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PAPER

N-(5,6,7-Trihydroquinolin-8-ylidene)-2-benzhydrylbenzenaminonickel halide complexes: synthesis, characterization and catalytic behavior towards ethylene polymerization⁺

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A series of N-(5,6,7-trihydroquinolinylidene)-2-benzhydrylbenzenamine ligands was synthesized and characterized by ¹H/¹³C NMR and IR spectroscopy, and by elemental analysis. These ligands reacted with NiCl₂ or NiBr₂(DME) to form the title halide complexes, which were also characterized by IR spectroscopy and elemental analysis. Single crystal X-ray diffraction revealed that the representative nickel complexes crystallized as centro-symmetric dimers with chloro-bridges linking distorted octahedral nickel centers. On activation with either methylaluminoxane (MAO) or diethylaluminium chloride (Et₂AlCl), all nickel pre-catalysts showed high activities for ethylene polymerization, producing polyethylene with narrow molecular weight distribution, consistent with single-site catalysis. The nature of the ligands and reaction parameters were investigated and discussed in terms of their influence on the catalytic behavior of these nickel pre-catalysts.

1. Introduction

Both ethylene oligomerization and polymerization play pivotal roles in today's petrochemical industry, and the products are tremendously important in our everyday life.1 Amongst the catalysts deployed, nickel-based complexes have enjoyed much success, acting as pre-catalysts in ethylene oligomerization (including ethylene dimerization).² By overcoming the problems associated with β -hydrogen elimination,³ the use of bis(imino)nickel halides proved to be a notable milestone in late-transition metal ethylene polymerization catalysis, achieving high activities and producing polyethylene with high molecular weight.⁴ Subsequently, variations of the bis(imino)nickel pre-catalyst model have been the focus of much attention. New systems were developed either by fine-tuning the substituents present on the parent ligand set,⁵ or by employing newly designed ligands such as bidentate N^N,6 N^P,7 N^O,8 P^O,9 or tridentate N^N^N,10 N^NO,11 N^P^N ligand sets.12 In general, these nickel pre-catalysts are not as attractive

for ethylene polymerization, as illustrated by the bis(imino)nickel halides,⁴ because mostly these newly developed systems induced ethylene oligomerization.⁵ However, inspired by the successful shift from bis(imino)nickel^{4,5} to pyridyliminonickel pre-catalysts,¹³ the N-(5,6,7-trihydro-quinolin-8-ylidene)arylaminonickel precatalysts have recently been explored, and interesting properties were observed for ethylene oligomerization when employing N-(2-Cl/Ph-5,6,7-trihydroquinolin-8-ylidene)arylamine¹⁴ and for ethylene polymerization with N-(5,6,7-trihydroquinolin-8-ylidene)-arylamines.¹⁵ Encouraged by these new findings, whereby the use of bulky substituents have stabilized the active species,¹⁶ the scope for using other 2-dibenzhydrylbenzenamines instead of the more common anilines was investigated. The resulting N-(5,6,7-trihydroquinolin-8-ylidene)-2-benzhydrylbenzenamines were then complexed with nickel halides, and the resulting N-(5,6,7-trihydroquinolin-8-ylidene)-2-benzhydrylbenzenaminonickel dichlorides were evaluated for ethylene polymerization catalysis. The nature of the ligands, as well as the reaction conditions employed, have been studied for their effects on the catalytic performance of the systems herein.

2. **Results and discussion**

2.1 Synthesis and characterization

N-(5,6,7-Trihydroquinolinylidene)-2-benzhydrylbenzenamine ligands can be easily prepared by the condensation of 5,6,7trihydroquinolin-8-one with bulky anilines in moderate yields (Scheme 1). All the compounds were characterized by FT-IR, ¹H and ¹³C NMR spectroscopy as well as by elemental analysis. Further reaction of the ligands with NiCl₂·6H₂O or NiBr₂·DME

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Scheme 1 Synthetic procedure.

afforded the title complexes, which were characterized by FT-IR and elemental analysis. In addition, the molecular structures of the complexes **Ni2** and **Ni3** were confirmed by single-crystal X-ray diffraction studies.

