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Synthesis, characterisation and ethylene oligomerization behaviour of *N*-(2-substituted-5,6,7-trihydroquinolin-8-ylidene)arylaminonickel dichlorides†

Jiangang Yu,[ac] Xinquan Hu,[b] Yanning Zeng,[c] Liping Zhang,[c] Caihua Ni,*[a] Xiang Hao[c] and Wen-Hua Sun*[c]

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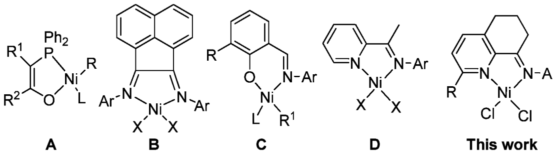
A series of *N*-(2-substituted-5,6,7-trihydroquinolin-8-ylidene)-arylaminonickel(II) dichlorides were synthesized by the one-pot stoichiometric reaction of nickel dichloride, 2-chloro- or 2-phenyl-substituted 5,6,7-trihydroquinolin-8-one, and the corresponding anilines. All nickel complexes were characterized by elemental and spectroscopic analysis. The molecular structures of representative nickel complexes, determined by the single-crystal X-ray diffraction, indicate the different coordination numbers around nickel either four with more bulky ligands or five with less bulky ligands. All nickel complexes, activated with ethylaluminium sesquichloride ($Et_3Al_2Cl_3$), showed high activities (up to 9.5×10^6 g mol^{-1} h^{-1}) in ethylene oligomerization for dimer and trimers.

Introduction

Ethylene oligomerization is one of most important industrial processes for producing linear alpha-olefins, in which a well-known process is the Shell Higher Olefin Process (SHOP) employing the nickel catalyst (**A**) (Scheme 1).[1] The interest in nickel catalysts for ethylene reactivity was resurrected with the observation that highly active ethylene polymerization catalyst of diiminonickel complexes (**B**)[2] and self-activating catalyst of neutral salicylaldiminonickel complexes (**C**).[3] In the past decade, papers of nickel complexes acting as catalysts in ethylene oligomerization and polymerization have mushroomed with extensive works of nickel complexes bearing bidentate ligands such as *N^N*,[4,5] *N^P*,[6] *N^O*,[7] *P^O*,[8] and tridentate ligands such as *N^N^N*,[4e,9] *N^N^O*,[4e,5e,10] *N^P^N*.[11]



Scheme 1 Model catalysts.

In general, *N,N*-bidentate Ni(II) complexes are more attractive due to their easy syntheses and better catalytic performances.

Within *N,N*-bidentate Ni(II) complexes, the 2-iminopyridinyl nickel halides (**D**) showed good activities in ethylene polymerization,[5a,b] and their derivatives showed activities for both oligomerization and polymerization.[5d,e] However, there is no research on the fused-cycloalkanonylpyridine for such 2-iminopyridines as ligands. In this work, the 2-chloro- and 2-phenyl-substituted 5,6,7-trihydroquinolin-8-ones[12] are used to form *N*-(2-substituted-5,6,7-trihydroquinolin-8-ylidene)-arylaminonickel dichlorides. The molecular structures of representative complexes are determined by single-crystal X-ray crystallography analysis, and indicate that the five-coordinated number is preferred for nickel complexes bearing *N*-(2-chloro-5,6,7-trihydroquinolin-8-ylidene)arylamines, whereas the four-coordinated number is found for nickel complexes ligating *N*-(2-phenyl-5,6,7-trihydroquinolin-8-ylidene)arylamines. All nickel catalysts are highly active in ethylene oligomerization in the presence of ethylaluminium sesquichloride ($Et_3Al_2Cl_3$). Herein the synthesis and characterisation of the title nickel complexes are reported along with their performance in ethylene oligomerisation.

