Journal of Organometallic Chemistry 708-709 (2012) 98–105

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

2-Substituted 8-(2-benzhydrylarylimino)-5,6,7-trihydroquinoline-*N*,*N*′ nickel dichlorides: Synthesis, characterization and catalytic behavior towards ethylene

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ARTICLE INFO

Article history:
Received 11 January 2012
Received in revised form
18 February 2012
Accepted 22 February 2012

Keywords:
2-Substituted 8-(2-benzhydrylarylimino)-5,6,7-trihydroquinoline-*N*,*N*′ nickel dichloride
Distorted trigonal bipyramidal geometry
Distorted tetrahedral geometry
Ethylene polymerization
Ethylene oligomerization

ABSTRACT

A series of 2-substituted 8-(2-benzhydrylarylimino)-5,6,7-trihydroquinolines (**L**) was synthesized and fully characterized, and their nickel chloride complexes, namely 2-substituted 8-(2-benzhydrylarylimino)-5,6,7-trihydroquinoline-*N*,*N*′ nickel dichlorides (**L**$NiCl_2$), were prepared and characterized by FT-IR and elemental analysis. The structures of representative complexes were confirmed by single crystal X-ray crystallography, which revealed a distorted trigonal bipyramidal geometry at the metal for complexes **Ni3** and **Ni5** containing an additional solvent molecule, and a distorted tetrahedral geometry for the complex **Ni8**. Upon activation with methylaluminoxane (MAO), all nickel pre-catalysts showed good activity for ethylene polymerization and considerable activity for ethylene oligomerization.

1. Introduction

The impressive catalytic performances of diiminonickel halide complexes initiated the resurrection of interest in late-transition metal complexes, particularly their use in ethylene oligo- and polymerization [1]. Extensive studies have been conducted over the past two decades through the modification of the substituents present at the diimine ligand [2–7]. Sticking to the concept of using N^N bidentate ligands, some *N*-heterocyclic compounds have been designed and successfully used in nickel-based pre-catalysts for ethylene oligomerization and/or polymerization [8–18]. In addition, numerous alternative nickel pre-catalysts have been reported, which employ various ligand types such as bidentate N^P [19–21], N^O [22–30], P^O [31,32], or tridentate N^N^N [33–46], N^N^O [47,48], N^P^N [49–51]. Within the N^N bidentate nickel pre-catalyst family, those bearing iminopyridyl ligation showed high activities for ethylene polymerization [8,9]. Interestingly, bimetallic analogues produced both polyethylenes and oligomers [52]. Recently, nickel halide complexes bearing arylimino-5,6,7-trihydroquinoline derivatives performed impressively for either ethylene oligomerization [53,54] or polymerization [55–57]. Furthermore, benzhydryl-substituted anilines were successfully used in forming imino-based ligands, and their late-transition metal pre-catalysts possessed enhanced catalytic activities in ethylene polymerization [7,58,59]. On extending this research, 2-substituted 8-(2-benzhydrylarylimino)-5,6,7-trihydro-quinolines are now synthesized and used herein to prepare the corresponding nickel chloride complexes. Upon activation with MAO, these nickel pre-catalysts showed good activity in ethylene polymerization and considerable activity in ethylene oligomerization.

2. Results and discussion

2.1. Synthesis and characterization

The 2-substituted 8-(2-benzhydrylarylimino)-5,6,7-trihydroquinoline ligands (**L1**–**L8**) used in this work were prepared in reasonable yields according to our previous literature synthesis [55] by reaction of the respective 2-benzhydrylanilines (Scheme 1). The obtained compounds were confirmed to be two isomers of similar ratio comprising the forms enamine (**L**′) and Schiff-base (**L**); the two

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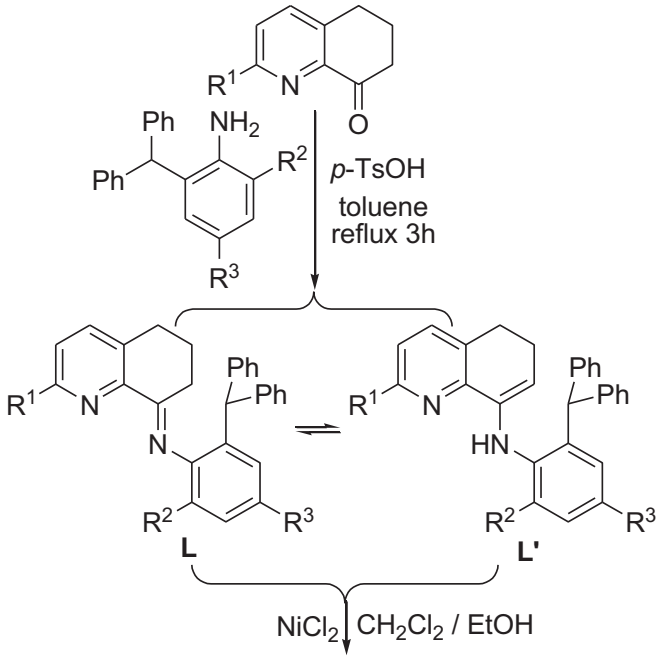
doi:10.1016/j.jorganchem.2012.02.031



R^2	R^3	R^1 = Ph	R^1 = Cl
Me	-CH(Ph)$_2$	**Ni1**	**Ni5**
Me	Me	**Ni2**	**Ni6**
-CH(Ph)$_2$	Me	**Ni3**	**Ni7**
-CH(Ph)$_2$	*i*Pr	**Ni4**	**Ni8**

Scheme 1. Synthetic procedure.

isomers were quickly isomerised at room temperature as evidenced by the different fractions on column separation which showed the same ratio of isomers as monitored by NMR measurements. Two co-existing isomers for enamine and Schiff-base have been observed in our previous work [55,60].

The mixture of each ligand (0.5 mmol) was reacted with an equivalent amount of $NiCl_2 \cdot 6H_2O$ in 5 mL ethanol and 2 mL dichloromethane at room temperature. After being stirred for 3 h, the resultant solution was mixed with 20 mL ether and further stirred to precipitate the yellow nickel complex. According to their FT-IR spectra, the peaks around 3350 cm^{-1} for the N–H and 1564 cm^{-1} for the C=C bond of enamine of free ligands disappeared from the FT-IR spectra of their nickel complexes, indicating the isomer transformation of enamine (**L′**) into Schiff-base derivatives occurred during coordination with the nickel centre. Checking their data of elemental analysis, most showed relative lower values of nitrogen contents than the theoretic data; and that could be due to problems with combustion in the series of ligands used, previously being observed in our research [61]. One, the molecular structures of the nickel complexes **Ni3**, **Ni5** and **Ni8** were further confirmed by single crystal X-ray diffraction studies.

2.2. Molecular structures

Single crystals of complex **Ni3** suitable for X-ray diffraction were obtained by re-crystallization from a saturated dichloromethane solution, and the molecular structure revealed the distorted trigonal bipyramidal geometry around the five-coordinated nickel atom; there is an additional water molecule of solvation (Fig. 1). Unlike their iminopyridylnickel chloride complexes which exist as dimers [53,54,62,63], a mono-ligated mononuclear nickel complex was observed due to the presence of the bulky benzhydryl substituents on the aryl$_{imino}$ group. The N2–C8 bond at 1.294 Å clearly showed double bond characteristics, consistent with coordination of the ligand as the Schiff-base form. The atoms Ni1, N1, C9, C8 and N2 formed a planar metallocycle with a slight deviation of 0.0555 Å for C8 and 0.0461 Å for C9 out of the plane. The phenyl plane linked on the imine was perpendicular to the fused pyridyl ring; selected bond lengths and angles are tabulated in Table 1.

Single crystals of complex **Ni5** were obtained by laying diethyl ether on to a DMF solution. The molecular geometry is very similar to that of **Ni3**, but with an additional DMF molecule present, which in this case is ligated to the nickel centre via its oxygen (Fig. 2). As shown for **Ni3**, the bond N2–C8 of **Ni5** at 1.280(5) Å was consistent with a double bond. Within the five-membered metallocyclic plane of Ni1, N1, C9, C8 and N2, the deviations were for C8 0.0740 Å and C9 0.0862 Å out of the plane. Again, the phenyl plane is almost perpendicular (99.1°) to the fused pyridinyl ring. Selected bond lengths and angles are listed in Table 1.