2.2 Molecular structures

Single crystals of Ni2·CH₃OH and Ni3·C₂H₅OH suitable for Xray diffraction analysis were obtained by laying diethyl ether onto dichloromethane/methanol or ethanol (v/v = 1 : 1) solutions of the respective complex at room temperature. Both complexes Ni2·CH₃OH and Ni3·C₂H₅OH crystallized as centro-symmetric dimers and their molecular structures show a distorted octahedral geometry at the nickel center, which is completed by the coordination of a solvent molecule. The molecular structures of complexes Ni2·CH₃OH and Ni3·C₂H₅OH are shown in Fig. 1 and 2, and the selected bond lengths and angles are tabulated in Table 1.

In both structures, the nickel centers are symmetrically bridged by two chloride atoms (Cl2 and Cl2i), and each is further coordinated by two nitrogen atoms (N1 and N2) from the ligand

Table 1 Selected bond lengths (Å) and angles (°) for Ni2·CH₃OH and Ni3·C₂H₅OH

	Ni2·CH ₃ OH	Ni3·C ₂ H ₅ OH
Bond lengths (Å)		
NiNi	3.449	3.425
Ni(1) - N(1)	2.056(3)	2.057(6)
Ni(1) - N(2)	2.134(3)	2.153(5)
Ni(1)-Cl(2)	2.4696(12)	2.3854(18)
Ni(1)-Cl(1)	2.4268(12)	2.398(2)
Ni(1)-O(1)	2.137(3)	2.153(5)
N(1)-C(1)	1.327(5)	1.324(10)
N(1)-C(5)	1.366(5)	1.348(9)
N(2)-C(9)	1.300(5)	1.282(8)
N(2)-C(10)	1.436(5)	1.428(8)
Bond angles (°)	. ,	
N(1)-Ni(1)-N(2)	78.66(13)	78.6(2)
N(1)-Ni(1)-O(1)	95.66(13)	91.3(2)
N(2)-Ni(1)-O(1)	88.33(12)	90.6(2)
N(1)-Ni(1)-Cl(1)	89.14(10)	90.52(18)
O(1) - Ni(1) - Cl(1)	170.97(9)	171.07(14)
N(2)-Ni(1)-Cl(1)	100.14(9)	98.36(16)
N(1)-Ni(1)-Cl(2)	174.69(10)	172.18(17)
O(1)-Ni(1)-Cl(2)	83.74(9)	84.72(14)
N(2)-Ni(1)-Cl(2)	96.05(9)	94.69(15)
Cl(1)-Ni(1)-Cl(2)	92.17(4)	94.48(7)



Fig. 1 ORTEP drawing of complex Ni2·CH₃OH.



Fig. 2 ORTEP drawing of complex Ni3· C_2H_3OH . Thermal ellipsoids are shown at 30% probability. Hydrogen atoms have been omitted for clarity.

as well as the oxygen from the solvent molecule. As shown in Fig. 1, there is a five-membered heteronickel-cycle constructed from Ni, N1, C5, C9 and N2, in which the C9 atom deviates by 0.0396 Å from the plane of the atoms N1, N2, and Ni1, whilst the C5 atom deviates by 0.0096 Å, i.e. the five atoms are almost in the same plane. The two Ni-N bond lengths are Ni-N1 (2.056 Å) and Ni–N2 (2.134 Å). The pyridyl and imino-phenyl planes are nearly perpendicular with a dihedral angle of 98.4°. There is no direct bonding between the two nickel atoms with an intramolecular distance of 3.4491 Å, which is similar to 3.4810 Å found in the [2,6-diethyl-N-(2-chloro-5,6,7-trihydroquinolin-8ylidene)phenylamino]nickel(II) dichloride.14 The axial chloride Cl1 forms stronger bonding with the nickel centre (Ni-Cl1, 2.4268 Å) than does the equatorial bridging chloride Cl2 [Ni-Cl2 (2.4696 Å)]. The Ni \cdots Ni length is 3.425 Å for Ni3 \cdot C₂H₅OH which is slightly shorter than that of Ni2·CH₃OH (3.449 Å) and the dihedral angle of pyridyl and imino-phenyl planes is 91.5°. The small differences between the molecular structures of Ni2·CH₃OH and $Ni3 \cdot C_2 H_5 OH$ are probably caused by the introduction of bulky substituents at the ortho-position of the N-aryl ring.

