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Synthesis, characterization and ethylene oligomerization behavior of *N*-(2-alkyl-5,6,7-trihydroquinolin-8-ylidene)arylaminonickel(II) dichlorides

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ABSTRACT

A series of *N*-(2-alkyl-5,6,7-trihydroquinolin-8-ylidene)arylaminonickel(II) dichloride complexes were synthesized in a one-pot reaction with nickel dichloride. All nickel complexes were characterized by elemental and spectroscopic analysis. The molecular structures of representative nickel complexes, as determined by the single crystal X-ray diffraction, are reported. All nickel complexes, when treated with ethylaluminium sesquichloride ($Et_3Al_2Cl_3$), showed high activities (up to 1.1×10^6 g mol^{-1} h^{-1}) for ethylene oligomerization, with good thermal stability at 80 °C at 10 atm ethylene. The influence of the reaction parameters on the catalytic behavior was investigated for these nickel-based systems, including variation of Al/Ni molar ratio and reaction temperature.

1. Introduction

α-Olefins originally manufactured by the Ziegler (Alfen) process are key intermediates for the synthesis of a wide range of chemical products. Over the past few decades, the preparation of ethylene oligomers catalyzed by transition metal complexes has undergone significant development, especially for those systems based on nickel. By the end of the 1970s, nickel complexes had been developed as catalysts for ethylene oligomerization by Keim et al. [1], which, in the 1980s, was industrialized in the form of the Shell Higher Olefin Process (SHOP), and is now a major process for the production of linear α-olefins via the oligomerization of ethylene [2]. In the 1990s, Brookhart et al. found that cationic diimino-nickel complexes performed with very good activity during ethylene polymerization and oligomerization [3–4], and this encouraged further extensive investigation into new pre-catalysts of other late-transition metal complexes [5]. Moreover, to improve catalyst performance, efforts were paid to both the modification of the original ligand set as well as exploration of new ligand types capable of producing high activity nickel catalysts, and numerous nickel complexes bearing bidentate ligands such as N^N [6–13], N^O [14–20], P^N [21–25], P^O [26–29] and tridentate ligands such as N^P^N [30–32], N^N^O [33–35], P^N^N [30,36,37], and N^N^N [38–43], have been prepared. A number of recent review articles have covered the progress of nickel complexes as catalysts for ethylene reactivity [44–47].

Within the *N,N*-bidentate Ni(II) family of complexes, the 2-iminopyridinyl nickel halides showed good activities for both ethylene oligomerization and polymerization [48–51]. Previous work in our group has reported a fused-cycloalkanylpyridine for such 2-iminopyridine ligation, *viz* *N*-(2-chloro-/2-phenyl-5,6,7-trihydroquinolin-8-ylidene) arylaminonickel dichlorides [52], which showed high activity in ethylene oligomerization. The nickel precatalysts bearing *N*-(5,6,7-trihydroquinolin-8-ylidene)arylamines, which have no substituent at the ortho-position of the 5,6,7-trihydroquinoline, however, performed high activities in ethylene polymerization [53]; moreover, their nickel analogs solely showed ethylene polymerization with verified substituents on the aryl groups within of *N*-(5,6,7-trihydroquinolin-8-ylidene)arylamines [54]. In comparison with the results obtained by nickel pre-catalysts ligated with *N*-(2-chloro- or 2-phenyl-5,6,7-trihydroquinolin-8-ylidene)arylamines, the scope of the nickel complexes bearing *N*-(2-alkyl-5,6,7-trihydroquinolin-8-ylidene)arylamines are necessarily investigated. Therefore, 2-alkyl-5,6,7-trihydroquinolin-8-ones are synthesized, reacted with various anilines and nickel dihalides to form the corresponding *N*-(2-alkyl-5,6,7-trihydroquinolin-8-ylidene)arylaminonickel dichlorides. The molecular structures of representative complexes have been determined by single-crystal X-ray crystallography. Upon activation with ethylaluminium sesquichloride ($Et_3Al_2Cl_3$, EASC), all the nickel pre-catalysts showed good activity towards ethylene oligomerization. The influence of the reaction parameters on the catalytic performance has been investigated in detail.