Results and discussion

Synthesis and characterisation

The reaction of 2-chloro/phenyl-5,6,7-trihydroquinolin-8-one with anilines gave two compounds due to partial migration of the double bonding of Schiff-base into inner cyclic 4,5-dihydroquinolin-8-arylamines, therefore the stepwise procedure

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[a] *School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, China. E-mail: nicaihua2000@163.com*
[b] *College of Chemical Engineering and Materials Science, Zhejiang University of Technology, Hangzhou 310014, China*
[c] *Key Laboratory of Engineering Plastics, Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. E-mail: whsun@iccas.ac.cn; Fax: +86-10-62618239*

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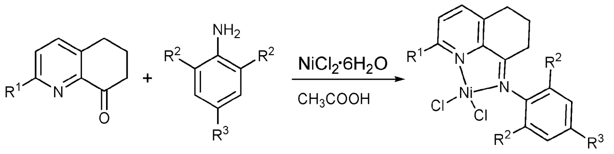

	Ni1	Ni2	Ni3	Ni4	Ni5	Ni6	Ni7	Ni8	Ni9	Ni10
R1	Cl	Cl	Cl	Cl	Cl	Ph	Ph	Ph	Ph	Ph
R2	Me	Et	iPr	Me	Et	Me	Et	iPr	Me	Et
R3	H	H	H	Me	Me	H	H	H	Me	Me

Scheme 2 Synthetic procedure of bidentate nickel complexes.

of preparing ligands and then forming nickel complexes is not suitable for the current work. To overcome the problem in synthesizing unstable ligands[11,13] or forming ligands in low yields,[14] one-pot reaction is an efficient methodology to form metal complex due to cation-induced assembly. Therefore, the title nickel complexes are formed in acceptable yields through the one-pot reactions of 2-chloro- (or phenyl-)5,6,7-trihydroquinolin-8-one, the corresponding anilines and $NiCl_2{\cdot}6H_2O$ in acetic acid (Scheme 2). All complexes were consistent with their elemental analyses, and their IR spectra with a strong band in the range 1550–1600 cm^{-1} which can be ascribed to the stretching vibration of C=N. The unambiguous molecular structures of **Ni2**, **Ni3**, **Ni8** and **Ni10** are confirmed by single-crystal X-ray crystallography.

Molecular structures

Crystals of **Ni2**, **Ni3**, **Ni8** and **Ni10** suitable for single-crystal X-ray crystallography have been obtained by laying diethyl ether on their ethanol solution at room temperature. The molecular structures indicate two kinds of coordination numbers around nickel atoms. The five-coordination around nickel atom is observed within complexes **Ni2** and **Ni3**, which are a chloro-bridged dimer or a monomeric nickel complex containing a coordinated ethanol, respectively. Within complexes **Ni8** and **Ni10**, they adapt four-coordination numbers with bidentate ligands and two chlorides. The coordination numbers are dependent on the steric hindrances associated with their ligands. The ligands with a bulky aryl group occupy more space around nickel and induce the lower coordination numbers for complexes **Ni8** and **Ni10**; the ligands bearing chloro-substituent form nickel complexes with five-coordination number, forming the chloro-bridged dimeric **Ni2** and monomer **Ni3** having an additional solvent. Such phenomena are commonly observed within other nickel complexes in the literature.[15] The molecular structures of **Ni2**, **Ni3**, **Ni8** and **Ni10** are shown in Fig. 1–4, and their selected bond lengths and angles are listed in Table 1.

The five-coordinated complexes **Ni2** and **Ni3** display the distorted bipyramidal coordination environment around nickel atom, whereas the four-coordinated complexes **Ni8** and **Ni10** adopt the distorted tetrahedral sphere. As shown in Table 1, the ligands embrace nickel atoms stronger in complexes **Ni8** and **Ni10** with shorter bond lengths of Ni–N and larger bond angles of N1–Ni–N2 than the analogous complexes **Ni2** and **Ni3** show. Regarding dimeric **Ni2**, there is no direct bonding between two nickel atoms with intramolecular distance 3.481 Å, which is quite similar to the data 3.475 Å observed in the analogous di-μ-chloro-bis(2-iminopyridinyl)dinickel dichlorides.[16]

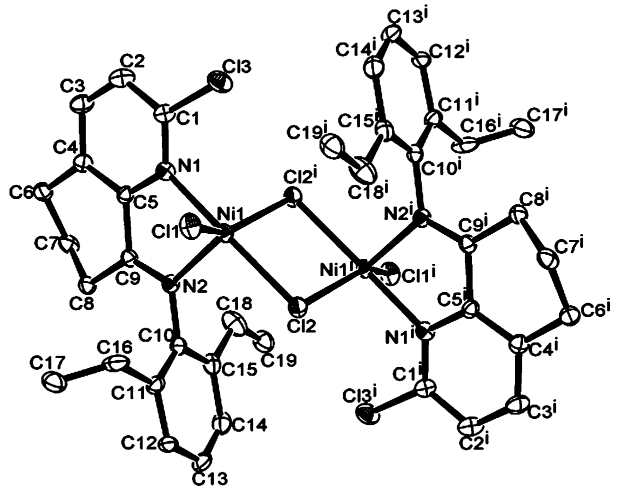

Fig. 1 ORTEP drawing of complex **Ni2** with thermal ellipsoids at 30% probability level. Hydrogen atoms have been omitted for clarity.

