
- 4 (a) A. L. Monteiro, M. B. de Souza and R. F. de Souza, *Polym. Bull.*, 1996, 36, 331; (b) S. A. Svejda and M. Brookhart, *Organometallics*, 1999, 18, 65; (c) L. Z. W.-H. Sun, Z. Ma, Y. L. Hu and C. X. Shao, *Chin. Chem. Lett.*, 2001, 12, 691; (d) W.-H. Sun, Z. Li, H. Hu, B. Wu, H. Yang, N. Zhu, X. Leng and H. Wang, *New J. Chem.*, 2002, 26, 1474; (e) F. Speiser, P. Braunstein and L. Saussine, *Organometallics*, 2004, 23, 2633; (f) J. Hou, W.-H. Sun, D. Zhang, L. Chen, W. Li, D. Zhao and H. Song, *J. Mol. Catal. A: Chem.*, 2005, 231, 221; (g) J. Hou, W.-H. Sun, S. Zhang, H. Ma, Y. Deng and X. Lu, *Organometallics*, 2006, 25, 236; (h) P. Chavez, I. G. Rios, A. Kermagoret, R. Pattacini, A. Meli, C. Bianchini and P. Braunstein, *Organometallics*, 2009, 28, 1776.
- 5 (a) M. Schmid, R. Eberhardt, M. Klinga, M. Leskelä and B. Rieger, Organometallics, 2001, 20, 2321; (b) H. Gao, W. Guo, F. Bao, G. Gui, J. Zhang, F. Zhu and Q. Wu, Organometallics, 2004, 23, 6273; (c) D. H. Camacho and Z. Guan, Macromolecules, 2005, 38, 2544; (d) D. Meinhard, P. Reuter and B. Pieger, Organometallics, 2007, 26, 751; (e) C. S. Popeney, A. Rheingold and L. Z. Guan, Organometallics, 2009, 28, 4452; (f) H. Liu, W. Zhao, X. Hao, C. Redshaw, W. Huang and W.-H. Sun, Organometallics, 2011, 30, 2418–2424; (g) F.-Z. Yang, Y.-C. Chen, Y.-F. Lin, K.-H. Yu, Y. Wang, S.-T. Liu and J.-T. Chen, Dalton Trans, 2009, 1243; (h) S. Zai, F. Liu, H. Gao, C. Li, G. Zhou, S. Cheng, L. Guo, L. Zhang, F. Zhu and Q. Wu, Chem. Commun., 2010, 46, 4321.
- 6 (a) W.-H. Sun, Z. Li, H. Hu, B. Wu, H. Yang, N. Zhu, X. Leng and H. Wang, *New J. Chem.*, 2002, 26, 1474; (b) Z. Guan and W. J. Marshall, *Organometallics*, 2002, 21, 3580; (c) F. Speiser, P. Braunstein, L. Saussine and R. Welter, *Organometallics*, 2004, 23, 2613; (d) F.

Speiser, P. Braunstein and L. Saussine, *Organometallics*, 2004, **23**, 2625; (e) Z. Weng, S. Teo and T. S. A. Hor, *Organometallics*, 2006, **25**, 4878.

- 7 (a) T. R. Younkin, E. F. Connor, J. I. Henderson, S. K. Friedrich, R. H. Grubbs and D. A. Bansleben, *Science*, 2000, 287, 460; (b) T. Hu, L.-M. Tang, X.-F. Li, Y.-S. Li and N.-H. Hu, *Organometallics*, 2005, 24, 2628; (c) D.-P. Song, W.-P. Ye, Y.-X. Wang, J.-Y. Liu and Y.-S. Li, *Organometallics*, 2009, 28, 5697; (d) B. A. Rodriguez, M. Delferro and T. J. Marks, *Organometallics*, 2008, 27, 2166; (e) D. Zhang, G.-X. Jin and N. Hu, *Chem. Commun.*, 2002, 574; (f) D. Zhang and G.-X. Jin, *Organometallics*, 2003, 22, 2851.