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2. Results and discussion

2.1. Synthesis and characterization

Initially, the preparation of the nickel compounds was attempted by first synthesizing the ligand set (2-methyl/isopropyl-5,6,7-trihydroquinolin-8-one plus aniline) followed by subsequent reaction with the nickel salts; however, this resulted in two compounds, namely cyclic 4,5-dihydroquinolin-8-arylamines, which were very unstable. To conquer this problem, a one-pot process involving 2-methyl- or 2-isopropyl-5,6,7-trihydroquinolin-8-one and the corresponding aniline together with $NiCl_2 \cdot 6H_2O$ in acetic acid, was undertaken to synthesize the target nickel complexes (Scheme 1).

All nickel complexes, which were formed in good yield, were characterized by FT-IR spectroscopy and by elemental analysis, In the FT-IR spectra, there is a strong band in the range 1550–1600 cm^{-1}, which can be ascribed to the stretching vibration of C=N. The molecular structures of complexes **Ni1**, **Ni4** and **Ni10** were confirmed by single crystal X-ray crystallography.

2.2. X-ray crystallographic studies

Single crystals of the nickel complexes **Ni1** and **Ni4** suitable for X-ray diffraction studies were obtained by slow diffusion of diethyl ether into methanol solution, while crystals of the complex **Ni10** were obtained by diffusion of diethyl ether into dichloromethane solution. The ORTEP diagrams of the molecular structures are shown in Figs. 1–3. The selected bond lengths and angles are listed in Table 1.

The five-coordinate complexes **Ni1** and **Ni4** are best described as distorted trigonal bipyramidal geometries at nickel, with the fifth coordination site occupied by the solvent (methanol) molecule.

Complex **Ni10** is a binuclear structure with centrosymmetric bridging Cl atoms, and the coordination geometry around the nickel center can again be described as a distorted trigonal bipyramidal. The ligands with a bulky iPr group occupy more space around nickel, which for **Ni10** creates slight differences in the bond lengths and bond angles of N1–Ni–N2 from those of **Ni1** and **Ni4**, and larger bond angles for N2–Ni1–Cl2, Cl1–Ni1–Cl2.

2.3. Ethylene oligomerization

In order to find the most suitable co-catalyst, pre-catalyst **Ni3** was screened using different co-catalysts such as methylaluminoxane (MAO), modified methylaluminoxane (MMAO), diethylaluminium chloride ($AlEt_2Cl$) and ethylaluminium sesquichloride ($Et_3Al_2Cl_3$, EASC) at 40 °C (only moderate activity was observed at 20 °C) under 10 atm ethylene (Table 2). In general, good observed activities were achieved on varying the co-catalysts, with the exception of the very low activity observed on combination with $AlEt_2Cl$. However, the benefit of using EASC was evident both in terms of catalytic activity and economic considerations, thus EASC was chosen as the co-catalyst for further investigations.

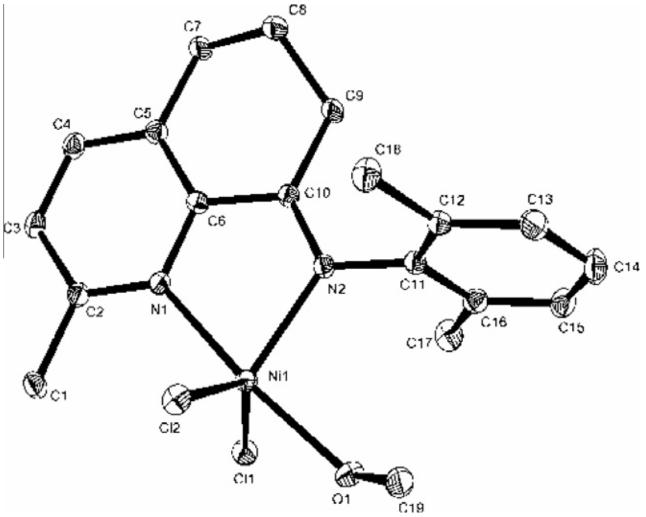


Fig. 1. ORTEP drawing of complex **Ni1** with thermal ellipsoids at 30% probability level. Hydrogen atoms have been omitted for clarity.

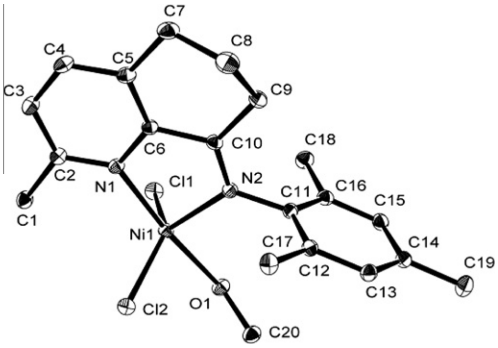


Fig. 2. ORTEP drawing of complex **Ni4** with thermal ellipsoids at 30% probability level. Hydrogen atoms have been omitted for clarity.