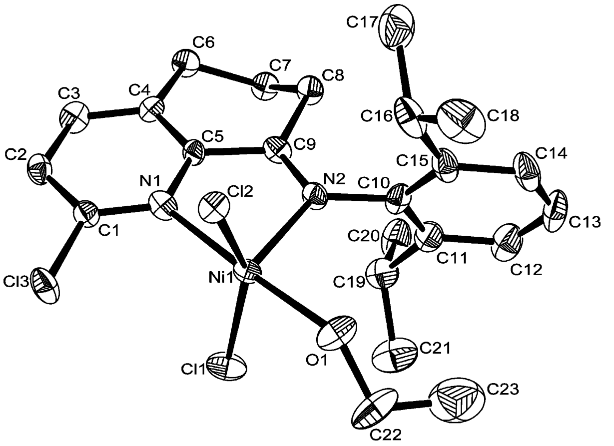

Fig. 2 ORTEP drawing of complex **Ni3** with thermal ellipsoids at 30% probability level. Hydrogen atoms have been omitted for clarity.

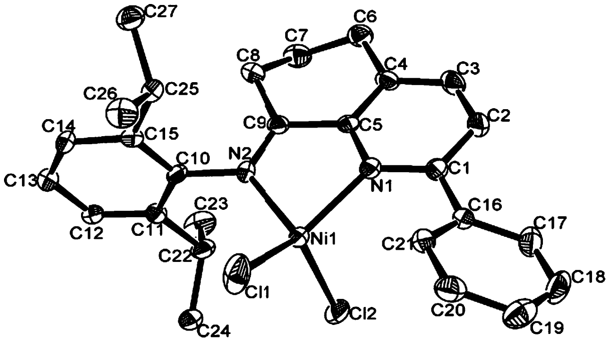

Fig. 3 ORTEP drawing of complex **Ni8** with thermal ellipsoids at 30% probability level. Hydrogen atoms have been omitted for clarity.

Ethylene oligomerization

Various alkylaluminiums such as MAO, MMAO, $AlEt_2Cl$ and ethylaluminium sesquichloride ($Et_3Al_2Cl_3$, EASC) have been

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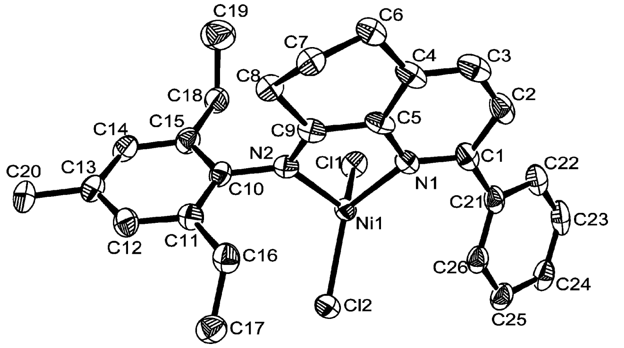

Fig. 4 ORTEP drawing of complex **Ni10** with thermal ellipsoids at 30% probability level. Hydrogen atoms have been omitted for clarity.