Single crystals of complex **Ni8** were grown by the slow diffusion of diethyl ester into a dichloromethane solution under nitrogen atmosphere. The molecular structure in this case revealed a distorted tetrahedral geometry around the nickel (Fig. 3). As shown for the above two complexes **Ni3** and **Ni5**, the bond N2–C8 of **Ni8** was 1.291(5) consistent with a coordinated C=N bond. The five-membered metallocycle comprising atoms Ni1, N1, C9, C8 and N2 is almost co-planar with the deviations of C8 of 0.0057 Å and C9 of 0.0023 Å, respectively. The dihedral angle between the phenyl and fused pyridinyl planes is 92.5°, indicating their near perpendicular feature. Selected bond lengths and angles are collected in Table 1.

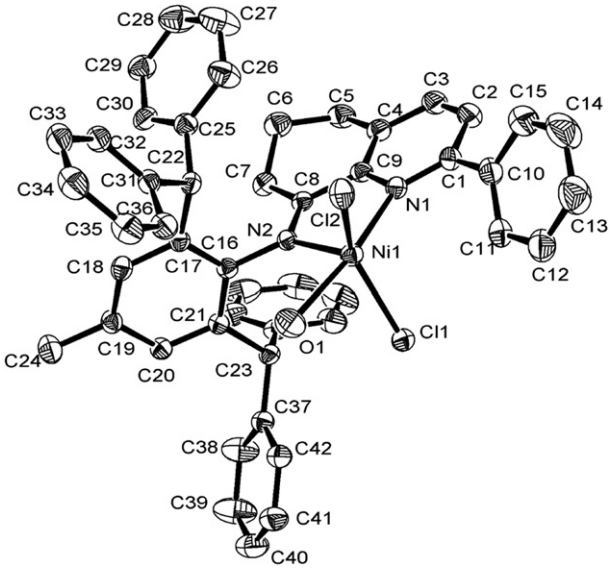


Fig. 1. ORTEP drawing of complex **Ni3**·H_2O. Thermal ellipsoids are shown at 30% probability. Hydrogen atoms have been omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for **Ni3**·H_2O, **Ni5**·DMF and **Ni8**.

	Ni3·H_2O	**Ni5**·DMF	**Ni8**
Bond lengths (Å)			
Ni(1)–N(1)	2.058(3)	2.112(3)	2.002(3)
Ni(1)–N(2)	2.007(2)	2.045(3)	2.024(3)
Ni(1)–Cl(1)	2.3209(9)	2.2777(13)	2.2083(13)
Ni(1)–Cl(2)	2.2624(10)	2.3129(13)	2.1916(13)
Ni(1)–O(1)	2.155(2)	2.077(3)	–
N(1)–C(1)	1.346(4)	1.321(5)	1.332(5)
N(1)–C(9)	1.370(4)	1.372(5)	1.354(5)
N(2)–C(8)	1.294(3)	1.280(5)	1.291(5)
N(2)–C(10)	1.457(4)	1.451(4)	1.452(4)
C(8)–C(9)	1.486(4)	1.482(5)	1.483(5)
Bond angles (°)			
N(1)–Ni(1)–N(2)	82.07(10)	78.89(12)	81.22(12)
N(1)–Ni(1)–O(1)	171.51(10)	172.60(12)	–
N(2)–Ni(1)–O(1)	89.91(10)	93.73(12)	–
N(1)–Ni(1)–Cl(1)	98.01(7)	93.87(9)	107.69(10)
O(1)–Ni(1)–Cl(1)	86.39(8)	88.64(9)	–
N(2)–Ni(1)–Cl(1)	102.16(7)	114.37(9)	111.38(8)
N(1)–Ni(1)–Cl(2)	94.70(8)	88.79(10)	107.54(11)
O(1)–Ni(1)–Cl(2)	86.04(8)	93.41(9)	–
N(2)–Ni(1)–Cl(2)	114.61(7)	102.60(9)	111.00(8)
Cl(1)–Ni(1)–Cl(2)	142.38(3)	142.76(5)	127.83(6)

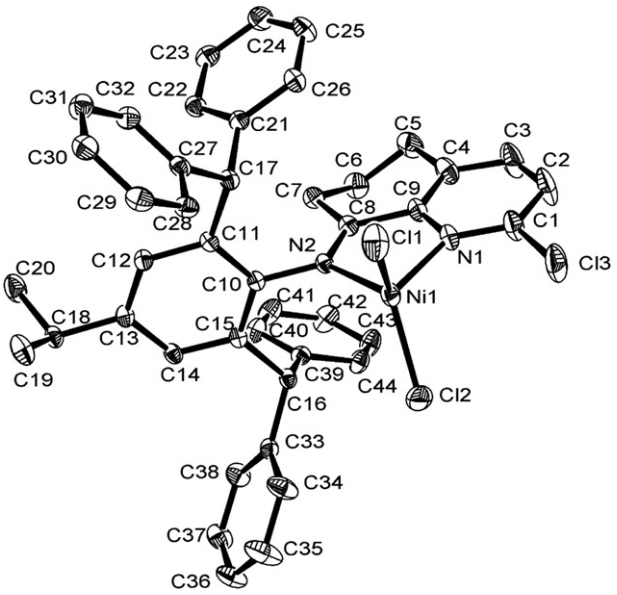


Fig. 3. ORTEP drawing of complex **Ni8**. Thermal ellipsoids are shown at 30% probability. Hydrogen atoms have been omitted for clarity.

2.3. Ethylene polymerization and oligomerization

The nickel(II) complex **Ni3** was used for the selection of a suitable co-catalyst (Table 2). Interestingly all co-catalysts, including methylaluminoxane (MAO), modified methylaluminoxane (MMAO), diethylaluminium chloride (Et_2AlCl) and ethylaluminium sesquichloride (EASC), could activate the system and produced both polyethylene and butenes. Upon activation with either MAO or MMAO, the polymerization activity was much higher than the dimerization due to preferred chain propagation with alumoxanes [7,12,53], whilst for the system employing either EASC or Et_2AlCl, the favoured reaction was dimerization rather than polymerization, attributed to enhanced β-H transfer elimination. The observed trends for the Tm values for the polyethylenes obtained was as follows: EASC (125.2 °C, entry 3 of Table 2), MMAO (122.1 °C, entry 2 of Table 2), Et_2AlCl (121.6 °C, entry 4 of Table 2), and MAO (111.1 °C, entry 1 of Table 2), indicating lower chain migration occurred for alkylaluminum and alumoxane having bulky substituents during the chain propagation. On comparison with results from analogous pre-catalysts [54–58], the introduction of 2-substituents (either Cl or Ph) on the 5,6,7-trihydroquinoline frameworks enhanced ethylene oligomerization [53,54], in contrast to non-substituted derived ligands for which solely ethylene polymerization was observed [55–58]. The current title nickel pre-catalysts showed a new catalytic feature in that they performed both ethylene oligomerization and polymerization, due to the deployment of bulky substituents on the anilines. The overall achievable catalytic activity was relatively lower than observed for previous systems [55–58,63,64], however they performed comparatively better when activation with either MAO or MMAO [65]. Therefore, the co-catalyst MAO was chosen for further studies.

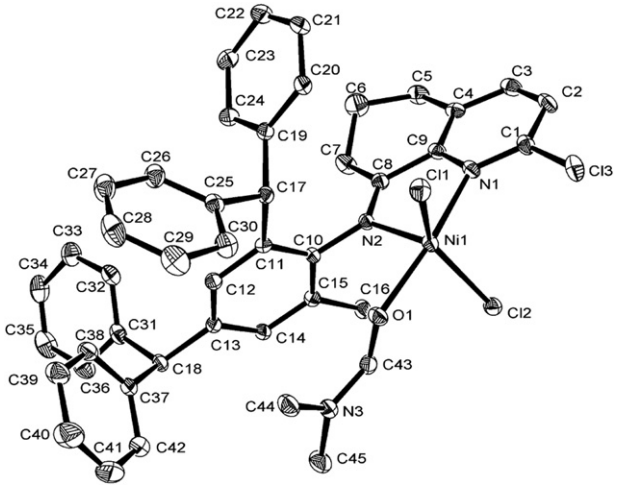


Fig. 2. ORTEP drawing of complex **Ni5**·DMF. Thermal ellipsoids are shown at 30% probability. Hydrogen atoms have been omitted for clarity.

Various experimental conditions were employed to improve the productivity and selectivity of the catalysts. The influence of the reaction parameters, including the molar ratio of [Al]/[Ni] and reaction temperature, was investigated using **Ni3**/MAO. An increase in the [Al]/[Ni] ratio from 500 to 1500 led to improvements in the catalytic activities. Increasing the [Al]/[Ni] ratio to 2000 caused a decrease in the activity (Entries 1–4 in Table 3). The highest activity was observed at 20 °C through running different temperature tests (Entries 3, 5 and 6 in Table 3). Elevating the reaction temperature resulted in deactivation, which can be ascribed to the instability of the active centre [3,5,7,66]. Furthermore, an investigation of the effect of time was carried out, and there was no obvious loss of catalyst activity on prolonged reaction time. This indicated a relatively long lifetime for the catalyst system **Ni3**/MAO.