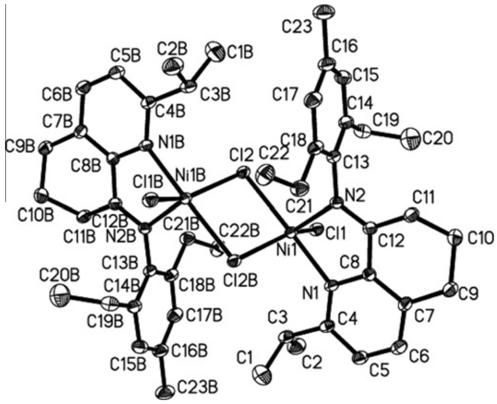
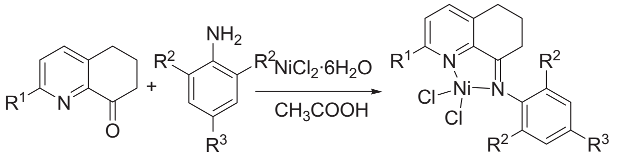


Fig. 3. ORTEP drawing of complex **Ni10** with thermal ellipsoids at 30% probability level. Hydrogen atoms have been omitted for clarity.



	Ni1	Ni2	Ni3	Ni4	Ni5	Ni6	Ni7	Ni8	Ni9	Ni10
R^1	Me	Me	Me	Me	Me	iPr	iPr	iPr	iPr	iPr
R^2	Me	Et	iPr	Me	Et	Me	Et	iPr	Me	Et
R^3	H	H	H	Me	Me	H	H	H	Me	Me

Scheme 1. Synthetic procedure of nickel complexes.

To evaluate the effects of the reaction conditions on the catalytic performance, detailed investigations with complex **Ni3** were carried out using different Al/Ni ratios and reaction temperatures; results are summarized in Table 3.

For the **Ni3**/EASC system, on changing of the Al/Ni molar ratio from 100 to 400 at 40 °C, the highest activity (1.79×10^5 g mol^{-1} (Ni)h^{-1}) was achieved with a Al/Ni molar ratio of 200. Furthermore,

Table 1
Selected bond lengths (Å) and angles (°) for complexes **Ni1**, **Ni4** and **Ni10**.

	Ni1	**Ni4**		**Ni10**
Bond lengths/(Å)			Bond lengths/	
Ni1–N2	2.032(3)	2.025(2)	(Å)	2.041(3)
Ni1–N1	2.072(3)	2.073(2)	Ni1–N2	2.068(3)
Ni1–O1	2.089(2)	2.097(2)	Ni1–N1	2.3063(11)
Ni1–Cl1	2.3039(12)	2.3002(11)	Ni1–Cl1	2.3596(12)
Ni1–Cl2	2.3151(14)	2.3130(13)	Ni1–Cl2	1.339(4)
N2–C10	1.287(4)	1.284(3)	N1–C4	1.353(5)
N2–C11	1.448(4)	1.445(3)	N1–C8	1.281(5)
N1–C2	1.335(4)	1.340(3)	N2–C12	1.437(4)
N1–C6	1.359(4)	1.358(3)	N2–C13	
Bond angles				
(°)	80.05(11)	80.10(9)	Bond angles (°)	80.26(12)
N2–Ni1–N1	93.84(11)	94.53(9)	N2–Ni1–N1	108.45(9)
N2–Ni1–O1	173.18(10)	174.10(8)	N2–Ni1–Cl1	89.82(9)
N1–Ni1–O1	110.98(8)	112.49(7)	N1–Ni1–Cl1	105.19(8)
N2–Ni1–Cl1	92.44(8)	92.47(7)	N2–Ni1–Cl2	91.71(9)
N1–Ni1–Cl1	86.89(8)	87.30(7)	N1–Ni1–Cl2	146.09(4)
O1–Ni1–Cl1	111.23(8)	107.96(7)	Cl1–Ni1–Cl2	
N2–Ni1–Cl2	93.81(8)	93.21(7)		
N1–Ni1–Cl2	91.23(8)	90.78(7)		
O1–Ni1–Cl2	137.78(4)	139.53(4)		
Cl1–Ni1–Cl2				