- 8 (a) W. Keim, Angew. Chem., Int. Ed. Engl., 1990, 29, 235; (b) J. Heinicke, M. He, A. Dal, H. Klein, O. Hetche, W. Keim, U. Flörke and H. Haupt, Eur. J. Inorg. Chem., 2000, 431; (c) J. Heinicke, M. Köhler, N. Peulecke and W. Keim, J. Catal., 2004, 225, 16; (d) C.-Y. Guo, N. Peulecke, K. R. Basvani, M. K. Kinderman and J. Heinicke, Macromolecules, 2010, 43, 1416; (e) C.-Y. Guo, N. Peulecke, K. R. Basvani, M. K. Kinderman and J. Heinicke, J. Polym. Sci., Part A: Polym. Chem., 2009, 47, 258.
- 9 (a) N. Ajellal, M. C. A. Kuhn, A. D. G. Boff, M. Hörner, C. M. Thomas, J.-F. Carpentier and O. L. Jr. Casagrande, *Organometallics*, 2006, **25**, 1213; (b) Y. Yang, P. Yang, C. Zhang, G. Li, X. J. Yang, B. Wu and C. Janiak, *J. Mol. Catal. A: Chem.*, 2008, **296**, 9; (c) S. O. Ojwach, I. A. Guzei, L. L. Benade, S. F. Mapolie and J. Darkwa, *Organometallics*, 2009, **28**, 2127; (d) L. Xiao, M. Zhang, R. Gao and W.-H. Sun, *Aust. J. Chem.*, 2010, **63**, 109.
- 10 X. Tang, W.-H. Sun, T. Gao, J. Hou, J. Chen and W. Chen, J. Organomet. Chem., 2005, 690, 1570.
- 11 R. L. Stapleton, J. Chai, N. J. Taylor and S. Collins, Organometallics, 2006, 25, 2514.
- 12 W.-H. Sun, S. Zhang and W. Zuo, C. R. Chim., 2008, 11, 307.
- 13 (a) T. V. Laine, K. Lappalainen, J. Liimatta, E. Aitola, B. Löfgren and M. Leskelä, *Macromol. Rapid Commun.*, 1999, **20**, 487; (b) G. J. P. Britovsek, S. P. D. Baugh, O. Hoarau, V. C. Gibson, D. F. Wass, A. J. P. White and D. J. Williams, *Inorg. Chim. Acta*, 2003, **345**, 279; (c) B. K. Bahuleyan, U. Lee, C.-S. Ha and I. Kim, *Appl. Catal.*, *A*, 2008, **351**, 36.
- 14 J. Yu, X. Hu, Y. Zeng, L. Zhang, C. Ni, X. Hao and W.-H. Sun, New J. Chem., 2011, 35, 178.
- 15 J. H. Groen, M. J. M. Vlaar, P. W. N. M. van Leeuwen, K. Vrieze and H. Kooijman, J. Organomet. Chem., 1998, 551, 67.
- 16 (a) J. D. Masuda, P. Wei and D. W. Stephan, *Dalton Trans.*, 2003, 3500; (b) D. Li, D. Cui, X. Zhang and A. Trifonov, *Dalton Trans.*, 2011, 40, 2151.
- 17 T. V. Laine, M. Klinga and M. Leskelä, Eur. J. Inorg. Chem., 1999, 959.
- 18 (a) T. Usami and S. Takayama, Polym. J., 1984, 16, 731.

- 19 (a) W.-H. Sun, S. Zhang, S. Jie, W. Zhang, Y. Li, H. Ma, J. Chen, K. Wedeking and R. Fröhlich, *J. Organomet. Chem.*, 2006, **691**, 4196; (b) L. Xiao, R. Gao, M. Zhang, Y. Li, X. Cao and W.-H. Sun, *Organometallics*, 2009, **28**, 2225; (c) M. Zhang, K. Wang and W.-H. Sun, *Dalton Trans.*, 2009, 6354.