Catalyst system **Ni3**/MAO exhibited the highest activities among these catalysts. The presence of two bulky benzhydryl substituents in both of the *ortho*-positions of the phenyl ring led to better activity than employing a methyl group as in **Ni2**/MAO. The role played by the steric bulk of the substituents in the catalysis procedure here is obviously different from the system employing *N*-(5,6,7-trihydroquinolin-8-ylidene)-2-benzhydrylarylamine-*N*,*N*′ nickel halide complexes without the 2-substituent [56]. This can be explained by the special requirements of the 2-substituents close to the active site of the catalyst. The fact that these complexes produce high molecular weight polymer with relatively high Tm values is a consequence of slow chain transfer relative to chain propagation [65]. The electron withdrawing chlorine substituent on the pyridine

Table 2
Selection of suitable co-catalyst based on **Ni3**.[a]

Entry	Co-cat.	Al/Ni	Polymer/g	Polymerization Activity[b]	Oligomerization activity[c]	Selectivity α-C4/C4	Tm °C[d]
1	MAO	1000	0.52	2.08	4.85	92	111.1
2	MMAO	1000	0.33	1.34	7.65	74	122.1
3	EASC	300	0.08	0.33	6.61	73	125.2
4	Et_2AlCl	300	0.13	0.52	8.37	78	121.6

[a] Reaction conditions: 5 μmol **Ni3**; 10 atm ethylene; 100 mL toluene; 20 °C; 30 min.
[b] 10^5 g mol(Ni)$^{-1}$ h^{-1}.
[c] 10^4 g mol(Ni)$^{-1}$ h^{-1}.
[d] Determined by DSC.

led to lower activities toward polymerization but relatively higher activities for ethylene oligomerization [64,67]. Dimerization of ethylene was the major reaction, and the selectivity for α-olefin products is high according to GC analysis [53,64,67].

3. Conclusion

A number of 2-substituted 8-(2-benzhydrylarylimino)-5,6,7-trihydroquinoline-*N*,*N*′ nickel dichlorides were synthesised to study their catalytic behaviour during ethylene polymerization and oligomerization. The results showed that all these nickel complexes exhibited good activity ($\leq 2.48 \times 10^5$ g mol (Ni)$^{-1}$ h^{-1}) for ethylene polymerization, producing relatively high Tm (>100 °C) products. Additionally, a small amount of C4 was obtained with high α-olefin selectivity. The results of this work confirm that enhancing the steric bulk of the *ortho*-aryl-substituents of the catalyst resulted in higher ratio of solid polymer to oligomer.

4. Experiment section

4.1. General considerations and materials

All manipulations involving air- and moisture- sensitive compounds were carried out under an atmosphere of dried and purified nitrogen with 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. High-purity ethylene was purchased from Beijing Yanshan Petrochemical Co. Other reagents were purchased from Aldrich, Acros, or local suppliers. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DMX 400 MHz instrument at ambient temperature, using TMS as an internal standard. IR spectra were recorded on a Perkin–Elmer System 2000 FT-IR spectrometer. Elemental analysis was carried out using a Flash EA 1112 micro-analyzer. GC analysis was performed with a VARIAN CP-3800 gas chromatograph equipped with a flame ionization detector and a 30 m (0.2 mm i.d., 0.25 μm film thickness) CP-Sil 5 CB column. The yield of oligomers was calculated by referencing with the mass of the solvent on the basis of the prerequisite that the mass of each fraction was approximately proportional to its integrated areas in the GC trace. Selectivity for the linear α-olefin was defined as (amount of linear α-olefin of all fractions)/(total amount of oligomer products) in percent. Melting points of polyethylenes were obtained from the second scanning run on Perkin–Elmer DSC-7 at a heating rate of 10 °C/min.

4.2. Syntheses and characterization

4.2.1. Synthesis of ligands

*4.2.1.1. 2-Phenyl-8-(2,4-dibenzhydryl-6-methylarylimino)-5,6,7-trihydroquinoline (**L1**) and N-(2-methyl-4,6-dibenzhydryl)-2-phenyl-5,6-dihydroquinolin-8-amine (**L1**′).* The following synthesis was a general procedure and the other ligands were obtained using the similar methods. A 10 mL toluene solution of 2-phenyl-5,6,7-trihydroquinolin-8-one (1 mmol, 0.223 g) and 2-methyl-4,6-dibenzhydrylaniline (1.1 mmol, 0.482 g) together with a catalytic amount of *p*-toluenesulfonic acid was refluxed for 3 h. The toluene was then evaporated under reduced pressure, and the residue was purified by alumina column chromatography [V (petroleum ether): V (dichloromethane) = 10:1]. The product was a pale yellow powder, which was collected in 43% yield (0.28 g, 0.43 mmol). M.p.: 128–130 °C ^{1}H NMR (400 MHz, $CDCl_3$ TMS) for **L1**: δ = 7.71 (d,

Table 3
Polymerization and oligomerization of ethylene.[a]

Entry	Complex	Al/Ni	*T*/°C	*t*/min	Polymer/g	Polymerization activity[b]	Oligomerization activity[c]	Selectivity α-C4/C4	Tm °C[d]
1	**Ni3**	500	20	30	0.18	0.72	2.83	90	113.6
2	**Ni3**	1000	20	30	0.52	2.08	4.85	92	111.1
3	**Ni3**	1500	20	30	0.62	2.48	9.51	92	111.8
4	**Ni3**	2000	20	30	0.47	1.89	3.18	94	110.0
5	**Ni3**	1500	40	30	0.38	1.52	8.73	88	100.3
6	**Ni3**	1500	60	30	0.26	1.04	6.95	87	98.8
7	**Ni3**	1500	20	10	0.16	1.92	4.12	92	110.5
8	**Ni3**	1500	20	20	0.35	2.10	8.77	93	110.7
9	**Ni3**	1500	20	40	0.76	2.28	11.2	91	110.2
10	**Ni1**	1500	20	30	0.41	1.64	4.02	93	120.0
11	**Ni2**	1500	20	30	0.32	1.28	1.44	93	121.4
12	**Ni4**	1500	20	30	0.45	1.80	9.88	94	111.4
13	**Ni5**	1500	20	30	trace	–	6.43	93	–
14	**Ni6**	1500	20	30	trace	–	3.01	90	–
15	**Ni7**	1500	20	30	0.17	0.68	13.4	97	113.8
16	**Ni8**	1500	20	30	0.44	1.76	10.2	93	111.9

[a] Reaction conditions: 5 μmol of Ni; MAO as co-catalyst; 10 atm of ethylene; 100 mL total volume of toluene.
[b] 10^5 g mol(Ni)$^{-1}$ h^{-1}.
[c] 10^4 g mol(Ni)$^{-1}$ h^{-1}.
[d] Determined by DSC.

J = 7.8 Hz, 1H, Py *H*), 7.27 (d, J = 7.46 Hz, 1H, Py *H*), 6.94–7.25 (m, 25H, *Ph*), 6.82 (s, 1H, N=C–*Ph*), 6.60 (s, 1H, N=C–*Ph*), 5.72 (s, 1H, –C*H*(Ph)$_2$), 5.43 (s, 1H, –C*H*(Ph)$_2$), 2.78, 2.61 (m, 2H, Py–CH_2–), 1.27 (m, 2H, N=C–CH_2–), 1.93 (s, 3H, Ph–CH_3), 1.14, 0.88 (m, 2H, –CH_2–) ppm; and for **L1′**: δ = 7.86 (d, J = 7.8 Hz, 1H, Py *H*), 7.57 (d, J = 7.9 Hz, 1H, Py *H*), 6.94–7.25 (m, 25H, *Ph*), 6.82 (s, 1H, C=N–*Ph*), 6.71 (s, 1H, C=N–*Ph*), 6.68 (s, 1H, –N*H*–), 5.68 (s, 1H, –C*H*(Ph)$_2$), 5.43 (s, 1H, –C*H*(Ph)$_2$), 4.62 (t, J = 4.3 Hz, 1H, –C=C*H*–), 2.87 (t, J = 7.5 Hz, 2H, Py–CH_2–), 2.34 (m, 2H, Py–CH2–CH_2–), 2.26 (s, 3H, Ph–CH_3), 1.88 (m, 2H, –CH_2–) ppm. ^{13}C NMR (100 MHz, $CDCl_3$ TMS) for **L1**: 166.3, 153.5, 149.8, 144.8, 143.1, 142.0, 140.8, 139.3, 138.5, 137.4, 135.5, 133.8, 130.9, 129.7, 128.9, 128.5, 128.3, 126.2, 56.6, 51.8, 27.7, 21.7, 18.8, 18.3 ppm; and for **L1′**: 157.2, 149.3, 144.6, 144.4, 144.2, 139.7, 137.6, 137.2, 130.3, 129.6, 129.5, 128.6, 128.2, 128.0, 127.5, 126.8, 126.1, 118.6, 99.7, 56.4, 52.0, 29.3, 28.6, 23.3 ppm. FT-IR (KBr, cm^{-1}): 3362, 3023, 2919, 2361, 1974, 1638, 1598, 1575, 1471, 1387, 1026, 739, 694. Anal. Calcd for $C_{48}H_{40}N_2$ (645): C, 89.40; H, 6.25; N, 4.34%. Found: C, 89.27; H, 6.13; N, 4.76%.