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

Entry	Pre-cat.	Co-cat.	Al/Ni	Act.[b]	C4 (%)	α-C_4 (%)
1	**Ni3**	EASC	200	1.79	100	91.7
2	**Ni3**	MAO	1000	1.48	100	82.9
3	**Ni3**	Et_2AlCl	200	0.21	100	86.4
4	**Ni3**	MMAO	1000	1.98	100	64.6

[a] Reaction conditions: 5 μmol of Ni; 10 atm ethylene; 40 °C; 30 min; 100 mL toluene.
[b] Activity: 10^5 g mol^{-1}(Ni) h^{-1}.

Table 3
Ethylene Oligomerization by **Ni3**/EASC.[a]

Entry	Pre-cat.	*T* (°C)	Al/Ni	*t* (min)	Act.[b]	α-C4 (%)	C4 (%)
1	**Ni3**	20	200	30	0.64	95.4	100
2	**Ni3**	60	200	30	2.29	88.6	100
3	**Ni3**	70	200	30	2.28	84.9	100
4	**Ni3**	80	200	30	4.3	80.3	100
5	**Ni3**	90	200	30	3.58	79.4	100
6	**Ni3**	40	100	30	0.43	83.5	100
7	**Ni3**	40	150	30	0.87	80.8	100
8	**Ni3**	40	250	30	1.06	94.1	100
9	**Ni3**	40	300	30	0.93	94.4	100
10	**Ni3**	40	400	30	0.87	98.2	100
11	**Ni3**	80	200	5	19.1	80.5	100
12	**Ni3**	80	200	10	10.6	74.2	100
13	**Ni3**	80	200	20	6.13	80.3	100

[a] Reaction conditions: 5 μmol of Ni; 10 atm. ethylene; 100 mL toluene.
[b] Activity: 10^5 g mol^{-1}(Ni) h^{-1}.

Table 4
Ethylene oligomerization by **Ni8**/EASC.[a]

Entry	*T* (°C)	Al/Ni	Act.[b]	α-C4 (%)	C4 (%)
1	60	200	1.03	92.2	100
2	80	200	1.93	86.2	100
3	90	200	1.75	82.2	100
4	40	100	0.33	97.1	100
5	40	200	0.89	95.8	100
6	40	300	0.41	96.9	100

[a] Reaction conditions: 5 μmol of Ni; 10 atm ethylene; 30 min.; 100 mL toluene.
[b] Activity: 10^5 g mol^{-1}(Ni) h^{-1}.

Table 5
Ethylene oligomerization by nickel pre-catalysts **Ni1**–**Ni10**.[a]

Entry	Pre-cat.	Act.[b]	C4 (%)	α-C4 (%)
1	**Ni1**	3.58	100	80.7
2	**Ni2**	3.85	100	79.4
3	**Ni3**	4.3	100	80.3
4	**Ni4**	5.74	100	74.4
5	**Ni5**	11.0	100	63.1
6	**Ni6**	1.61	100	87.4
7	**Ni7**	1.93	100	92.7
8	**Ni8**	3.09	100	86.2
9	**Ni9**	3.87	100	84.1
10	**Ni10**	6.88	100	73.9

[a] Reaction condition: 5 μmol of Ni; 10 atm ethylene; EASC, Al/Ni = 20; 80 °C; 30 min; 100 mL toluene.
[b] Activity: 10^5 g mol^{-1}(Ni) h^{-1}.

it was found that the selectivity for α-olefins tended to increase with increasing Al/Ni molar ratio. On fixing the Al/Ni molar ratio at 200, the influence of temperature was evaluated. On increasing the temperature from 20 to 90 °C, the activity increased until the temperature reached 90 °C, whereupon the activity decreased slightly. The highest activity of 4.30×10^5 g mol^{-1}(Ni) h^{-1} was observed at 80 °C. It was also observed that the selectivity for α-olefins decreased on increasing the temperature.

Catalyst lifetimes were also investigated (entry 11–13, Table 3), with the activity reaching 1.91×10^6 g mol^{-1}(Ni) h^{-1} at 5 min, but decreasing rapidly with the time. This is tentatively attributed to the presence of the electron-rich substituents at R^1, which increase the electronic density, compared to that in our previous systems [52].