Table 1 Selected bond lengths (Å) and angles (°) for complexes **Ni2**, **Ni3**, **Ni8** and **Ni10**

	Ni2	**Ni3**	**Ni8**	**Ni10**
Bond lengths/Å				
Ni1–N1	2.077(5)	2.077(9)	2.044(6)	2.018(5)
Ni1–N2	2.030(4)	2.054(8)	2.012(6)	2.011(5)
Ni1–Cl1	2.2766(16)	2.278(3)	2.202(3)	2.2166(17)
Ni1–Cl2	2.3789(17)	2.324(3)	2.234(2)	2.1992(18)
N2–C9	1.289(7)	1.292(13)	1.293(9)	1.276(7)
N2–C10	1.464(7)	1.460(13)	1.451(9)	1.440(7)
N1–C1	1.327(7)	1.327(13)	1.367(10)	1.345(8)
N1–C5	1.352(7)	1.379(12)	1.362(10)	1.360(8)
Ni1–O1	—	2.038(8)	—	—
Bond angles (°)				
N2–Ni1–N1	79.10(18)	79.8(3)	81.6(3)	82.0(2)
N2–Ni1–Cl1	110.73(14)	102.5(3)	106.79(19)	104.65(15)
N1–Ni1–Cl1	93.77(13)	89.4(3)	137.8(2)	123.12(14)
N2–Ni1–Cl2	97.11(14)	107.6(3)	110.2(2)	112.34(14)
N1–Ni1–Cl2	171.25(13)	89.6(2)	96.68(19)	100.04(14)
Cl1–Ni1–Cl2	94.95(6)	149.20(12)	117.29(13)	126.21(7)
O1–Ni1–N2	—	99.0(3)	—	—
O1–Ni1–N1	—	176.1(3)	—	—
O1–Ni1–Cl1	—	87.3(2)	—	—

evaluated as activators to activate the complex **Ni3** in ethylene oligomerization (entries 1–4 in Table 2). The system employing EASC as cocatalyst exhibits highest activity (entry 4 in Table 2), which is consistent to its analogues of iminopyridinyl-nickel catalysts.[17] Therefore, the EASC is used as activator for selecting optimum reaction parameters such as ratios of aluminium to nickel (entries 4–8 in Table 2), reaction temperatures (entry 6, entries 9–11 in Table 2) and lifetime of the active species (entry 6, entries 12–15 in Table 2).

The **Ni3**/EASC is studied with changing Al/Ni molar ratios from 200 to 600 (entries 4–8 in Table 2) at 20 °C, shows best value of 8.7×10^6 g mol^{-1}(Ni) h^{-1} with the molar ratio of Al/Ni = 400 : 1 (entry 6 in Table 2). The molar ratio of Al/Ni = 400 : 1, both catalytic activity and α-olefin and butuene selectivity are observed greatest at 20 °C (entry 6 in Table 2); and the catalytic system behave a lower activity and worse α-olefin selectivity along with increasing reaction temperature (entries 9–11 in Table 2), such phenomena were also observed by other nickel catalysts.[4e,9b,18] Prolonging reaction time (entries 6, 12–13 in Table 2), the activity is slightly decreased meanwhile the amount of hexenes are mainly increased. These results indicate no inducing period of ethylene oligomerization, and the active species are slowly deactivated. Therefore, other nickel procatalysts are investigated at 20 °C with the molar ratio of Al/Ni = 400 : 1, and all catalytic performances are tabulated in Table 3.

Even though the complex **Ni2** is dinuclear as a solid, the active species of all nickel catalysts are generally considered as their monomeric species. Therefore, two series of active species are formed regarding to the differences of their ligands with R^1 substituent. Two sets of data are comparable on the base of ligands with R^1 substituent (chloro for the nickel complexes **Ni1–Ni5** and Ph for the nickel complexes **Ni6–Ni10**). Their activities decrease in the order of 2,6-di(*i*-Pr) > 2,6-di(Et) > 2,6-di(Me) > 2,6-di(Et)-4-Me > 2,4,6-tri(Me) with R^1 = Cl; meanwhile, with R^1 = Ph, the activities decrease in the order of 2,6-di(*i*-Pr) > 2,6-di(Et) > 2,6-di(Me), and 2,6-di(Et)-4-Me > 2,4,6-tri(Me). Such phenomena are consistent with observations in literature that bulky alkyl substituents help solubility of procatalysts for better activity.[18b,19] Interestingly, catalysts **Ni4** and **Ni9** (R^2 and R^3 = Me) which showed the

Table 2 Ethylene oligomerization by **Ni3** with various alkylaluminiums[a]