*4.2.1.2. 2-Phenyl-8-(2-benzhydryl-4,6-dimethylarylimino)-5,6,7-trihydroquinoline (**L2**) and N-(2,4-methyl-6-dibenzhydryl)-2-phenyl-5,6-dihydroquinolin-8-amine (**L2′**).* This compound was prepared according to the method described for **L1**. The product was a yellow powder and the yield was 45% (0.22 g, 0.45 mmol). M.p.: 148–149 °C ^{1}H NMR (400 MHz, $CDCl_3$ TMS) for **L2**: δ = 7.69 (d, J = 8.1 Hz, 1H, Py *H*), 7.56 (d, J = 8.0 Hz, 1H, Py *H*), 7.03–7.22 (m, 15H, Ph), 6.88 (s, 1H, N=C–*Ph*), 6.61 (s, 1H, C=N–*Ph*), 5.75 (s, 1H, –C*H*(Ph)$_2$), 2.73, 2.58 (m, 2H, Py–CH_2–), 2.22 (s, 3H, Ph–CH_3), 2.00 (s, 3H, Ph–CH_3), 1.91, 1.57 (m, 2H, N=C–CH$_2$), 1.13, 0.83 (m, 2H, –CH$_2$–) ppm; and for **L2′**: δ = 8.08 (d, J = 7.8 Hz, 1H, Py *H*), 7.54 (d, J = 7.9 Hz, 1H, Py *H*),7.03–7.22(m, 15H, *Ph*), 6.97 (s, 1H, C=N–*Ph*), 6.65 (s, 1H, –N–*H*), 6.61 (s, 1H, C=N–*Ph*), 5.67 (s, 1H, –C*H*(Ph)$_2$), 4.59 (t, J = 4.8 Hz, 1H, C=CH–), 2.85 (t, J = 7.5 Hz, 2H, Py–CH_2–), 2.32 (m, 2H, C=CH–CH_2–), 2.31 (s, 3H, Ph–CH_3), 2.23 (s, 2H, Ph–CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$ TMS) for **L2**: 167.3, 156.4, 149.3, 144.5, 141.9, 139.3, 138.2, 137.7, 135.5, 133.8, 130.9, 129.2, 128.6, 128.1, 127.8, 126.8, 125.9, 122.0, 52.2, 30.5, 29.1, 21.6, 21.5, 18.0 ppm; and for **L2′**: 153.5, 146.6, 143.1, 139.8, 138.7, 137.4, 136.5, 135.0, 131.6, 130.4, 129.6, 128.8, 128.4, 128.0, 127.5, 126.1, 124.9, 118.5, 97.9, 51.8, 27.7, 21.4, 21.2, 18.5 ppm. FT-IR (KBr, cm^{-1}): 3362, 3024, 2917, 2362, 1974, 1640, 1598, 1575, 1470, 1387, 1246, 760, 695. Anal. Calcd for $C_{36}H_{32}N_2$ (492): C, 87.77; H, 6.55; N, 5.69%. Found: C, 87.88; H, 6.31; N, 5.77%.

*4.2.1.3. 2-Phenyl-8-(2,6-dibenzhydryl-4-methylarylimino)-5,6,7-trihydroquinoline (**L3**) and N-(2,6-dibenzhydryl-4-methyl)-2-phenyl-5,6-dihydroquinolin-8-amine (**L3′**).* This compound was prepared according to the method described for **L1**. The product was a yellow powder isolated in 44% yield (0.28 g, 0.44 mmol). M.p.: 187–189 °C ^{1}H NMR (400 MHz, $CDCl_3$ TMS) for **L3**: δ = 7.56 (d, J = 8.0 Hz, 1H, Py *H*), 7.52 (d, J = 8.0 Hz, 1H, Py *H*), 7.03–7.22 (m, 20H, Ph), 6.79 (s, 2H, C=N–*Ph*), 5.61 (s, 2H, –C*H*(Ph)$_2$), 2.36 (t, J = 5.88 Hz, 2H, Py–CH_2–), 2.22 (s, 3H, Ph–CH_3), 1.12 (t, J = 5.70 Hz, 2H, N=C–CH$_2$–), 0.71 (m, 2H, –CH$_2$–) ppm; and for **L3′**: δ = 8.12 (d, J = 8.1 Hz, 1H, Py *H*), 7.76 (d, J = 7.9 Hz, 1H, Py *H*), 7.11–7.39(m, 20H, Ph), 6.83 (s, 2H, C=N–*Ph*), 6.47 (s, 1H, –N–*H*), 5.88 (s, 2H, –C*H*(Ph)$_2$), 4.49 (t, J = 4.6 Hz, 1H, C=CH–), 2.78 (t, J = 7.7 Hz, 2H, Py–CH_2–), 2.23 (s, 3H, Ph–CH_3), 2.16 (m, 2H, –CH_2–) ppm. ^{13}C NMR (100 MHz, $CDCl_3$ TMS) for **L3**: 168.3, 154.5, 150.2, 147.5, 145.2, 143.1, 139.8, 137.5, 136.2, 132.3, 131.2, 130.2, 128.7, 128.3, 127.7, 126.6, 125.8, 120.7, 52.6, 33.4, 29.4, 28.7, 20.9 ppm; and for **L3′**: 153.4, 149.3, 143.5, 139.6, 139.2, 136.6, 135.5, 131.1, 130.7, 130.1, 129.8, 128.8, 128.6, 128.4, 128.0, 126.9, 126.0, 118.5, 99.4, 51.5, 27.6, 21.8, 21.6 ppm. FT-IR (KBr, cm^{-1}): 3354, 3024, 2944, 2361, 1949, 1629, 1598, 1574, 1493, 1386, 1025, 763, 692. Anal. Calcd for $C_{48}H_{40}N_2$ (645): C, 89.40; H, 6.25; N, 4.34%. Found: C, 89.29; H, 6.41; N, 4.16%.

*4.2.1.4. 2-Phenyl-8-(2,6-dibenzhydryl-4-isopropylarylimino)-5,6,7-trihydroquinoline (**L4**) and N-(2,6-dibenzhydryl-4-(1-methylethyl))-2-phenyl-5,6-dihydroquinolin-8-amine (**L4′**).* This compound was prepared according to the method described for **L1**. The product was a yellow powder and the yield was 37% (0.25 g, 0.37 mmol). M.p.: 134–135 °C ^{1}H NMR (400 MHz, $CDCl_3$ TMS) for **L4′**: δ = 8.09 (d, J = 7.8 Hz, 1H, Py *H*), 7.37 (d, J = 7.9 Hz, 1H, Py *H*), 7.04–7.27 (m, 20H, *Ph*), 6.78 (s, 2H, N=C–*Ph*), 5.46 (s, 2H, –C*H*(Ph)$_2$), 2.73 (m, 1H, –C*H*(CH$_3$)$_2$), 2.35 (t, J = 7.9 Hz, 2H, Py–CH_2–), 1.97 (t, J = 5.8 Hz, 2H, N=C–CH_2–), 1.04 (d, 6H, –CH(CH_3)$_2$), 0.73 (m, 2H, –CH_2–) ppm; and for **L4′**: δ = 7.74 (d, J = 7.8 Hz, 1H, Py *H*), 7.47 (d, J = 7.9 Hz, 1H, Py *H*), 7.01–7.27(m, 25H, *Ph*), 6.83 (s, 2H, C=N–*Ph*), 6.43 (s, 1H, –N*H*–), 5.80 (s, 2H, –C*H*(Ph)$_2$), 4.45 (t, J = 4.5 Hz, 1H, –C=C*H*–), 2.75 (t, J = 7.5 Hz, 2H, Py–CH_2–), 2.72 (m, 1H, –C*H*(CH$_3$)$_2$), 2.13 (m, 2H, –C=CH–CH_2–), 1.09 (d, J = 6.9 Hz, 6H, –CH(CH_3)$_2$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$ TMS) for **L4**: 164.7, 143.0, 140.0, 139.3, 138.6, 138.0, 129.8, 129.7, 129.4, 129.2, 128.9, 128.6, 128.2, 127.4, 126.7, 126.2, 126.0, 124.1, 52.7, 40.1, 33.3, 29.2, 24.1, 22.9 ppm; and for **L4′**: 156.8, 153.3, 150.4, 148.1, 146.8, 144.9, 143.4, 142.6, 142.2, 138.7, 128.4, 128.3, 127.6, 127.0, 126.9, 126.6, 126.4, 126.2, 99.2, 52.4, 39.2, 33.9, 30.0, 24.1 ppm. FT-IR (KBr, cm^{-1}): 3349, 3023, 2955, 2344, 1978, 1634, 1600, 1572, 1492, 1386, 1025, 741, 695. Anal. Calcd for $C_{50}H_{44}N_2$ (673): C, 89.25; H, 6.59; N, 4.16%. Found: C, 89.11; H, 6.29; N, 4.07%.