Based on the optimum conditions found for the nickel complex **Ni3** with R^1 = Me, the screening conditions of a representative nickel complex with R^1 = iPr (**Ni8**) were selected. The results are summarized in Table 4.

Thus, at a fixed Al/Ni molar ratio of 200 at 80 °C, all the nickel complexes (**Ni1**–**Ni10**) showed good activities and high selectivity for α-olefins (Table 5). The activities of the nickel complexes with R^1 = Me decreased in the order, **Ni5** > **Ni4** > **Ni3** > **Ni2** > **Ni1**. Bulky substituted ligands protected the active species, thereby affording the highest activity [55]. This explanation also served to explain the activity trend observed for the nickel complexes with R^1 = iPr, which decreased in the order **Ni10** > **Ni9** > **Ni8** > **Ni7** > **Ni6**. The activities observed for **Ni6**–**Ni10** (R^1 = iPr) were lower than those of **Ni1**–**Ni5** (R^1 = Me), due to the steric and electronic influence of R^1 at the nickel center [55–57].

3. Conclusion

A series of *N*-(2-substituted 5,6,7-trihydroquinolin-8-ylidene) arylaminonickel(II) dichloride complexes were synthesized and fully characterized. Upon activation with EASC, all nickel(II) complexes exhibited good activity for ethylene oligomerization with enhanced thermal stability at 80 °C and high selectivity for α-C4. Catalysts bearing 2-Me substituted ligands generally showed better activities than did their analogs ligating by 2-*i*Pr substituted ligands. Less bulky substituents on the aryl group resulted in better catalytic activities, and additional substituents in the *para*-position of the aryl group (from aniline) afforded higher activity.

4. Experimental

4.1. General considerations

All manipulations of air and/or moisture sensitive compounds were performed under nitrogen atmosphere using standard Schlenk techniques. All solvents were routinely purified and distilled before use. Methylaluminoxane (MAO, 1.46 M solution in toluene) and modified methylaluminoxane (MMAO, 1.93 M in heptane, 3A) were purchased from AkzoNobel Corp. Diethylaluminium chloride (Et_2AlCl, 0.79 M in toluene) and ethylaluminium sesquichloride (EASC, 0.87 M in toluene) were freely obtained from Beijing Yansan Petrochemical Co. Elemental analysis was conducted on a Flash EA 1112 microanalyzer. IR spectra were recorded on a Perkin–Elmer System 2000 FT-IR spectrometer using KBr disks in the range 4000–400 cm^{-1}. Gas chromatograph (GC) analysis was performed with a VARIAN CP-3800 gas chromatograph equipped with a flame ionization detector and a 30 m column (0.2 mm inert diameter, 0.25 μm film thickness).

4.2. Synthesis of nickel complexes Ni1–Ni10

4.2.1. 2,6-Dimethyl-N-(2-methy-5,6,7-trihydroquinolin-8-ylidene)phenylaminonickel(II) dichloride (Ni1)

To a 25 ml two-necked round bottom flask, were added 2-methyl-5,6,7-trihydroquinolin-8-one (1 mmol), 2,6-dimethylaniline (1.0 mmol), $NiCl_2 \cdot 6H_2O$ (1.0 mmol) and glacial acetic acid (10 ml). The mixture was stirred at reflux temperature for 5 h, and then the acid was removed under reduced pressure. The residue was dissolved in 10 ml methanol, and **Ni1** was precipitated when 50 ml of diethyl ether was added. After filtration, the solid was washed with diethyl ether (3 × 5 mL), and dried under vacuum. The resultant yellow solid weighted 0.275 g (69.8% yield). FT-IR (KBr disk, cm^{-1}): 2970, 2911, 2855, 2362, 2336, 1622, 1595, 1480, 1274, 1223, 1203, 822, 778, 773, 662. *Anal.* Calc. for $C_{18}H_{20}Cl_2N_2Ni$ (393.96): C, 54.88; H, 5.12; N, 7.11. Found: C, 54.56; H, 5.20; N, 6.74%.