2.3 Ethylene polymerization

The ethylene polymerization behavior of these nickel complexes was investigated. Trace quantities of oligomers were found during

 Table 2
 Polymerization of ethylene in the presence of MAO^a

Entry	Pre-cat.	T/ °C	Al/Ni	t/ min	Polymer/ g	Activity ^b	$M_{\rm w}{}^c$ / kg mol ⁻¹	$M_{\rm w}/M_{\rm n}{}^c$	$T_{\rm m}^{d}/^{\rm o}{\rm C}$	Branches/1000C ^e
1	Ni1	20	500	30	3.20	1.28	12.0	2.6	114.6	176
2	Ni1	20	600	30	8.15	3.26	7.7	1.8	102.9	132
3	Ni1	20	750	30	14.15	5.66	5.7	2.2	95.6	113
4	Ni1	20	1000	30	11.84	4.74	5.2	2.0	93.6	141
5	Ni1	20	1500	30	11.63	4.65	5.4	2.0	80.8	150
6	Ni1	30	750	30	9.61	3.84	10.6	2.0	103.5	113
7	Ni1	40	750	30	6.86	2.74	4.1	2.3	88.8	150
8	Ni1	50	750	30	3.27	1.31	2.5	2.3	77.9	186
9	Ni1	20	750	10	4.61	5.17	7.9	2.4	92.3	115
10	Ni1	20	750	20	9.03	5.42	7.0	2.7	98.7	121
11	Ni1	20	750	40	16.67	4.00	6.8	2.5	90.9	136
12	Ni2	20	750	30	10.48	4.19	4.8	2.3	58.9	127
13	Ni3	20	750	30	2.31	0.92	6.7	2.1	61.2	181
14	Ni4	20	750	30	1.62	0.65	7.4	1.9	64.9	226
15	Ni5	20	750	30	7.52	3.01	6.3	1.9	95.2	123
16	Ni6	20	750	30	5.46	2.18	7.0	2.6	90.5	136
17	Ni7	20	750	30	1.94	0.78	7.3	2.5	60.8	209
18	Ni8	20	750	30	1.42	0.57	6.8	1.8	64.1	246

^{*a*} Reaction conditions: 5 µmol of Ni; 10 atm of ethylene; 100 mL toluene. ^{*b*} 10⁶ g(PE)·mol(Ni)⁻¹·h⁻¹. ^{*c*} Determined by GPC. ^{*d*} Determined by DSC. ^{*e*} Determined by FT-IR.

the polymerization process through GC detection. Different cocatalysts were employed to activate the pre-catalyst. Both MAO and EtAlCl₂ showed higher activity than did other alkylaluminium reagents and thus were selected for further study. All the catalysts exhibited very low activity when the ethylene pressure was 1 bar, thus subsequent entries were performed with 10 bar ethylene as the routine condition. Herein, the effect of ligand environment on catalytic behavior was investigated in further detail. Also the molar ratio of Al/Ni, the temperature, and the reaction time have been considered. The pre-catalysts showed high catalytic activity (up to 10^6) for ethylene polymerization.

2.3.1 Ethylene polymerization in the presence of MAO. The influence of the reaction parameters, including the molar ratio of Al/Ni, the reaction time and the reaction temperature, were investigated using the Ni1/MAO system. On variation of the Al/Ni from 500 to 1500 (entries 1-5 in Table 2), the catalyst showed the highest activity at an optimum ratio of 750, namely $\leq 5.66 \times 10^{6} \text{ g(PE)} \cdot \text{mol}(\text{Ni})^{-1} \cdot \text{h}^{-1}$ (entry 3 in Table 2). The molecular weight distributions were relatively narrow, with values in the region of about 2.00, suggesting fairly well controlled behavior. It was found that when the ratio of Al/Ni was raised to 750, the molecular weights remained almost unaffected. This indicated that the amount of MAO is enough to activate the pre-catalyst at the ratio of 750. Also the influence of the reaction temperature was investigated (entries 6 and 7, 8 in Table 2) at the constant molar ratio of Al/Ni = 750. The activity decreased with increasing reaction temperature. It was found that the polymer of highest molecular weight was attainable at 30 °C (Fig. 3). When the temperature was raised to 50 °C, only a small amount of wax was obtained possessing a very low molecular weight of about 2500. Thus, the activity decreased sharply and the resultant polymer possessed lower molecular weight than runs conducted at room temperature, which is similar to results for other late-transition iminopyridyl-based pre-catalysts.¹⁷ The present system is much more sensitive to temperature than the N-(5,6,7-trihydroquinolin-8-ylidene)arylamine nickel complexes previously reported by our



Fig. 3 GPC traces of polyethylene produced by **Ni1**/MAO catalytic system (a: T = 30 °C, entry 6; b: T = 20 °C, entry 3; c: T = 40 °C, entry 7; d: T = 50 °C, entry 8 in Table 2).