*4.2.1.5. 2-Chloro-8-(2,4-dibenzhydryl-6-methylarylimino)-5,6,7-trihydroquinoline (**L5**) and N-(2-methyl-4,6-dibenzhydryl)-2-chloro-5,6-dihydroquinolin-8-amine (**L5′**).* This compound was prepared according to the method described for **L1**. The product was a yellow powder isolated in 41% yield (0.25 g, 0.41 mmol). M.p.: 140–141 °C ^{1}H NMR (400 MHz, $CDCl_3$ TMS) for **L5**: δ = 7.40 (d, J = 7.8 Hz, 1H, Py *H*), 7.27 (d, J = 7.9 Hz, 1H, Py *H*), 6.94–7.25 (m, 20H, *Ph*), 6.78 (s, 1H, N=C–*Ph*), 6.55 (s, 1H, N=C–*Ph*), 5.57 (s, 1H, –C*H*(Ph)$_2$), 5.39 (s, 1H, –C*H*(Ph)$_2$), 2.66, 2.50 (m, 2H, Py–CH_2–), 1.96, 1.44 (m, 2H, N=C–CH_2–), 1.93 (s, 3H, Ph–CH_3), 1.45, 0.95 (m, 2H, –CH_2–) ppm; and for **L5′**: δ = 7.38 (d, J = 7.8 Hz, 1H, Py *H*), 7.24 (d, J = 7.9 Hz, 1H, Py *H*), 6.94–7.25(m, 20H, *Ph*), 6.87 (s, 1H, C=N–*Ph*), 6.76 (s, 1H, C=N–*Ph*), 6.30 (s, 1H, –N*H*–), 5.59 (s, 1H, –C*H*(Ph)$_2$), 5.39 (s, 1H, –C*H*(Ph)$_2$), 4.55 (t, J = 4.6 Hz, 1H, –C=C*H*–), 2.76 (t, J = 7.8 Hz, 2H, Py–CH_2–),2.25 (m, 2H, Py–CH$_2$–CH_2–), 2.23 (s, 3H, Ph–CH_3), 1.88 (m, 2H, –CH_2–) ppm. ^{13}C NMR (100 MHz, $CDCl_3$ TMS) for **L5**: 165.8, 150.2, 148.1, 146.9, 144.3, 143.4, 142.1, 140.8, 140.0, 137.8, 137.4, 136.9, 135.8, 133.7, 130.8, 130.2, 129.5, 128.3, 126.2, 124.7, 56.6, 52.1, 27.2, 21.5, 18.7, 18.1 ppm; and for **L5′**: 152.8, 150.4, 150.1, 148.3, 144.7, 144.6, 144.1, 143.4, 143.2, 137.6, 132.1, 129.6, 129.2, 128.9, 128.2, 127.9, 126.4, 126.1, 125.9, 122.1, 99.4, 56.4, 51.9, 30.3, 27.2, 21.5 ppm. FT-IR (KBr, cm^{-1}): 3348, 3028, 2893, 2329, 1978, 1639, 1599, 1573, 1474, 1331, 1124, 755, 696. Anal. Calcd for $C_{42}H_{35}ClN_2$ (602): C, 83.63; H, 5.85; N, 4.64%. Found: C, 83.47; H, 5.77; N, 4.72%.

*4.2.1.6. 2-Chloro-8-(2-benzhydryl-4,6-dimethylarylimino)-5,6,7-trihydroquinoline (**L6**) and N-(2,4-methyl-6-dibenzhydryl)-2-chloro-5,6-dihydroquinolin-8-amine (**L6′**).* This compound was prepared according to the method described for **L1**. The product was a yellow powder isolated in 54% yield (0.24 g, 0.54 mmol). M.p.: 178–179 °C ^{1}H NMR (400 MHz, $CDCl_3$ TMS) for **L6**: δ = 7.43 (d, J = 8.1 Hz, 1H, Py *H*), 7.30 (d, J = 8.0 Hz, 1H, Py *H*), 7.03–7.22 (m, 20H, Ph), 6.87 (s, 1H, N=C–*Ph*), 6.60 (s, 1H, C=N–*Ph*), 5.73 (s, 1H, –C*H*(Ph)$_2$), 2.64, 2.45 (m, 2H, Py–CH_2–), 2.23 (s, 3H, Ph–CH_3), 2.21 (s, 3H, Ph–CH_3), 1.89, 1.12 (m, 2H, N=C–CH$_2$), 1.42, 0.90 (m, 2H, –CH$_2$–) ppm; and for **L6′**: δ = 7.37 (d, J = 7.8 Hz, 1H, Py *H*), 7.25 (d, J = 7.9 Hz, 1H, Py *H*),7.03–7.22(m, 10H, *Ph*), 6.95 (s, 1H, C=N–*Ph*), 6.65 (s, 1H, C=

N–*Ph*), 6.30 (s, 1H, –N–*H*), 5.60 (s, 1H, –*CH*(Ph)$_2$), 4.53 (t, J = 4.6 Hz, 1H, C=CH–), 2.76 (t, J = 7.7 Hz, 2H, Py–C*H*$_2$–), 2.23 (s, 3H, Ph–C*H*$_3$), 2.12 (s, 2H, Ph–C*H*$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$ TMS) for **L6**: 164.4, 149.8, 145.8, 144.0, 142.8, 139.6, 135.4, 133.3, 131.4, 129.9, 129.4, 128.7, 127.9, 127.6, 51.7, 29.8, 28.3, 26.8, 20.7, 17.5 ppm; and for **L6′**: 150.0, 147.7, 143.1, 141.7, 137.2, 136.9, 135.6, 134.6, 130.4, 129.2, 128.2, 127.7, 125.8, 121.7, 98.8, 51.6, 29.4, 28.5, 20.9, 18.0 ppm. FT-IR (KBr, cm^{-1}): 3350, 3053, 2952, 2335, 1974, 1635, 1602, 1575, 1494, 1345, 1224, 747, 696. Anal. Calcd for $C_{30}H_{27}ClN_2$ (450): C, 79.89; H, 6.03; N, 6.21%. Found: C, 80.14; H, 5.93; N, 6.45%.

*4.2.1.7. 2-Chloro-8-(2,6-dibenzhydryl-4-methylarylimino)-5,6,7-trihydroquinoline (**L7**) and N-(2,6-dibenzhydryl-4-methyl)-2-chloro-5,6-dihydroquinolin-8-amine (**L7′**).* This compound was prepared according to the method described for **L1**. The product was a yellow powder and the yield was 46% (0.28 g, 0.46 mmol). M.p.: 156–158 °C ^{1}H NMR (400 MHz, $CDCl_3$ TMS) for **L7**: δ = 7.34 (d, J = 8.1 Hz, 1H, Py *H*), 7.27 (d, J = 8.0 Hz, 1H, Py *H*), 7.03–7.22 (m, 20H, Ph), 6.70 (s, 2H, C=N–*Ph*), 5.34 (s, 2H, –*CH*(Ph)$_2$), 2.21 (t, J = 5.88 Hz, 2H, Py–C*H*$_2$–), 2.15 (s, 3H, Ph–C*H*$_3$), 0.80 (t, J = 5.70 Hz, 2H, N=C–CH$_2$–), 0.46 (m, 2H, –CH$_2$–) ppm; and for **L7′**: δ = 7.36 (d, J = 8.1 Hz, 1H, Py *H*), 7.29 (d, J = 7.9 Hz, 1H, Py *H*),7.03–7.22(m, 20H, Ph), 6.76 (s, 2H, C=N–*Ph*), 6.08 (s, 1H, –N–*H*), 5.73 (s, 2H, –*CH*(Ph)$_2$), 4.38 (t, J = 4.6 Hz, 1H, C=CH–), 2.63 (t, J = 7.7 Hz, 2H, Py–C*H*$_2$–), 2.20 (s, 3H, Ph–C*H*$_3$), 1.98 (m, 2H, –C*H*$_2$–) ppm. ^{13}C NMR (100 MHz, $CDCl_3$ TMS) for **L7**: 167.1, 150.1, 146.8, 144.6, 142.9, 140.0, 136.2, 132.2, 131.5, 130.1, 129.7, 128.4, 128.1, 126.0, 51.8, 31.0, 28.5, 21.4, 20.2 ppm; and for **L7′**: 150.8, 149.9, 149.3, 147.2, 142.7, 135.5, 130.1, 129.2, 129.0, 128.5, 128.1, 126.2, 125.9, 125.5, 90.1, 51.6, 33.2, 28.1, 22.7 ppm. FT-IR (KBr, cm^{-1}): 3348, 3025, 2935, 2329, 1978, 1633, 1601, 1576, 1493, 1378, 1221, 818, 699. Anal. Calcd for $C_{42}H_{35}ClN_2$ (602): C, 83.63; H, 5.85; N, 4.64%. Found: C, 83.82; H, 5.96; N, 4.34%.