						Product distribution (%)[c]		
Entry	Cocatalyst	Al/Ni	*T*/°C	*t*/min	Activity[b]	C4/∑	α-C4/C4	C6/∑
1	MAO	1000	20	30	0.31	87.1	98.0	12.9
2	MMAO	1000	20	30	0.93	86.9	89.0	13.1
3	$AlEt_2Cl$	200	20	30	0.94	84.3	84.3	15.7
4	EASC	200	20	30	4.54	92.5	> 99.0	7.5
5	EASC	300	20	30	5.1	89.4	97.1	10.6
6	EASC	400	20	30	8.7	89.6	> 99.0	10.4
7	EASC	500	20	30	5.9	88.0	> 99.0	12.0
8	EASC	600	20	30	5.4	85.1	> 99.0	14.9
9	EASC	400	40	30	7.6	77.9	94.2	22.1
10	EASC	400	60	30	6.5	81.2	87.4	18.8
11	EASC	400	80	30	5.8	73.9	76.7	26.1
12	EASC	400	20	10	9.5	91.5	> 99.0	8.5
13	EASC	400	20	20	9.0	86.7	> 99.0	13.3
14	EASC	400	20	40	5.8	87.5	> 99.0	12.5
15	EASC	400	20	50	4.7	86.8	> 99.0	13.2

[a] Reaction conditions: 5 μmol of Ni; 10 atm of ethylene; 100 mL of toluene. [b] Activity, 10^6 g mol^{-1}(Ni) h^{-1}. [c] Determined by GC. ∑ donates the total amount of oligomers.

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Table 3 Oligomerization of ethylene with all nickel procatalysts/EASC[a]

			Product distribution (%)[c]		
Entry	Cat.	Activity[b]	C4/∑	α-C4/C4	C6/∑
1	**Ni1**	3.7	88.5	98.0	11.5
2	**Ni2**	7.1	87.0	90.1	13.0
3	**Ni3**	8.7	89.6	> 99.0	10.4
4	**Ni4**	2.4	79.3	> 99.0	20.7
5	**Ni5**	2.5	89.1	94.4	10.9
6	**Ni6**	3.1	84.5	90.2	15.5
7	**Ni7**	3.4	84.5	87.1	15.5
8	**Ni8**	4.1	85.8	85.6	14.2
9	**Ni9**	2.5	79.5	89.7	20.5
10	**Ni10**	4.0	87.7	83.1	12.3

[a] Reaction conditions: 5 μmol of Ni; Al/Ni = 400; 10 atm of ethylene; 30 min; 20 °C; 100 mL of toluene. [b] Activity, 10^6 g mol^{-1}(Ni) h^{-1}. [c] Determined by GC. ∑ donates the total amount of oligomers.

lowest activities with producing more hexene. This phenomena were caused by the various substituents of R^1 and R^2. As shown in Table 3, the activities by **Ni6–Ni10** (R^1 = Ph, entries 6–10 in Table 3) were much smaller than those by **Ni1–Ni5** (R^1 = Cl, entries 1–5 in Table 3) due to steric influence of R^1 around nickel centre.[20]

Experimental

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 Akzo Nobel Corp. Diethylaluminium chloride (Et_2AlCl_2, 0.79 M in toluene) and ethylaluminium sesquinochroride (EASC, 0.87 M in toluene) were purchased from Beijing Yansan Petrochemical Co. Elemental analysis is conducted on a Flash EA 1112 microanalyzer. IR spectra are recorded on a Perkin-Elmer System 2000 FT-IR spectrometer using KBr discs in the range 4000–400 cm^{-1}. Gas chromatography (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).

Synthesis and characterisation of complexes Ni1–Ni10

All nickel complexes are prepared in the same manner. In typically synthesizing the complex **Ni1**, the mixture of 2-chloro-5,6,7-trihydroquinolin-8-one (1.0 mmol), 2,6-dimethylaniline (1.0 mmol) and $NiCl_2{\cdot}6H_2O$ (1.0 mmol) in glacial acetic acid (10 mL) is refluxed for 3 h. Acid was removed under reduced pressure, and the residue was dissolved in 10 mL methanol. Unreacted $NiCl_2$ was removed by filtration. 50 mL of diethyl ether was added to precipitate **Ni1**. After filtrated and washed with diethyl ether (3 × 5 mL), the collected solid was dried under vacuum.