4.2.2. 2,6-Diethyl-N-(2-methy-5,6,7-trihydroquinolin-8-ylidene)phenylaminonickel(II) dichloride (Ni2)

By using a similar procedure as described for **Ni1**, 2-methyl-5,6,7-trihydroquinolin-8-one (0.162 g, 1.0 mmol), 2,6-diethylaniline (0.150 g, 1.0 mmol), $NiCl_2 \cdot 6H_2O$ (0.238 g, 1.0 mmol) were added into 10 ml glacial acetic acid, and the complex **Ni2** was obtained as a yellow powder, 0.285 g, 67.5% yield. FT-IR (KBr disk, cm^{-1}): 2964, 2932, 2879, 2362, 2336, 1625, 1598, 1481, 1453, 1274, 1223, 1215, 816, 774, 666. *Anal.* Calc. for $C_{20}H_{24}Cl_2N_2Ni$ (422.02): C, 56.92; H, 5.73; N, 6.64. Found: C, 56.46; H, 6.03; N, 6.34%.

4.2.3. 2,6-Diisopropyl-N-(2-methy-5,6,7-trihydroquinolin-8-ylidene)phenylaminonickel(II) dichloride (Ni3)

By using a similar procedure as described for **Ni1**, 2-methyl-5,6,7-trihydroquinolin-8-one (0.162 g, 1.0 mmol), 2,6-diisopropylaniline (0.178 g, 1.0 mmol), $NiCl_2 \cdot 6H_2O$ (0.238 g, 1.0 mmol) were added into 10 ml glacial acetic acid, and the complex **Ni3** was obtained as a yellow powder, 0.361 g, 80.2% yield. FT-IR (KBr disk, cm^{-1}): 2963, 2928, 2866, 2362, 2335, 1622, 1594, 1479, 1449, 1277, 809, 773, 667. *Anal.* Calc. for $C_{22}H_{28}Cl_2N_2Ni$ (450.07): C, 58.71; H, 6.27; N, 6.22. Found: C, 58.51; H, 6.00; N, 5.77%.

4.2.4. 2,4,6-Trimethyl-N-(2-methy-5,6,7-trihydroquinolin-8-ylidene)phenylaminonickel(II) dichloride (Ni4)

By using a similar procedure as described for **Ni1**, 2-methyl-5,6,7-trihydroquinolin-8-one (0.162 g, 1.0 mmol), 2,4,6-trimethylaniline (0.136 g, 1.0 mmol), $NiCl_2 \cdot 6H_2O$ (0.238 g, 1.0 mmol) were added into 10 ml glacial acetic acid, and the complex **Ni4** was obtained as a yellow powder, 0.281 g, 68.8% yield. FT-IR (KBr disk, cm^{-1}): 3118, 2948, 1749, 1724, 1633, 1600, 1485, 1380, 1223, 856, 828, 795, 666. *Anal.* Calc. for $C_{19}H_{22}Cl_2N_2Ni$ (407.99): C, 55.93; H, 5.44; N, 6.87. Found: C, 55.51; H, 5.49; N, 5.84%.

4.2.5. 2,6-Diethyl-4-methyl-N-(2-methy-5,6,7-trihydroquinolin-8-ylidene)phenylaminonickel(II) dichloride (Ni5)

By using a similar procedure as described for **Ni1**, 2-methyl-5,6,7-trihydroquinolin-8-one (0.162 g, 1.0 mmol), 2,6-diethyl-4-methylaniline (0.164 g, 1.0 mmol), $NiCl_2 \cdot 6H_2O$ (0.238 g, 1.0 mmol) were added into 10 ml glacial acetic acid, and the complex **Ni5** was obtained as a yellow powder, 0.232 g, 53.1% yield. FT-IR (KBr disk, cm^{-1}): 2960, 2875, 1664, 1630, 1596, 1480, 1455,1272, 1214, 1135, 859, 829, 668. *Anal.* Calc. for $C_{21}H_{26}Cl_2N_2Ni$ (436.04): C, 57.84; H, 6.01; N, 6.42. Found: C, 57.51; H, 5.80; N, 6.04%.

4.2.6. 2,6-Dimethyl-N-(2-isopropyl-5,6,7-trihydroquinolin-8-ylidene)phenylaminonickel(II) dichloride (Ni6)

By using a similar procedure as described for **Ni1**, 2-isopropyl-5,6,7-trihydroquinolin-8-one (0.190 g, 1.0 mmol), 2,6-dimethylaniline (0.122 g, 1.0 mmol), $NiCl_2 \cdot 6H_2O$ (0.238 g, 1.0 mmol) were added into 10 ml glacial acetic acid, and the complex **Ni6** was obtained as a yellow powder, 0.249 g, 59.1% yield. FT-IR (KBr disk, cm^{-1}): 3021, 2952, 2867, 2361, 1628, 1599, 1224, 1205, 1043, 866, 836, 793, , 677. *Anal.* Calc. for $C_{20}H_{24}Cl_2N_2Ni$ (422.02): C, 56.92; H, 6.73; N, 6.64. Found: C, 56.46; H, 6.23; N, 6.34%.