*4.2.1.8. 2-Chloro-8-(2,6-dibenzhydryl-4-isopropylarylimino)-5,6,7-trihydroquinoline (**L8**) and N-(2,6-dibenzhydryl-4-(1-methylethyl))-2-chloro-5,6,-dihydroquinolin-8-amine (**L8′**): this compound was prepared according to the method described for **L1**.* The product was a yellow powder isolated in 42% yield (0.27 g, 0.42 mmol). M.p.: 102–104 °C ^{1}H NMR (400 MHz, $CDCl_3$ TMS) for **L8**: δ = 7.40 (d, J = 7.8 Hz, 1H, Py *H*), 7.30 (d, J = 7.9 Hz, 1H, Py *H*), 7.04–7.27 (m, 20H, *Ph*), 6.73 (s, 2H, N=C–*Ph*), 5.45 (s, 2H, –*CH*(Ph)$_2$), 2.70 (m, 1H, –*CH*(CH$_3$)$_2$), 2.64 (t, J = 7.9 Hz, 2H, Py–C*H*$_2$–), 1.96, 2.22 (t, J = 5.8 Hz, 2H, N=C–C*H*$_2$–), 1.04 (d, 6H, –CH(C*H*$_3$)$_2$), 0.68 (m, 2H, –C*H*$_2$–) ppm; and for **L8′**: δ = 7.59 (d, J = 7.8 Hz, 1H, Py *H*), 7.37 (d, J = 7.9 Hz, 1H, Py *H*), 7.04–7.27(m, 20H, *Ph*), 6.80 (s, 2H, C=N–*Ph*), 6.09 (s, 1H, –N*H*–), 5.74 (s, 2H, –*CH*(Ph)$_2$), 4.39 (t, J = 4.6 Hz, 1H, –C=C*H*–), 2.76 (t, J = 7.8 Hz, 2H, Py–C*H*$_2$–), 2.17 (m, 1H, –*CH*(CH$_3$)$_2$), 2.00 (m, 2H, –C*H*$_2$–), 1.05 (d, 6H, –CH(C*H*$_3$)$_2$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$ TMS) for **L8**: 166.9, 144.7, 144.1, 143.2, 143.0, 131.9, 130.1, 129.7, 128.4, 128.1, 127.9, 126.9, 126.5, 126.1, 51.9, 39.5, 33.8, 28.5, 24.1, 22.8 ppm; and for **L8′**: 150.4, 150.1, 148.0, 146.2, 142.6, 140.0, 138.5, 137.2, 136.4, 136.1, 130.1, 126.5, 126.1, 125.8, 100.7, 51.8, 31.7, 31.0, 27.4, 20.2 ppm. FT-IR (KBr, cm^{-1}): 3348, 3061, 2955, 2361, 1976, 1640, 1600, 1575, 1493, 1377, 1136, 746, 697. Anal. Calcd for $C_{44}H_{39}ClN_2$ (630): C, 83.72; H, 6.23; N, 4.44%. Found: C, 83.55; H, 6.49; N, 4.16%.

4.2.2. Synthesis of nickel complexes

*4.2.2.1. 2-Phenyl-8-(2,4-dibenzhydryl-6-methylarylimino)-5,6,7-trihydroquinoline-N,N′ nickel dichloride (**Ni1**).* As a general synthetic procedure, 0.118 g (0.5 mmol) $NiCl_2 \cdot 6H_2O$ was dissolved in 5 mL ethanol, and a mixture of 0.322 g (0.5 mmol) 2-methyl-4,6-dibenzhydryl-*N*-(2-phenyl-5,6,7-trihydroquinolin-8-ylidene)phenylamine (**L1**) and *N*-(2-methyl-4,6-dibenzhydryl)-2-phenyl-5,6-dihydroquinolin-8-amine (**L1′**) was dissolved in 2 mL CH_2Cl_2. A mixture of the above two solutions was stirred for 3 h, and then 20 mL ether was poured into the mixture to precipitate the complex. The yellow precipitate was collected by filtration, washed with diethyl ether (3 × 5 mL), and dried under vacuum at 60 °C to afford the nickel complex (**Ni1**) in 87% (0.33 g) isolated yield. FT-IR (KBr, disk, cm^{-1}): 3057, 3026, 2166, 2029, 1621, 1593, 1493, 1447, 1145, 739, 699. Anal. Calcd for $C_{48}H_{40}Cl_2N_2Ni$ (774): C, 74.44; H, 5.21; N, 3.62%. Found: C, 74.03; H, 5.29; N, 3.27%.

*4.2.2.2. 2-Phenyl-8-(2-benzhydryl-4,6-dimethylarylimino)-5,6,7-trihydroquinoline-N,N′ nickel dichloride (**Ni2**).* Using the same procedure as for the synthesis of **Ni1**, but using the mixture **L2** and **L2′** instead of **L1** and **L1′** in the reaction with $NiCl_2$; the nickel complex **Ni2** was collected as yellow powder in 0.28 g (91%). FT-IR (KBr, disk, cm^{-1}): 3028, 2918, 2168, 1977, 1622, 1593, 1468, 1448, 1212, 751, 697. Anal. Calcd for $C_{36}H_{32}Cl_2N_2Ni$ (622): C, 69.49; H, 5.18; N, 4.50%. Found: C, 69.41; H, 5.06; N, 4.05%.

*4.2.2.3. 2-Phenyl-8-(2,6-dibenzhydryl-4-methylarylimino)-5,6,7-trihydroquinoline-N,N′ nickel dichloride (**Ni3**).* Using the same procedure as for the synthesis of **Ni1**, but replacing the mixture of **L1** and **L1′** by a 0.5 mmol mixture of **L3** and **L3′**; the nickel complex **Ni3** was isolated as a yellow powder was formed in 0.34 g (89%). FT-IR (KBr, disk, cm^{-1}): 3028, 2920, 2165, 2029, 1617, 1600, 1467, 1446, 1127, 752, 699. Anal. Calcd for $C_{48}H_{40}Cl_2N_2Ni$ (774): C, 74.44; H, 5.21; N, 3.62%. Found: C, 74.36; H, 5.61; N, 3.17%.

*4.2.2.4. 2-Phenyl-8-(2,6-dibenzhydryl-4-isopropylarylimino)-5,6,7-trihydroquinoline-N,N′ nickel dichloride (**Ni4**).* Similarly, using a 0.5 mmol mixture of **L4** and **L4′** in the equimolar reaction with $NiCl_2$, the nickel complex **Ni4** was collected as a yellow powder in 0.37 g (93%). FT-IR (KBr, disk, cm^{-1}): 3026, 2891, 2167, 2028, 1638, 1598, 1493, 1468, 1125, 749, 697. Anal. Calcd for $C_{50}H_{44}Cl_2N_2Ni$ (802): C, 74.83; H, 5.53; N, 3.49%. Found: C, 74.46; H, 5.64; N, 3.15%.

*4.2.2.5. 2-Chloro-8-(2,4-dibenzhydryl-6-methylarylimino)-5,6,7-trihydroquinoline-N,N′ nickel dichloride (**Ni5**).* The stoichiometric reaction of a 0.5 mmol mixture of **L5** and **L5′** and $NiCl_2$ produced the nickel complex **Ni5** as a yellow powder in 0.34 g (94%). FT-IR (KBr, disk, cm^{-1}): 3027, 2895, 2167, 2030, 1639, 1600, 1493, 1448, 1124, 747, 699. Anal. Calcd for $C_{42}H_{35}Cl_3N_2Ni$ (733): C, 68.84; H, 4.81; N, 3.82%. Found: C, 68.93; H, 4.72; N, 3.44%.