[2,6-Dimethyl-*N*-(2-chloro-5,6,7-trihydroquinolin-8-ylidene) phenylamino]nickel(II) dichloride (**Ni1**) was obtained as green powder in 51.1% yield. IR (KBr; cm^{-1}): 3345, 2931, 1567 (νC=N), 1488, 1409, 1341, 1239, 1123, 1028, 866, 783, 675, 616, 502, 403. Anal. calcd for $C_{17}H_{17}Cl_3N_2Ni$(414): C, 49.27; H, 4.14; N, 6.76%. Found: C, 49.21; H, 4.41; N, 6.49%. MS-ESI: calcd for $C_{17}H_{17}Cl_3N_2Ni$ *m*/*z* 411.9, found *m*/*z* 377.0 $(M - Cl)^+$.

[2,6-Diethyl-*N*-(2-chloro-5,6,7-trihydroquinolin-8-ylidene) phenylamino]nickel(II) dichloride (**Ni2**) was obtained as green powder in 55.0% yield. IR (KBr; cm^{-1}): 3049, 2963, 2930, 2875, 1581 (νC=N), 1449, 1262, 1237, 1190, 1156, 1124, 864, 817, 781, 676, 641, 521. Anal. calcd for $C_{19}H_{21}Cl_3N_2Ni$(442): C, 51.58; H, 4.78; N, 6.33%. Found: C, 51.53; H, 5.12; N, 6.05%. MS-ESI: calcd for $C_{19}H_{21}Cl_3N_2Ni$ *m*/*z* 440.0, found *m*/*z* 405.0 $(M - Cl)^+$.

[2,6-Bis(1-methylethyl)-*N*-(2-chloro-5,6,7-trihydroquinolin-8-ylidene)phenylamino]nickel(II) dichloride (**Ni3**) was obtained as green powder in 62.9% yield. IR (KBr; cm^{-1}): 3350, 2961, 2927, 2867, 1618, 1581 (νC=N), 1453, 1268, 1238, 1189, 1127, 1038, 928, 877, 816, 779, 550. Anal. calcd for $C_{21}H_{25}Cl_3N_2Ni$(470): C, 53.61; H, 5.36; N, 5.95%. Found: C, 53.25; H, 5.21; N, 6.03%. MS-ESI: calcd for $C_{21}H_{25}Cl_3N_2Ni$ *m*/*z* 468.0, found *m*/*z* 433.0 $(M - Cl)^+$.

[2,4,6-Trimethyl-*N*-(2-chloro-5,6,7-trihydroquinolin-8-ylidene) phenylamino]nickel(II) dichloride (**Ni4**) was obtained as green powder in 65.2.0% yield. IR (KBr; cm^{-1}): 2923, 1575 (νC=N), 1412, 1235, 1210, 1122, 1035, 1011, 817, 680, 562, 505. Anal. calcd for $C_{18}H_{19}Cl_3N_2Ni$(428): C, 50.46; H, 4.47; N, 6.54%. Found: C, 50.34; H, 4.76; N, 6.91%. MS-ESI: calcd for $C_{18}H_{19}Cl_3N_2Ni$ *m*/*z* 426.0, found *m*/*z* 391.0 $(M - Cl)^+$.

[2,6-Diethyl-4-methyl-*N*-(2-chloro-5,6,7-trihydroquinolin-8-ylidene)phenylamino]nickel(II) dichloride (**Ni5**) was obtained as green powder in 71.0% yield. IR (KBr; cm^{-1}): 2956, 2933, 2872, 2854, 1626, 1578 (νC=N), 1444, 1341, 1243, 1142, 1121, 922, 858, 646, 501. Anal. calcd for $C_{20}H_{23}Cl_3N_2Ni$(456): C, 52.63; H, 5.08; N, 6.14%. Found: C, 52.38; H, 5.29; N, 6.02%. MS-ESI: calcd for $C_{20}H_{23}Cl_3N_2Ni$ *m*/*z* 454.0, found *m*/*z* 419.0 $(M - Cl)^+$.

[2,6-Dimethyl-*N*-(2-phenyl-5,6,7-trihydroquinolin-8-ylidene) phenylamino]nickel(II) dichloride (**Ni6**) was obtained as green powder in 60.5% yield. IR (KBr; cm^{-1}): 3272, 2928, 1558 (νC=N), 1401, 1341, 1162, 1122, 1034, 1009, 815, 763, 679, 614, 482. Anal. calcd for $C_{23}H_{22}Cl_2N_2Ni$(456): C, 60.58; H, 4.86; N, 6.14%. Found: 60.76; H, 5.02; N, 6.33%. MS-ESI: calcd for $C_{23}H_{22}Cl_2N_2Ni$ *m*/*z* 454.0, found *m*/*z* 419.0 $(M - Cl)^+$.