group,¹⁵ thus revealing that the active centre formed by this kind of pre-catalyst possessing bulky substituents at the ortho-position is more unstable at higher temperatures. The ¹³C NMR spectrum for Ni1/MAO (entry 3 in Table 2) showed 100 branches/1000 carbons (Fig. 4).¹⁸ The formation of the highly branched PEs obtained was due to β-hydrogen migration, which occurred at the active nickel species.¹⁹ Furthermore, the influence of the reaction time was studied, and in general, the catalytic activities slowly decreased on prolonging the reaction time, indicating a relative long lifetime of the active species. The other complexes herein were also screened under these optimized conditions (entries 12, 13 and 14 in Table 2). The activity decreased sharply when the ortho-position of the phenyl ring was occupied by the bulky dibenzhydryl [-CH(Ph)₂] group. Contrastingly, the substituent at the para-position played a relatively minor role in influencing the catalytic activity of the ethylene polymerization (Ni1>Ni2>Ni3>Ni4). When the halogen at nickel is bromide, the activities showed much lower values than did the corresponding nickel chloride complexes; similar trends with the other ligand variations were noted (Ni5>Ni6>Ni7>Ni8).



2.3.2 Ethylene polymerization in the presence of Et₂AlCl. Using Et₂AlCl as co-catalyst rather than MAO, the complexes performed with a relatively lower activity toward ethylene polymerization. The influence of the reaction parameters on the catalytic activities, including the molar ratio of Et₂AlCl and the reaction temperature, were investigated with complex Ni1. The detailed results are summarized in Table 3. The results showed a similar tendency as for those observed when using MAO, but the PDI of the waxes were somewhat narrower. The molecular weights were higher than using MAO (entries 20 and 24-30 in Table 3). Also both the ratio of Al/Ni and the temperature played important roles in the polymerization behavior. The optimum ratio of Al/Ni was found to be 150, whilst increasing the reaction temperature from 20 °C to 40 °C (entries 21, 22 and 23 in Table 3) led to an obvious decrease in the activity and the isolation of lower molecular weight polymers (Fig. 5). It is interesting that the T_m values were lower than the entries using MAO though the wax possessed higher molecular weight. This can be attributed to the higher degree of branching, which can be detected and calculated via IR spectroscopic analysis.20

3. Conclusions

A number of bulky substituents were introduced to the N-(5,6,7-trihydroquinolinylidene)-2-benzhydrylbenzenamines-Ni(II) pre-

Table 3 Polymerization of ethylene in the presence of Et₂AlCl^a



Fig. 5 GPC traces of polyethylene produced by Ni1/Et₂AlCl catalytic system (a: T = 30 °C, entry 22; b: T = 20 °C, entry 20; c: T = 40 °C, entry 23 in Table 3).

catalyst family to study their influence on the catalytic behavior during ethylene polymerization. The results showed that all these nickel complexes exhibited high activity (up to 5.66×10^6 g mol(Ni)⁻¹·h⁻¹) for ethylene polymerization, producing highly branched wax-like products with narrow molecular weight distribution. The molecular weight can be easily controlled through ligand modification, *i.e.* substituent variation. Complexes bearing one bulky substituent [-CH(Ph)₂] at an *ortho*-position of the *N*aryl ring (Ni1 and Ni2) exhibited higher activities than did the complexes with two bulky substituents [-CH(Ph)₂] at both *ortho*positions of the *N*-aryl ring (Ni3 and Ni4), which illustrates the fine balance steric bulk plays on the catalytic performance of these nickel-based ethylene polymerization systems.

4. Experimental section

4.1 General considerations and materials

All work involving air or moisture-sensitive compounds was carried out under nitrogen atmosphere using standard Schlenk techniques. Toluene was dried by refluxing with sodium and distilled under nitrogen. Methylaluminoxane (MAO, 1.46 M in toluene) was purchased from Albemarle and diethylaluminium chloride (Et₂AlCl, 0.50 M in toluene) was purchased from Acros