*4.2.2.6. 2-Chloro-8-(2-benzhydryl-4,6-dimethylarylimino)-5,6,7-trihydroquinoline-N,N′ nickel dichloride (**Ni6**).* Similarly, the stoichiometric reaction of a 0.5 mmol mixture of **L6** and **L6′** and $NiCl_2$ produced the nickel complex **Ni6** as a yellow powder in 0.27 g (94%). FT-IR (KBr, disk, cm^{-1}): 3028, 2917, 2167, 1973, 1636, 1600, 1493, 1448, 1124, 747, 698. Anal. Calcd for $C_{30}H_{27}Cl_3N_2Ni$ (580): C, 62.06; H, 4.69; N, 4.82%. Found: C, 62.41; H, 4.43; N, 4.77%.

*4.2.2.7. 2-Chloro-8-(2,6-dibenzhydryl-4-methylarylimino)-5,6,7-trihydroquinoline-N,N′ nickel dichloride (**Ni7**).* Similarly, the stoichiometric reaction of a 0.5 mmol mixture of **L7** and **L7′** and $NiCl_2$ produced the nickel complex **Ni7** as a yellow powder in 0.33 g (92%). FT-IR (KBr, disk, cm^{-1}): 3027, 2893, 2167, 2030, 1639, 1601, 1476, 1448, 1125, 748, 697. Anal. Calcd for $C_{42}H_{35}Cl_3N_2Ni$ (733): C, 68.84; H, 4.81; N, 3.82%. Found: C, 69.02; H, 4.77; N, 3.69%.

*4.2.2.8. 2-Chloro-8-(2,6-dibenzhydryl-4-isopropylarylimino)-5,6,7-trihydroquinoline-N,N′ nickel dichloride (**Ni8**).* Similarly, the stoichiometric reaction of a 0.5 mmol mixture of **L8** and **L8′** and $NiCl_2$ produced the nickel complex **Ni8** as a yellow powder in 0.34 g (89%). FT-IR (KBr, disk, cm^{-1}): 3027, 2919, 2168, 1975, 1638, 1602,

Table 4
Crystal data and structure refinement for **Ni3**·H_2O, **Ni5**·DMF and **Ni8**.

	Ni3·H_2O	**Ni5**·DMF	**Ni8**
Empirical formula	$C_{48}H_{41}Cl_2N_2NiO$	$C_{45}H_{42}Cl_3N_3NiO$	$C_{44}H_{39}Cl_3N_2Ni$
Fw	791.44	805.88	760.83
T (K)	173(2)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Rhombohedral	Triclinic	Monoclinic
Space group	R-3	P-1	P2(1)/n
a (Å)	39.007(6)	9.2107(18)	12.324(3)
b (Å)	39.007(6)	12.339(3)	9.761(2)
c (Å)	16.546(3)	18.142(4)	31.826(6)
α (°)	90	83.77(3)	90
β (°)	90	75.34(3)	100.73(3)
γ (°)	120	87.96(3)	90
V (Å^3)	21,803(6)	1982.8(7)	3761.6(13)
Z	18	2	4
D_{calcd}, (g cm^{-3})	1.085	1.350	1.343
μ (mm^{-1})	0.543	0.730	0.763
F (000)	7434	840	1584
Crystal size (mm)	0.70 × 0.30 × 0.30	0.27 × 0.19 × 0.07	0.30 × 0.26 × 0.22
θ range (°)	1.04–26.37	1.17–26.38	1.30–26.38
Limiting indices	$-48 \le h \le 48$	$-11 \le h \le 11$	$-15 \le h \le 15$
	$-48 \le k \le 48$	$-15 \le k \le 15$	$-12 \le k \le 9$
	$-20 \le l \le 20$	$-22 \le l \le 22$	$-39 \le l \le 39$
No. of rflns collected	82,860	15,102	31,977
No. of unique rflns [R(int)]	9905 (0.0576)	8043 (0.0385)	7663 (0.0534)
Completeness to θ (%)	100%	98.9%	99.5%
Abs corr.	Empirical	Empirical	Empirical
Data/restraints/params	9905/19/499	8043/0/478	7663/0/451
Goodness of fit on F^2	1.789	1.203	1.338
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0771$	$R1 = 0.0647$	$R1 = 0.0703$
	$wR2 = 0.2353$	$wR2 = 0.1640$	$wR2 = 0.1744$
R indices (all data)	$R1 = 0.0825$	$R1 = 0.0767$	$R1 = 0.0781$
	$wR2 = 0.2408$	$wR2 = 0.1861$	$wR2 = 0.1873$
Largest diff peak and hole (e Å^{-3})	0.884 and −0.843	1.102 and −0.511	0.447 and −0.470

1494, 1448, 1126, 747, 698. Anal. Calcd for $C_{44}H_{39}Cl_3N_2Ni$ (761): C, 69.46; H, 5.17; N, 3.68%. Found: C, 69.30; H, 5.23; N, 3.58%.

4.3. X-ray crystallographic studies

X-ray studies of single crystals of **Ni3**·H_2O, **Ni5**·DMF and **Ni8** were carried out on a Rigaku Saturn724+ CCD with graphite-monochromatic Mo Kα 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 SHELXL-97 package [68]. Details of the X-ray structure determinations and refinements are provided in Table 4.

4.4. General procedure for ethylene polymerization and dimerization

Ethylene polymerization and dimerization at 10 atm of ethylene pressure was carried out in a stainless steel autoclave (250 mL capacity) equipped with a mechanical stirrer and a temperature controller. After 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 temperature reached to the set value, the co-catalyst and additional toluene (maintaining total volume as 100 mL in reactor) then was injected into the reactor via a syringe. The ethylene pressure was tuned to 10 atm, and maintained by constant feeding of ethylene. After the desired time, the ethylene was released and a little amount of solution was collected, which was then analyzed by gas chromatography (GC) for determining the composition and mass distribution of oligomers obtained. Also the reaction solution was quenched by acidic ethanol containing 10% hydrochloric acid, the precipitated polymer was collected by filtration, and washed with ethanol and water for several times, and then dried in a vacuum until to constant weight.

Appendix A. Supplementary material

CCDC 861932, 861933 and 861934 contain the supplementary crystallographic data for the complexes **Ni3**, **Ni5** and **Ni8**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

[1] L.K. Johnson, C.M. Killian, M. Brookhart, J. Am. Chem. Soc. 117 (1995) 6414–6415.
[2] C.M. Killian, L.K. Johnson, M. Brookhart, Organometallics 16 (1997) 2005–2007.
[3] D.P. Gates, S.A. Svejda, E. Onate, C.M. Killian, L.K. Johnson, P.S. White, M. Brookhart, Macromolecules 33 (2000) 2320–2334.
[4] M. Schmid, R. Eberhardt, M. Klinga, M. Leskela, B. Rieger, Organometallics 20 (2001) 2321–2330.
[5] B.K. Bahuleyan, G.W. Son, D.-W. Park, C.-S. Ha, I. Kim, J. Polym. Sci. Part A: Polym. Chem. 46 (2008) 1066–1082.
[6] L. Li, M. Jeon, S.Y. Kim, J. Mol. Catal. A: Chem. 303 (2009) 110–116.
[7] H. Liu, W. Zhao, X. Hao, C. Redshaw, W. Huang, W.-H. Sun, Organometallics 30 (2011) 2418–2424.
[8] T.V. Laine, K. Lappalainen, J. Liimatta, E. Aitola, B. Löfgren, M. Leskelä, Macromol. Rapid Commun. 20 (1999) 487–491.
[9] T.V. Laine, U. Piironen, K. Lappalainen, M. Klinga, E. Aitola, M. Leskel, J. Organomet. Chem. 606 (2000) 112–124.
[10] X. Tang, Y. Cui, W.-H. Sun, Z. Miao, S. Yan, Polym. Int. 53 (2004) 2155–2161.
[11] S. Song, T. Xiao, T. Liang, F. Wang, C. Redshaw, W.-H. Sun, Catal. Sci. Technol. 1 (2011) 69–75.