[2,6-Diethyl-*N*-(2-phenyl-5,6,7-trihydroquinolin-8-ylidene) phenylamino]nickel(II) dichloride (**Ni7**) was obtained as green powder in 66.9% yield. IR (KBr; cm^{-1}): 3272, 2933, 1555 (νC=N), 1400, 1341, 1166, 1122, 1034, 1009, 679, 614, 494. Anal. calcd for $C_{25}H_{26}Cl_2N_2Ni$(484): C, 62.03; H, 5.41; N, 5.79%. Found: 62.21; H, 5.64; N, 5.91%. MS-ESI: calcd for $C_{25}H_{26}Cl_2N_2Ni$ *m*/*z* 482.0, found *m*/*z* 447.1 $(M - Cl)^+$.

[2,6-Bis(1-methylethyl)-*N*-(2-phenyl-5,6,7-trihydroquinolin-8-ylidene)phenylamino]nickel(II) dichloride (**Ni8**) was obtained as green powder in 71.0% yield. IR (KBr; cm^{-1}): 3358, 2969, 1557 (νC=N), 1406, 1341, 1027, 762, 677, 616, 508, 403. Anal. calcd for $C_{27}H_{30}Cl_2N_2Ni$(442): C, 63.32; H, 5.90; N, 5.47%. Found: C, 63.63; H, 5.97; N, 5.54%. MS-ESI: calcd for $C_{27}H_{30}Cl_2N_2Ni$ *m*/*z* 510.1, found *m*/*z* 475.1.1 $(M - Cl)^+$.

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Table 4 Crystal data and structure refinement for **Ni2**, **Ni3·CH_2CH_3OH**, **Ni8** and **Ni10**

	2Ni2	**Ni3·CH_2CH_3OH**	**Ni8**	**Ni10**
Empirical formula	$C_{38}H_{42}Cl_6N_4Ni_2$	$C_{23}H_{31}Cl_3N_2NiO$	$C_{27}H_{30}Cl_2N_2Ni$	$C_{26}H_{28}Cl_2N_2Ni$
Formula weight	884.88	516.56	512.14	498.11
T/K	173(2)	173(2)	293(2)	173(2)
Wavelength/Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$Pbca$	$C2/c$
a/Å	9.4118(19)	11.597(2)	15.896(3)	31.488(6)
b/Å	18.517(4)	17.402(4)	16.770(3)	10.033(2)
c/Å	11.063(2)	12.326(3)	18.790(4)	15.549(3)
α (°)	90	90	90	90
β (°)	93.02(3)	95.83(3)	90	102.20(3)
γ (°)	90	90	90	90
V/Å^3	1925.3(2)	2450.9(9)	5009.0(18)	4801.2(17)
Z	2	4	8	8
D_{calcd}/g cm^{-3}	1.526	1.400	1.358	1.378
μ/mm^{-1}	1.428	1.136	1.005	1.047
F(000)	912	1080	2144	2080
Crystal size/mm	0.30 × 0.20 × 0.04	0.30 × 0.13 × 0.08	0.20 × 0.24 × 0.10	0.17 × 0.13 × 0.07
θ range [°]	2.15–27.47	1. 78–27.42	2.07–27.44	2.13–25.50
Limiting indices	$-12 \leq h \leq 11$	$-15 \leq h \leq 12$	$-18 \leq h \leq 20$	$-38 \leq h \leq 38$
	$-24 \leq k \leq 19$	$-22 \leq k \leq 22$	$-21 \leq h \leq 17$	$-12 \leq k \leq 12$
	$-14 \leq l \leq 14$	$-12 \leq l \leq 15$	$-24 \leq h \leq 24$	$-18 \leq l \leq 18$
No. of rflns collected	15 557	19 496	37 551	27 177
No. unique rflns [R(int)]	4403 (0.0672)	5525 (0.0983)	5709(0.0906)	4466(0.0755)
No. of params	262	303	289	327
Completeness to θ [%]	99.8%	99.1%	99.8%	99.9%
Goodness of fit on F^2	1.347	1.412	1.463	1.377
Final R indices [$I > 2\sum(I)$]	$R_1 = 0.0845$	$R_1 = 0.1587$	$R_1 = 0.1399$	$R_1 = 0.0908$
	w$R_2 = 0.1972$	w$R_2 = 0.3174$	w$R_2 = 0.2849$	w$R_2 = 0.1570$
R indices (all data)	$R_1 = 0.0966$	$R_1 = 0.1804$	$R_1 = 0.1515$	$R_1 = 0.0959$
	w$R_2 = 0.2036$	w$R_2 = 0.3330$	w$R_2 = 0.2953$	w$R_2 = 0.1591$
Largest diff peak and hole/e Å^{-3}	0.683 and −0.829	0.630 and −0.620	0.559 and −0.871	0.400 and −0.327