- 20 (a) J.-Y. Liu, Y. Zheng, Y.-G. Li, L. Pan, Y.-S. Li and N.-H. Hu, J. Organomet. Chem., 2005, 690, 1233; (b) W.-H. Sun, P. Hao, G. Li, S. Zhang, W. Wang, J. Yi, M. Asma and N. Tang, J. Organomet. Chem., 2007, 692, 4506.
- 21 (a) L. C. Simon, R. S. Mauler and R. F. de Souza, J. Polym. Sci., Part A: Polym. Chem., 1999, 37, 4656; (b) G. J. P. Britovsek, M. Bruce, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. Mastroianni, S. J. McTavish, C. Redshaw, G. A. Solan, S. Stromberg, A. J. P. White and D. J. Williams, J. Am. Chem. Soc., 1999, 121, 8728; (c) D.-J. Byun and S. Y. Kim, Macromolecules, 2000, 33, 1921; (d) G. J. P. Britovsek, S. A. Cohen, V. C. Gibson and M. van Meurs, J. Am. Chem. Soc., 2004, 126, 10701; (e) M. van Meurs, G. J. P. Britovsek, V. C. Gibson and S. A. Cohen, J. Am. Chem. Soc., 2005, 127, 9913.
- 22 G. B. Galland, R. F. de Souza, R. S. Mauler and F. F. Nunes, Macromolecules, 1999, 32, 1620.
- 23 (a) R. Chen and S. F. Mapolie, J. Mol. Catal. A: Chem., 2003, 193, 33; (b) B. K. Bahuleyan, B. R. Jermy, I. Y. Ahn, H. Suh, D.-W. Park, C. S. Ha and I. Kim, Catal. Commun., 2009, 11, 252; (c) M. W. Wegner, A. K. Ott and B. Rieger, Macromolecules, 2010, 43, 3624.
- 24 Ethylene polymerization by Ni3/MAO was also conducted in hexane within a 5 L autoclave. Reaction conditions: 37.5 µmol of Ni; 10 atm of ethylene; 20 °C; 30 min; Al/Ni = 1000:1; 2.5 L hexane. The polymerization activity is 6.4×10^6 g (PE) mol(Ni)⁻¹ h⁻¹.
- 25 (a) K. P. Tellmann, V. C. Gibson and D. J. Williams, Organometallics, 2005, 24, 280; (b) B. K. Bahuleyan, G. W. Son, D.-W. Park, C.-S. Ha and I. Kim, J. Polym. Sci., Part A: Polym. Chem., 2008, 46, 1066.
- 26 M. Helldörfer, W. Milius and H. G. Alt, J. Mol. Catal. A: Chem., 2003, 197, 1.
- 27 D. P. Gates, S. A. Svejda, E. Oñate, C. M. Killian, L. K. Johnson, P. S. White and M. Brookhart, *Macromolecules*, 2000, 33, 2320.
- 28 (a) I. Göttker-Schnetmann, P. Wehrmann, C. Röhr and S. Meching, Organometallics, 2007, 26, 2348; (b) S. Jie, S. Zhang and W.-H. Sun, Eur. J. Inorg. Chem., 2007, 5584; (c) G. J. P. Britovsek, S. Mastroianni, Gregory. A. Solan, S. P. D. Baugh, C. Redshaw, V. C. Gibson, A. J. P. White, D. J. Williams and M. R. J. Elsegood, Chem.–Eur. J., 2000, 6, 2221; (d) W.-H. Sun, S. Jie, S. Zhang, W. Zhang, Y. Song, H. Ma, J. Chen, K. Wedeking and R. Fröhlich, Organometallics, 2006, 25, 666.
- 29 G. M. Sheldrick, SHELXTL-97, Program for the Refinement of Crystal Structures University of Göttingen: Göttingen, Germany, 1997.