4.2.7. 2,6-Diethyl-N-(2-isopropyl-5,6,7-trihydroquinolin-8-ylidene)phenylaminonickel(II) dichloride (Ni7)

By using a similar procedure as described for **Ni1**, 2-isopropyl-5,6,7-trihydroquinolin-8-one (0.190 g, 1.0 mmol), 2,6-diethylaniline (0.150 g, 1.0 mmol), $NiCl_2 \cdot 6H_2O$ (0.238 g, 1.0 mmol) were added into 10 ml glacial acetic acid, and the complex **Ni7** was obtained as a yellow powder, 0.303 g, 67.4% yield. FT-IR (KBr disk, cm^{-1}): 2967, 2928, 2881, 2361, 1627, 1595, 1478, 1450, 1280, 1217, 1048, 865, 810, 675. *Anal.* Calc. for $C_{22}H_{28}Cl_2N_2Ni$ (450.07): C, 58.71; H, 6.27; N, 6.22. Found: C, 58.46; H, 6.24; N, 5.86%.

4.2.8. 2,6-Diisopropyl-N-(2-isopropyl-5,6,7-trihydroquinolin-8-ylidene)phenylaminonickl(II) dichloride (Ni8)

By using a similar procedure as described for **Ni1**, 2-isopropyl-5,6,7-trihydroquinolin-8-one (0.190 g, 1.0 mmol), 2,6-isopropylaniline (0.178 g, 1.0 mmol), $NiCl_2 \cdot 6H_2O$ (0.238 g, 1.0 mmol) were added into 10 ml glacial acetic acid, and the complex **Ni8** was obtained as a yellow powder, 0.326 g, 68.2% yield. FT-IR (KBr disk, cm^{-1}): 2965, 2927, 2870, 2361, 1623, 1598, 1484, 1459, 1217, 1188, 1052, 828, 806, 767. *Anal.* Calc. for $C_{24}H_{32}Cl_2N_2Ni$ (478.12): C, 60.29; H, 6.75; N, 5.86. Found: C, 59.88; H,6.85; N, 5.42%.

4.2.9. 2,4,6-Trimethyl-N-(2-isopropyl-5,6,7-trihydroquinolin-8-ylidene)phenylaminonickel(II) dichloride (Ni9)

By using a similar procedure as described for **Ni1**, 2-isopropyl-5,6,7-trihydroquinolin-8-one (0.190 g, 1.0 mmol), 2,4,6-trimethylaniline (0.136 g, 1.0 mmol), $NiCl_2 \cdot 6H_2O$ (0.238 g, 1.0 mmol) were added into 10 ml glacial acetic acid, and the complex **Ni9** was obtained as a yellow powder 0.281 g, 64.2% yield. FT-IR (KBr disk, cm^{-1}): 2959, 2916, 2871, 1622, 1596, 1470, 1452, 1225, 1140, 1041, 852, 672. *Anal.* Calc. for $C_{21}H_{26}Cl_2N_2Ni$ (436.04): C, 57.84; H, 6.01; N, 6.42. Found: C, 57.58; H, 6.04; N, 6.17%.

4.2.10. 2,6-Diethyl-4-methyl-N-(2-isopropyl-5,6,7-trihydroquinolin-8-ylidene)phenylaminonickel(II) dichloride (Ni10)

By using a similar procedure as described for **Ni1**, 2-isopropyl-5,6,7-trihydroquinolin-8-one (0.190 g, 1.0 mmol), 2,6-diethyl-4-methylaniline (0.164 g, 1.0 mmol), $NiCl_2 \cdot 6H_2O$ (0.238 g, 1.0 mmol) were added into 10 ml glacial acetic acid, and the complex **Ni10** was obtained as a yellow powder, 0.334 g, 72.0% yield. FT-IR (KBr disk, cm^{-1}): 2966, 2931, 2874, 1621, 1589, 1480, 1460, 1214, 1140, 1046, 864, 832, 654. *Anal.* Calc. for $C_{23}H_{30}Cl_2N_2Ni$ (464.10): C, 59.52; H, 6.52; N, 6.04. Found: C, 59.44; H, 6.71; N, 5.89%.