[2,4,6-Trimethyl-*N*-(2-phenyl-5,6,7-trihydroquinolin-8-ylidene)-phenylamino]nickel(II) dichloride (**Ni9**) was obtained as green powder in 78.0% yield. IR (KBr; cm^{-1}): 2247, 2927, 1566 (νC=N), 1406, 1342, 1214, 1124, 1034, 1010, 681, 615, 480. Anal. calcd for $C_{24}H_{24}Cl_2N_2Ni$(470): C, 61.32; H, 5.15; N, 5.96%. Found: C, 61.44; H, 5.39; N, 6.20%. MS-ESI: calcd for $C_{24}H_{24}Cl_2N_2Ni$ m/z 468.0, found m/z 433.1 $(M - Cl)^+$.

[2,6-Diethyl-4-methyl-*N*-(2-phenyl-5,6,7-trihydroquinolin-8-ylidene)phenylamino]nickel(II) dichloride (**Ni10**) was obtained as green powder in 81.6% yield. IR (KBr; cm^{-1}): 3305, 2601, 1567 (νC=N), 1417, 1344, 1234, 1120, 1033, 764, 682, 504. Anal. calcd for $C_{26}H_{28}Cl_2N_2Ni$(498): C, 62.69, H, 5.67; N, 5.62%. Found: C, 62.76, H, 5.54; N, 5.69%. MS-ESI: calcd for $C_{26}H_{28}Cl_2N_2Ni$ m/z 496.1, found m/z 461.1 $(M - Cl)^+$.

General procedure for ethylene oligomerization at 10 atm of ethylene pressure

Ethylene oligomerization was performed in a stainless steel autoclave (300 mL capacity) equipped with gas ballast through a solenoid clave for continuous feeding of ethylene at constant pressure. 50 mL of toluene was added into the autoclave under ethylene atmosphere. The catalyst was dissolved in 20 mL toluene in a Schlenk tube with stirring. When the desired reaction temperature was reached, the catalyst dissolved in 20 mL toluene, the desired amount of cocatalyst and the remained toluene (total volume was 100 mL) were added in turn by syringes. Ethylene at the desired pressure was introduced to start the reaction. After stirred for the desired period of time, the reaction was stopped with ceasing the ethylene inputting. The autoclave was cooled in an ice-water bath, and then the pressure was released. 2 mL the reaction solution was collected and terminated by addition of 4 mL 10% aqueous hydrogen chloride. The organic was collected and analyzed by gas chromatography (GC) to determine the composition and mass distribution of the oligomers. The remaining reaction solution was quenched with 5% hydrogen chloride ethanol.

X-Ray crystallographic studies

Single crystals of **Ni2**, **Ni3·CH_2CH_3OH**, **Ni8** and **Ni10** suitable for X-ray diffraction analysis were obtained by laying diethyl ether on their ethanol solution at room temperature. With graphite-monochromatic Mo Ka 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. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC 779268 (**Ni2**), 779269 (**Ni3·CH_2CH_3OH**), 779270 (**Ni8**) and 779271 (**Ni10**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/c0nj00516a

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Conclusions

The molecular structures of nickel complexes revealed a four-coordination number around nickel with 2-phenyl substituted ligands, and five-coordination number around nickel with 2-chloro substituted ligands. All title nickel catalysts perform high activities in ethylene oligomerization with high selectivity of butenes and hexenes; and catalysts bearing 2-chloro substituted ligands generally show better activity than their analogues ligating 2-Ph substituted ligands.

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