Entry	Pre-cat.	T∕ °C	Al/Ni	t/ min	Polymer/ g	Activity ^b	$M_{ m w}{}^c$ / kg mol ⁻¹	$M_{\rm w}/M_{\rm n}{}^c$	$T_{\rm m}^{\ \ d}/^{\circ}{ m C}$	Branches/1000C ^e
19	Ni1	20	100	30	5.75	2.30	5.8	1.8	82.0	175
20	Ni1	20	150	30	10.28	4.11	3.7	2.2	69.3	210
21	Ni1	20	250	30	9.49	3.80	3.8	1.8	64.9	240
22	Ni1	30	150	30	6.79	2.72	4.2	1.9	72.7	227
23	Ni1	40	150	30	1.93	0.77	3.4	1.8	56.4	260
24	Ni2	20	150	30	10.08	4.03	4.0	2.0	60.8	184
25	Ni3	20	150	30	3.15	1.26	9.1	1.9	61.2	229
26	Ni4	20	150	30	2.80	1.12	6.8	1.7	63.8	193
27	Ni5	20	150	30	5.75	2.30	7.2	1.9	89.9	154
28	Ni6	20	150	30	5 49	2.20	7.0	1.9	84.2	144
29	Ni7	20	150	30	2.74	1.10	7.0	1.7	60.8	219
30	Ni8	20	150	30	1.97	0.79	7.7	1.8	64.8	189

^{*a*} Reaction conditions: 5 μmol of Ni; 10 atm of ethylene; 100 mL toluene. ^{*b*} 10⁶ g(PE)·mol(Ni)⁻¹·h⁻¹. ^{*c*} Determined by GPC. ^{*d*} Determined by DSC. ^{*e*} Determined by FT-IR.

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. ¹H and ¹³C NMR spectra were recorded on a Bruker DMX 400 MHz instrument at ambient temperature, using TMS as an internal standard. IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer. Elemental analysis was carried out using a Flash EA 1112 microanalyzer. Molecular weights (M_w) and molecular 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. 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

4.2.1 Synthesis of ligands.

2-Methyl-4,6-dibenzhydryl-N-(5,6,7-trihydroquinolin-8-ylidene)phenylamine (L1). A 15 mL toluene solution of 5,6,7trihydroquinolin-8-one (2 mmol, 0.294 g) and 2-methyl-4,6dibenzhydrylaniline (2.2 mmol, 0.966 g) together with a catalytic amount of p-toluenesulfonic acid was refluxed for 3 h. The toluene was then evaporated at reduced pressure, and the residue was purified by alumina column chromatography [V (petroleum ether): V (dichloromethane) = 5:1]. The product was a yellow powder, which was collected in 38% yield. Mp 84-86 °C. ¹H NMR (400 MHz, CDCl₃ TMS): δ 8.73 (d, J = 4.3 Hz, 1H, Py *Hm*), 8.33 (d, J = 7.5 Hz, 1H, Py Hm), 7.46 (t, J = 5.8 Hz, 1H, Py Hp), 6.88– 7.29 (m, 20H, Ph-H), 6.78 (s, 1H, Ph-H), 6.56 (s, 1H, Ph-H), 5.62 (s, 1H, p-CH(Ph)₂), 5.40 (s, 1H, o-CH(Ph)₂), 2.69, 2.52 (m, 2H, $-N = CCH_2$), 1.95 (s, 3H, Ph-CH₃), 2.06, 1.25 (m, 2H, py-CH₂-), 1.60, 1.05 (m, 2H, -CH₂-) ppm.¹³C NMR (100 MHz, CDCl₃ TMS): δ 165.8, 148.4, 146.9, 144.5, 144.3, 144.0, 142.8, 137.2, 136.8, 136.7, 133.3, 129.9, 129.2, 128.8, 128.6, 127.8, 127.5, 125.8, 125.7, 125.4, 56.1, 51.6, 30.3, 28.9, 21.0, 17.8 ppm. FT-IR (KBr, cm⁻¹): 3344 (w), 2925 (m), 2027 (w), 1640 (s, C=N), 1598 (m), 1564 (m), 1492 (vs), 1032 (s), 738 (vs). Anal. Calcd for C₄₂H₃₆N₂ (568): C, 88.69; H, 6.38; N, 4.93%. Found: C, 88.54; H, 6.41; N, 5.10%.