[12] S. Song, Y. Li, C. Redshaw, F. Wang, W.-H. Sun, J. Organomet. Chem. 696 (2011) 3772–3778.
[13] T. Xiao, J. Lai, S. Zhang, X. Hao, W.-H. Sun, Catal. Sci. Technol. 1 (2011) 462–469.
[14] R. Gao, L. Xiao, X. Hao, W.-H. Sun, F. Wang, Dalton Trans. (2008) 5645–5651.
[15] S. Song, T. Xiao, C. Redshaw, X. Hao, F. Wang, W.-H. Sun, J. Organomet. Chem. 696 (2011) 2594–2599.
[16] W. Zhang, W.-H. Sun, B. Wu, S. Zhang, H. Ma, Y. Li, J. Chen, P. Hao, J. Organomet. Chem. 691 (2006) 4759–4767.
[17] C. Shao, W.-H. Sun, Z. Li, Y. Hu, L. Han, Catal. Comm. 3 (2002) 405–410.
[18] X. Tang, W.-H. Sun, T. Gao, J. Hou, J. Chen, W. Chen, J. Organomet. Chem. 690 (2005) 1570–1580.
[19] Z. Guan, W.J. Marshall, Organometallics 21 (2002) 3580–3586.
[20] F. Speiser, P. Braunstein, L. Saussine, R. Welter, Organometallics 23 (2004) 2613–2624.
[21] Z. Weng, S. Teo, T.S.A. Hor, Organometallics 25 (2006) 4878–4882.
[22] T.R. Younkin, E.F. Connor, J.I. Henderson, S.K. Friedrich, R.H. Grubbs, D.A. Bansleben, Science 287 (2000) 460–462.
[23] D.-P. Song, W.-P. Ye, Y.-X. Wang, J.-Y. Liu, Y.-S. Li, Organometallics 28 (2009) 5697–5704.
[24] B.A. Rodriguez, M. Delferro, T.J. Marks, Organometallics 27 (2008) 2166–2168.
[25] D. Zhang, G.-X. Jin, Organometallics 22 (2003) 2851–2854.
[26] C. Wang, S. Friedrich, T.R. Younkin, R.R. Li, R.H. Grubbs, D.A. Bansleben, M.W. Day, Organometallics 17 (1998) 3149–3151.
[27] T. Hu, L.-M. Tang, X.-F. Li, Y.-S. Li, N.-H. Hu, Organometallics 24 (2005) 2628–2632.
[28] A. Kermagoret, P. Braunstein, Dalton Trans. (2008) 1564–1573.
[29] J. Hou, W.-H. Sun, D. Zhang, L. Chen, W. Li, D. Zhao, H. Song, J. Mol. Catal. A: Chem. 231 (2005) 221–223.
[30] D.-P. Song, J.-Q. Wu, W.-P. Ye, H.-L. Mu, Y.-S. Li, Organometallics 29 (2010) 2306–2314.
[31] J. Heinicke, N. Peulecke, M. Kohler, M. He, W. Keim, J. Organomet. Chem. 690 (2005) 2449–2457.
[32] M. Stefan, Angew. Chem. Int. Ed. 40 (2001) 534–540.
[33] W.-H. Sun, S. Jie, S. Zhang, W. Zhang, Y. Song, H. Ma, J. Chen, K. Wedeking, R. Frohlich, Organometallics 25 (2006) 666–667.
[34] M. Zhang, S. Zhang, P. Hao, S. Jie, W.-H. Sun, P. Li, X. Lu, Eur. J. Inorg. Chem. 35 (2007) 3816–3826.
[35] Y. Chen, P. Hao, W. Zuo, K. Gao, W.-H. Sun, J. Organomet. Chem. 693 (2008) 1829–1840.
[36] L. Xiao, R. Gao, M. Zhang, Y. Li, X. Cao, W.-H. Sun, Organometallics 28 (2009) 2225–2233.
[37] R. Gao, Y. Li, F. Wang, W.-H. Sun, M. Bochmann, Eur. J. Inorg. Chem. 27 (2009) 4149–4156.
[38] W.-H. Sun, P. Hao, G. Li, S. Zhang, W. Wang, J. Yi, M. Asma, N.J. Tang, J. Organomet. Chem. 692 (2007) 4506–4518.
[39] M. Zhang, P. Hao, W. Zuo, S. Jie, W.-H. Sun, J. Organomet. Chem. 693 (2008) 483–491.
[40] M. Zhang, R. Gao, X. Hao, W.-H. Sun, J. Organomet. Chem. 693 (2008) 3867–3877.
[41] N. Ajellal, M.C.A. Kuhn, A.D.G. Boff, M. Hörner, C.M. Thomas, J.-F. Carpentier, O.L. Casagrande Jr., Organometallics 25 (2006) 1213–1216.
[42] Y. Yang, P. Yang, C. Zhang, G. Li, X.J. Yang, B. Wu, C. Janiak, J. Mol. Catal. A: Chem. 296 (2008) 9–17.
[43] S.O. Ojwach, I.A. Guzei, L.L. Benade, S.F. Mapolie, J. Darkwa, Organometallics 28 (2009) 2127–2133.
[44] L. Xiao, M. Zhang, R. Gao, W.-H. Sun, Aust. J. Chem. 63 (2010) 109–115.
[45] W. Zhang, Y. Wang, J. Yu, C. Redshaw, X. Hao, W.-H. Sun, Dalton Trans. 40 (2011) 12856–12865.
[46] X. Chen, L. Zhang, J. Yu, X. Hao, H. Liu, W.-H. Sun, Inorg. Chim. Acta 370 (2011) 156–163.
[47] W.-H. Sun, X. Tang, T. Gao, B. Wu, W. Zhang, H. Ma, Organometallics 23 (2004) 5037–5047.
[48] H. Liu, L. Zhang, L. Chen, C. Redshaw, Y. Li, W.-H. Sun, Dalton Trans. 40 (2011) 2614–2621.
[49] J. Hou, W.-H. Sun, S. Zhang, H. Ma, Y. Deng, X. Lu, Organometallics 25 (2006) 236–244.
[50] R.L. Stapleton, J. Chai, N.J. Taylor, S. Collins, Organometallics 25 (2006) 2514–2524.
[51] C. Zhang, W.-H. Sun, Z.-X. Wang, Eur. J. Inorg. Chem. 23 (2006) 4895–4902.
[52] S. Jie, D. Zhang, T. Zhang, W.-H. Sun, J. Chen, Q. Ren, D. Liu, G. Zheng, W. Chen, J. Organomet. Chem. 690 (2005) 1739–1749.
[53] J. Yu, X. Hu, Y. Zeng, L. Zhang, C. Ni, X. Hao, W.-H. Sun, New J. Chem. 35 (2011) 178–183.
[54] W. Chai, J. Yu, L. Wang, X. Hu, C. Redshaw, W.-H. Sun, Inorg. Chim. Acta 385 (2012) 21–26.
[55] J. Yu, Y. Zeng, W. Huang, X. Hao, W.-H. Sun, Dalton Trans. 40 (2011) 8436–8443.
[56] X. Hou, Z. Cai, X. Chen, L. Wang, C. Redshaw, W.-H. Sun, Dalton Trans. 41 (2012) 1617–1623.
[57] L. Zhang, X. Hao, W.-H. Sun, C. Redshaw, ACS Catal. 1 (2011) 1213–1220.
[58] J. Yu, H. Liu, W. Zhang, X. Hao, W.-H. Sun, Chem. Commun. 47 (2011) 3257–3259.
[59] W. Zhao, J. Yu, S. Song, W. Yang, H. Liu, X. Hao, C. Redshaw, W.-H. Sun, Polymer 53 (2012) 130–137.
[60] D. Li, S. Li, D. Cui, X. Zhang, J. Organomet. Chem. 695 (2010) 2781–2788.
[61] C. Redshaw, D. Homden, D.L. Hughes, J.A. Wright, M.R.J. Elsegood, Dalton Trans. (2009) 1231–1242.
[62] K. Nienkemper, V.V. Kotov, G. Kehr, G. Erker, R. Fröhlich, Eur. J. Inorg. Chem. (2006) 366–379.
[63] T. Irrgang, S. Keller, H. Maisel, W. Kretschmer, R. Kempe, Eur. J. Inorg. Chem. (2007) 4221–4228.
[64] C. Bianchini, G. Giambastiani, G. Mantovani, A. Meli, D. Mimeau, J. Organomet. Chem. 689 (2004) 1356–1361.
[65] C. Bianchini, G. Giambastiani, L. Luconi, A. Meli, Coord. Chem. Rev. 254 (2010) 431–455.
[66] A. Koppl, H.G. Alt, J. Mol. Catal. A: Chem. 154 (2000) 45–53.
[67] J.M. Benito, E. de Jesús, J.F. de la Mata, J.C. Flores, R. Gómez, P. Gómez-Sal, Organometallics 25 (2006) 3876–3887.
[68] G.M. Sheldrick, SHELXTL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.