Table 6
Crystal data and structure refinement for **Ni1**, **Ni4** and **Ni10**.

	Ni1·CH_3OH	**Ni4**·CH_3OH	**Ni10**
Empirical formula	$C_{19}H_{24}Cl_2N_2NiO$	$C_{20}H_{25}Cl_2N2NiO$	$C_{46}H_{60}Cl_4N_4Ni_2$
Formula weight	426.01	439.01	928.20
T (K)	173(2)	293(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system, space group	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$
a (Å)	9.5570(19)	9.3985(19)	13.605(3)
b (Å)	10.730(2)	11.088(2)	14.196(3)
c (Å)	10.858(2)	11.367(2)	15.482(3)
α (°)	65.41(3)	63.92(3)	67.48(3)
β (°)	78.80(3)	77.70(3)	80.63(3)
γ (°)	70.50(3)	70.02(3)	73.42(3)
V (Å^3)	952.4(3)	997.1(3)	2642.3(9)
Z	2	2	2
D_{calc} (g cm^{-3})	1.485	1.462	1.167
μ (mm^{-1})	1.308	1.252	0.946
$F(000)$	444	458	976
Crystal size (mm)	0.55 × 0.47 × 0.19	0.42 × 0.37 × 0.21	0.56 × 0.45 × 0.29
θ Range (°)	2.07–27.51	2.00–30.04	1.56–27.49
Limiting indices	$-12 \leqslant h \leqslant 12$	$-13 \leqslant h \leqslant 13$	$-17 \leqslant h \leqslant 15$
	$-13 \leqslant k \leqslant 13$	$-15 \leqslant k \leqslant 15$	$-17 \leqslant k \leqslant 18$
	$-14 \leqslant l \leqslant 14$	$-15 \leqslant l \leqslant 16$	$-20 \leqslant l \leqslant 20$
No. of reflections collected	8477	15528	23573
No. unique rflns (R_{int})	4315(0.0376)	5795(0.0384)	12007(0.0438)
Number of parameters	231	240	505
Completeness to θ (%)	98.7	99.3	99.0
Goodness of fit on F^2	1.089	1.036	1.060
Final R indices $[I > 2\sum(I)]$	$R_1 = 0.0497$	$R_1 = 0.0517$	$R_1 = 0.0597$
	$wR_2 = 0.1407$	$wR_2 = 0.1531$	$wR_2 = 0.1662$
R indices (all data)	$R_1 = 0.0555$	$R_1 = 0.0547$	$R_1 = 0.0707$
	$wR_2 = 0.1506$	$wR_2 = 0.1589$	$wR_2 = 0.1746$
Largest diff peak and hole (e Å^{-3})	0.729 and -0.690	1.948 and −0.725	0.567 and −0.840

4.3. X-ray crystallographic studies

Single crystals of **Ni1**·CH_3OH, **Ni4**·CH_3OH and **Ni10** suitable for X-ray diffraction analysis were obtained by laying diethyl ether on methanol solutions at room temperature. 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. [58] Details of the X-ray structure determinations and refinements are provided in Table 6.

4.4. General procedure for ethylene oligomerization

Ethylene oligomerization was carried out in a stainless steel autoclave (300 mL capacity) equipped with an ethylene pressure control system, a mechanical stirrer and a temperature controller. When the desired reaction temperature was reached, under ethylene atmosphere, toluene, the desired amount of co-catalyst, and a toluene solution of the catalytic precursor (the total volume was 100 mL) were injected into the reactor with syringes in this order, and then the ethylene pressure was increased to 10 atm, and maintained at this level by constant feeding of ethylene. After the desired reaction period, the reactor was cooled with ice-water bath and the excess ethylene was vented. Small amounts of the reaction solution were collected and quenched by addition of drops of 10% aqueous hydrogen chloride. The organic layer was analyzed by gas chromatography (GC) for determining the composition and mass distribution of the oligomers obtained.

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Appendix A. Supplementary material

CCDC 846647, 846648 and 846649 contain the supplementary crystallographic data for complexes **Ni1**, **Ni4** and **Ni10**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.12.008.

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