2,4-Dimethyl-6-benzhydryl-N-(5,6,7-trihydroquinolin-8-ylidene)phenylamine (L2). This compound was prepared according to the method described for 1. The product was a yellow powder and the yield was 48%. Mp 80-82 °C. ¹H NMR (400 MHz, CDCl₃ TMS): δ 8.73 (d, J = 4.1 Hz, 1H, Py Hm), 7.46 (d, J = 7.5 Hz, 1H, Py Hm), 7.25 (t, J = 6.1 Hz, 1H, Py Hp), 7.04–7.22 (m, 10H, Ph-H), 6.88 (s, 1H, Ph-H), 6.59 (s, 1H, Ph-H), 5.65 (s, 1H, -CH(Ph)₂), 2.66, 2.47 (m, 2H, $-N = CCH_2$), 2.21 (s, 3H, *o*-Ph-CH₃), 1.99 (s, 3H, p-Ph-CH₃), 1.91, 1.14 (m, 2H, Py-CH₂-), 1.42, 0.89 (m, 2H, -CH₂-) ppm. ¹³C NMR (100 MHz, CDCl₃ TMS): δ 166.1, 150.0, 148.7, 146.5, 143.2, 137.1, 131.6, 130.1, 129.7, 129.1, 128.3, 128.0, 126.0, 124.8, 51.9, 30.5, 29.3, 21.3, 21.0, 18.1 ppm. FT-IR (KBr, cm⁻¹): 3342 (w), 2921 (m), 2017 (w), 1638 (s, C=N),1599 (m), 1564 (m), 1444 (vs), 1189 (s), 1031 (s), 744 (vs). Anal. Calcd for C₃₀H₂₈N₂ (416): C, 86.50; H, 6.78; N, 6.72%. Found: C, 86.62; H, 6.83; N, 6.88%.

2,6-Dibenzhydryl-4-methyl-N-(5,6,7-trihydroquinolin-8-ylidene)phenylamine (L3). This compound was prepared according to the method described for **1**. The product was a yellow powder isolated in 42% yield. Mp 103–104 °C. ¹H NMR (400 MHz, CDCl₃ TMS): δ 8.74 (d, J = 4.1 Hz, 1H, Py Hm), 7.41 (d, J = 7.6 Hz, 1H, Py *Hn*), 7.41 (t, J = 6.0 Hz, 1H, Py *Hp*), 7.05–7.37 (m, 20H, Ph-*H*), 6.69 (s, 2H, Ph-*H*), 5.51 (s, 2H, -*CH*(Ph)₂), 2.28 (t, J = 5.9 Hz, 2H, -*C*=N-*CH*₂-), 2.16 (s, 3H, Ph-*CH*₃), 0.86 (t, J = 6.1 Hz, 2H, Py-*CH*₂-), 0.54 (m, 2H, -*CH*₂-) ppm. ¹³C NMR (100 MHz, CDCl₃ TMS): δ 168.4, 148.5, 144.8, 142.8, 137.0, 132.4, 130.1, 129.7, 129.1, 128.4, 128.0, 126.1, 125.9, 124.7, 51.7, 31.1, 29.1, 21.4, 20.5 ppm. FT-IR (KBr, cm⁻¹): 3345 (w), 2929 (m), 2029 (m), 1734 (s), 1637 (s, C=N), 1598 (m), 1562 (m), 1493 (vs), 1238 (s), 1033 (vs), 746 (vs). Anal. Calcd for C₄₂H₃₆N₂ (568): C, 88.69; H, 6.38; N, 4.93%. Found: C, 88.57; H, 6.33; N, 4.86%.

2,6-Dibenzhydryl-4-(1-methylethyl)-N-(5,6,7-trihydro-quinolin-8-ylidene)phenylamine (L4). This compound was prepared according to the method described for 1. The product was collected in 45% yield as a yellow powder. Mp 96-98 °C. ¹H NMR (400 MHz, CDCl₃ TMS): δ 8.74 (d, J = 4.0 Hz, 1H, Py *Hm*), 7.41 (d, J = 7.6 Hz, 1H, Py Hm), 7.27 (t, J = 6.1 Hz, 1H, Py Hp), 7.03–7.24 (m, 20H, Ph-H), 6.72 (s, 2H, Ph-H), 5.51 (s, 1H, -CH(Ph)₂), 2.69 (m, 1H, $-CH_2(CH_3)_2$), 2.27 (t, J = 5.9 Hz, 2H, $-N = CCH_2$ -), 1.05 (d, J = 6.8 Hz, 6H, -CH₃), 0.88 (t, J = 6.0 Hz, 3H, Py-CH₂-), 0.55 (m, 2H, -CH₂-) ppm. ¹³C NMR (100 MHz, CDCl₃ TMS): δ 167.3, 144.0, 143.3, 142.8, 139.3, 132.5, 129.8, 129.6, 129.1, 128.5, 128.0, 126.7, 126.4, 126.0, 51.9, 33.6, 33.2, 24.1, 21.3, 19.8 ppm. FT-IR (KBr, cm⁻¹): 3338 (w), 2957 (m), 1976 (m), 1735 (s), 1639 (s, C=N), 1598 (s), 1570 (m), 1446 (vs), 1030 (s), 742 (vs). Anal. Calcd for C₄₄H₄₀N₂ (596): C, 88.55; H, 6.76; N, 4.69%. Found: C, 88.34; H, 6.78; N, 4.80%.

