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2-[1-(2,6-Dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(arylimino)ethyl] pyridylnickel(II) halides: Synthesis, characterization and ethylene oligomerization behavior

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1. Introduction

Late-transition metal pre-catalysts have attracted much attention with respect to ethylene polymerization and oligomerization in last two decades, and notable achievements are reflected in a number of review articles [1-6]. The resurrection of latetransition metal complex pre-catalysts for ethylene reactivity was initiated after pioneer work on nickel or palladium complexes bearing α -diimine ligands [7–9], together with work on iron or cobalt complexes containing bis(imino)pyridines [10,11], and subsequently, the number of research papers has mushroomed, and these employ a variety metals [12–16] such as iron, cobalt, nickel, or palladium and various ligand sets. In general, it has proved possible to control their catalytic behavior in ethylene oligomerization and/or polymerization through modifying the ligand backbones [17] or the *N*-bound aryl groups [18–25]. α-Diimine ligands are well-known in the area of ethylene polymerization and oligomerization due to their important feature of easily varied steric and

ABSTRACT

A series of nickel(II) halide complexes ligated by 2-[1-(2,6-dibenzhydryl-4-methyl-phenylimino)ethyl]-6-[1-(arylimino)-ethyl]pyridines was synthesized and characterized by FT–IR spectroscopy and elemental analysis. Single-crystal X-ray crystallographic studies revealed that the nickel halide complexes possess pseudo square-pyramidal geometry at nickel. Following screening with the co-catalysts Et₂AlCl, MAO, MMAO and ethylaluminum sesquichloride (EASC, Et₃Al₂Cl₃), EASC was chosen as the co-catalyst of choice, and activities as high as 2.5×10^6 g mol⁻¹ (Ni) h⁻¹ were observed for ethylene oligomerization. The influence of the ligands and of the reaction parameters on the catalytic behavior of the nickel precatalysts was investigated.

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electronic properties [26–28]. In addition, much academic work focuses on elucidating the reactive species [29-36] and on the formation of self-activating catalysts [37,38]. This is particularly the case for bis(imino)pyridyl derivatives, which have also made a huge impact on the ethylene polymerization and oligomerizaion field. We have been attracted by the use of N^N bi-dentate pre-catalysts and have designed a number of new ligand sets, namely 2-(2pyridyl)quinoxaline [39], 2-ethylcarboxylate-6-iminopyridine [40], and pyrazolyliminophosphorane [41]. In addition, we also reported some new N^N^N tridentate ligands, such as 2-imino-1,10-phenanthrolines [42,43], 2-benzimidazolyl-6-(1-(arylimino) ethyl)pyridines [44-47], 2-quinoxalinyl-6-imino-pyridines [48], 2-(benzimidazol-2-yl)-1,10-phenanthrolines [49], 2-(benzoxazolyl)-1,10-phenanthrolines [50] and 8-(1-aryliminoethylidene) quinaldines [51]. By employing these ligands, numerous metal complex pre-catalysts have been developed, and some of them have performed with high catalytic activities in either the oligomerization or polymerization of ethylene.

Recently nickel complex pre-catalysts bearing bi-dentate ligands have been highlighted due to their high activity and enhanced thermo-stability, which has been achieved via the use of unsymmetrical bulky diimines [52]. Interestingly, the alternative bi-dentate ligands N-(5,6,7-trihydroquinolin-8-ylidene)arylamines, when coordinated to nickel exhibited different ethylene

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reactivity, and high polymerization was achieved by derivatives bearing ligands without substituents at their 2-positions [53,54]. By contrast, high oligomerization activity was observed when employing 2-substituted N-(5,6,7-trihydroquinolin-8-ylidene) arylamines [55] or tridentate pyrazolyl [56-58]. On extending the work with bulky unsymmetrical diimino nickel pre-catalysts [52]. a number of bulky unsymmetrical bis(imino)pyridines were developed for iron and cobalt and were found to be highly active and thermally-stable [59,60]. Given this, the synthesis of bulky unsymmetrical bis(imino)pyridylnickel complexes became an attractive target, with a view to examining their catalytic behavior. Herein, the nickel complexes, 2-[1-(2,6-dibenzhydryl-4methylphenylimino)ethyl]-6-[1-(arylimino)ethyl]pyridyl nickel(II) dibromide or dichloride, are synthesized and fully characterized. When activated with ethylaluminum sesquichloride (EASC, Et₃Al₂Cl₃), all nickel complex pre-catalysts performed with high activity and good selectivity in ethylene dimerization.

2. Results and discussion

2.1. Synthesis and characterization of the nickel(II) complexes (Ni1–Ni10)

The ligands 2-[1-(2,6-dibenzhydryl-4-methylphenylimino) ethyl]-6-[1-(arylimino) ethyl]pyridines (**L1–L5**), were prepared by the reported procedures [60,61], The stoichiometrical reaction of the ligands (**L1–L5**) with (1,2-dimethoxyethane)nickel bromide or chloride in ethanol led to the corresponding nickel(II) halides in good yields (Scheme 1). The elemental analysis data of all the nickel complexes are consistent with their formula. In the FT–IR spectra, the C=N stretching vibration bands of the nickel(II) complexes appear in the range of 1583–1588 cm⁻¹ instead of those observed in the region 1635–1642 cm⁻¹ for the free ligands [59], indicating the effective coordination to nickel.

2.2. Crystal structures

To confirm the unambiguous molecular structures, single-crystals of the complexes **Ni4**, **Ni5** and **Ni6** were grown from their dichloromethane solutions layered with diethylether at room temperature. A pseudo square-pyramidal geometry at nickel was observed for all three nickel complexes; their selected bond lengths and angles are tabulated together in Table 1, and the molecular structures of three nickel complexes are shown in Figs. 1–3, respectively.