4.2.2 Synthesis of nickel complexes.

General procedure. NiCl₂·6H₂O or (DME)NiBr₂ (0.5 mmol) was dissolved in 10 mL ethanol and added to the solution of the ligand (0.5 mmol) in 5 mL CH₂Cl₂ (but not ethanol because of inferior solubility). The mixture was stirred overnight, and then ether was poured into the mixture to precipitate the complex. The precipitant was collected by filtration, washed with diethyl ether (3 × 5 mL), and dried under vacuum at 60 °C.

2-Methyl-4,6-dibenzhydryl-*N***-(5,6,7-trihydroquinolin-8-ylidene)phenylaminonickel(II) dichloride** (Ni1) (yellow, 0.31 g, 91% yield): FT-IR (KBr, disk, cm⁻¹): 3026 (m), 2028 (w),1976 (w), 1623 (s, C==N), 1584 (s), 1494 (vs), 1029 (s), 730(vs). Anal. Calcd for $C_{42}H_{36}Cl_2N_2Ni$ (698): C, 72.23; H, 5.20; N, 4.01%. Found: C, 72.43; H, 5.09; N, 4.04%.

2,4-Dimethyl-6-benzhydryl-*N***-(5,6,7-trihydroquinolin-8-ylidene)phenylaminonickel(II) dichloride (Ni2)**(yellow, 0.25 g, 93% yield): FT-IR (KBr, disk, cm⁻¹): 3190 (w), 2920 (m), 2030 (m), 1622 (s, C=N), 1583 (s), 1451 (vs), 1212 (s), 1033 (s), 746 (vs). Anal. Calcd for $C_{30}H_{28}Cl_2N_2Ni$ (546): C, 65.97; H, 5.17; N, 5.13%. Found: C, 65.89; H, 5.16; N, 5.10%.

2,6-Dibenzhydryl-4-methyl-*N*-**(5,6,7-trihydroquinolin-8-ylide-ne)phenylamineonickel(II) dichloride (Ni3)** (yellow, 0.33 g, 94% yield): FT-IR (KBr, disk, cm⁻¹): 2919 (m), 2030 (m), 1624 (s, C=N), 1584 (s), 1494 (vs), 1208 (s), 1029 (vs), 753 (vs). Anal. Calcd for $C_{42}H_{36}Cl_2N_2Ni$ (698): C, 72.23; H, 5.20; N, 4.01%. Found: C, 71.88; H, 5.17; N, 4.24%.

2,6-Dibenzhydryl-4-(1-methylethyl)-*N*-(**5,6,7-trihydro-quinolin-8-ylidene)phenylaminonickel(II) dichloride (Ni4)** (yellow, 0.35 g, 96% yield): FT-IR (KBr, disk, cm⁻¹): 2957 (m), 1975 (m), 1620 (s, C=N), 1581 (s), 1449 (vs), 1129 (s), 747 (vs). Anal. Calcd for $C_{44}H_{40}Cl_2N_2Ni$ (698): C, 72.75; H, 5.55; N, 3.86%. Found: C, 72.34; H, 5.21; N, 3.62%. **2,4-Dimethyl-6-benzhydryl-***N***-(5,6,7-trihydroquinolin-8-ylidene)phenylaminonickel(II) dibromide (Ni6)** (yellow, 0.27 g, 84% yield): FT-IR (KBr, disk, cm⁻¹): 2965 (m), 2036 (m), 1622 (s, C=N), 1580 (s), 1451 (vs), 1213 (vs), 1033 (vs), 740 (vs). Anal. Calcd for $C_{30}H_{28}Br_2N_2Ni$ (635): C, 56.74; H, 5.09; N, 4.41%. Found: C, 56.94; H, 5.06; N, 4.38%.

2,6-Dibenzhydryl-4-methyl-*N***-(5,6,7-trihydroquinolin-8-ylidene)phenylaminonickel(II) dibromide (Ni7)** (yellow, 0.31 g, 80% yield): FT-IR (KBr, disk, cm⁻¹): 2911 (m), 2029 (m), 1620 (s, C=N), 1582 (s), 1494 (vs), 1208 (s), 1132 (vs), 742 (vs). Anal. Calcd for $C_{42}H_{36}Br_2N_2Ni$ (787): C, 64.08; H, 4.61; N, 3.56%. Found: C, 63.87; H, 4.55; N, 3.46%.

2,6-Dibenzhydryl-4-(1-methylethyl)-*N***-(5,6,7-trihydro-quinolin-8-ylidene)phenylaminonickel(II) dibromide (Ni8)** (yellow, 0.33 g, 80% yield): FT-IR (KBr, disk, cm⁻¹): 2955 (m), 1978 (m), 1605 (s, C==N), 1578 (s), 1448 (vs), 1129 (s), 748 (vs). Anal. Calcd for $C_{44}H_{40}Br_2N_2Ni$ (815): C, 64.82; H, 4.95; N, 3.44%. Found: C, 65.03; H, 5.12; N, 3.76%.

4.3 X-ray crystallographic studies

Single crystals of Ni2·CH₃OH and Ni3·C₂H₅OH suitable for Xray diffraction analyses were obtained by laying diethyl ether on dichloromethane/methanol (v/v = 1 : 1) solution at room temperature. X-ray studies were carried out on a Rigaku Saturn724+ CCD with graphite-monochromatic Mo-K α radiation (k = 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 SHELXL-97 package.²¹ Details of the X-ray structure determinations and refinements are provided in Table 4.

4.4 General procedure for ethylene polymerization

A 250 mL stainless steel autoclave, equipped with a mechanical stirrer and a temperature controller, was evacuated by a vacuum pump and back-filled three times with N_2 and twice with ethylene. 50 mL toluene was added under ethylene atmosphere, and the nickel pre-catalyst in 30 mL toluene was injected. When the desired reaction temperature was reached, the required amount of co-catalyst (MAO or Et₂AlCl) and additional toluene (maintaining total volume as 100 mL in reactor) were added by syringe. A pressure of 10 atm ethylene was then rapidly reached and maintained through a solenoid clave, the mixture was vigorously stirred during the ethylene polymerization. After the desired reaction time, the reaction solution was quenched by the addition of acidic ethanol, and the precipitated polymer was washed with ethanol and water several times, and then dried in vacuum until of constant weight.

Table 4 Crystal data and structure refinement for Ni2-CH₃OH and Ni3-C₂H₃OH

	Ni2·CH ₃ OH	$Ni3 \cdot C_2H_5OH$
Empirical formula	C ₆₂ H ₆₄ Cl ₄ N ₄ Ni ₂ O ₂	C ₈₈ H ₈₂ Cl ₄ N ₄ Ni ₂ O ₂
Fw	1156.39	1486.8
T/K	173(2)	173(2)
λ/Å	0.71073	0.71073
Cryst system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a/Å	14.895(3)	16.059(2)
b/Å	15.229(3)	17.764(3)
c/Å	15.550(3)	15.868(3)
α (°)	90	90
β (°)	103.64(3)	108.03(4)
γ (°)	90	90
$V/Å^3$	3427.6(12)	4304.0(6)
Z	2	2
Dcalcd, $(g \text{ cm}^{-3})$	1.120	1.147
μ/mm^{-1}	0.744	0.607
F(000)	1208	1556
Cryst size/mm	$0.30 \times 0.26 \times 0.19$	$0.21 \times 0.18 \times 0.06$
θ range (°)	1.70-25.35	1.33-25.34
Limiting indices	$-16 \le h \le 17$	$-17 \le h \le 19$
	$-18 \le k \le 18$	$-21 \le k \le 19$
	$-18 \le l \le 16$	$-17 \le l \le 19$
No. of rflns collected	25 336	17 249
No. unique rflns [R(int)]	6266 (0.0526)	7802 (0.0826)
Completeness to θ (%)	99.8%	99.2%
Abs corr	None	None
Data/restranints/params	6266/0/335	7802/0/451
Goodness of fit on F ²	1.147	1.049
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0641$	$R_1 = 0.1030$
	$wR_2 = 0.1859$	$wR_2 = 0.2662$
R indices (all data)	$R_1 = 0.0723$	$R_1 = 0.1398$
	$wR_2 = 0.1924$	$wR_2 = 0.2920$
Largest diff peak and hole/e $Å^{-3}$	0.571 and -0.543	0.700 and -0.999

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