In complex **Ni4** as shown in Fig. 1, three coordinated nitrogen atoms and two bromides are situated around the nickel center. The

Table	1	
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Bond lengths (Å) and bond angles (°) for complexes **Ni4**, **Ni5** and **Ni6**.

	$\textbf{Ni4} \left(X = Br \right)$	$\textbf{2Ni5} \; (X=Br)$		Ni6 (X = Cl)
		Ni5	Ni5A	
Bond lengths (Å)				
Ni(1) - N(1)	2.193(4)	2.166(6)	2.155(7)	2.155(3)
Ni(1)-N(2)	1.955(4)	1.999(6)	1.957(7)	1.974(3)
Ni(1)-N(3)	2.141(4)	2.147(6)	2.149(7)	2.139(3)
Ni(1)-X(1)	2.3712(10)	2.3747(14)	2.3585(14)	2.2185(13)
Ni(1)-X(2)	2.4338(10)	2.4468(15)	2.4748(13)	2.3118(13)
N(1) - C(6)	1.294(6)	1.303(9)	1.279(10)	1.288(5)
N(1) - C(10)	1.421(6)	1.470(10)	1.435(11)	1.454(5)
N(2) - C(1)	1.341(6)	1.312(9)	1.334(11)	1.336(5)
N(2) - C(5)	1.357(6)	1.332(9)	1.378(11)	1.340(5)
N(3)-C(8)	1.271(6)	1.258(10)	1.310(11)	1.280(5)
N(3)-C(43)	1.461(6)	1.456(9)	1.424(11)	1.447(5)
Bond angles (°)				
N(2)-Ni(1)-N(3)	77.45(17)	76.4(2)	77.5(3)	77.60(13)
N(2)-Ni(1)-N(1)	76.42(17)	76.3(2)	77.3(3)	76.32(13)
N(3)-Ni(1)-N(1)	150.97(16)	148.5(2)	149.7(3)	149.14(13)
N(2)-Ni(1)-X(1)	156.60(13)	160.5(2)	160.17(18)	159.52(12)
N(3) - Ni(1) - X(1)	101.47(12)	101.54(18)	99.16(18)	100.57(10)
N(1)-Ni(1)-X(1)	97.51(11)	98.92(16)	98.79(17)	98.11(9)
N(2) - Ni(1) - X(2)	91.44(12)	90.89(19)	90.42(18)	88.99(11)
N(3) - Ni(1) - X(2)	94.88(11)	95.84(19)	96.66(17)	98.27(10)
N(1)-Ni(1)-X(2)	98.20(10)	99.99(16)	100.07(16)	97.49(9)
Br(1)-Ni(1)-X(2)	111.88(3)	108.61(5)	109.41(5)	111.38(6)

N(1), N(2), N(3) and one bromine atom, Br(1), are located in a square plane, and bond angles almost form a right angle such as N(2)–Ni(1)–Br(2), 91.44(12)°. In addition, the Ni–N_{imino} bond lengths are almost equal, with Ni(1)–N(1), 2.193(4) Å and Ni(1)–N(3) 2.141(4) Å, which both are longer than the Ni–N_{pyridine} bond, Ni(1)–N(2), 1.955(4) Å. The bond lengths of N(1)–C(6) 1.294(6) Å and N(3)–C(8) 1.271(6) Å are indicative of the double bonding characteristic of the C=N moiety.

There are two independent molecules of complex **Ni5** in the solid state, and the molecular structures are shown in Fig. 2. The N(2)-Ni(1)-Br(2) bond angle is 90.89(19)° and the N(2A)-Ni(1A)-Br(2A) bond angle is 90.42(18)°, which in both cases more closely approach a right angle than the angles observed in complex **Ni4**. Moreover, the Ni(1)-N(2) and Ni(1A)-N(2A) bond lengths are significantly shorter than the other two Ni-N bond lengths in complex **Ni5**, indicating stronger coordination. Other structural features of complex **Ni5** are similar to those of **Ni4**, with the slight differences caused by the diethyl substituents of **Ni5** versus the dimethyl of **Ni4**.

The structure of the chloride complex **Ni6** was also determined and is shown in Fig. 3. A similar coordination geometry around the



Scheme 1. Synthesis of nickel(II) complexes.



Fig. 1. ORTEP drawing of complex Ni4 with thermal ellipsoids at 30% probability level. Hydrogen atoms have been omitted for clarity.



Fig. 2. ORTEP drawing of complex Ni5 with thermal ellipsoids at 30% probability level. Hydrogen atoms have been omitted for clarity.



Fig. 3. ORTEP drawing of complex Ni6 with thermal ellipsoids at 30% probability level. Hydrogen atoms have been omitted for clarity.

nickel center is observed, closely approaching that observed for **Ni5**, with bonding of Ni(1)–N(2) being stronger than either Ni(1)–N(1) and Ni(1)–N(3) in **Ni6**. The Ni–Cl bond lengths are commonly longer than the Ni–Br bonds of their analogs **Ni4** and **Ni5**, indicating the weaker bonding of the chloride to the nickel center.

2.3. Ethylene dimerization by nickel(II) pre-catalysts

When regarding the influence of the bromide and chloride ligation, the two series of nickel complexes can be considered separately. Given that the anionic influence probably does not affect the nature of the alkylaluminium co-catalysts, one bromide complex **Ni4** was selected to screen for a suitable co-catalyst.

2.3.1. Co-catalysts selection

The influence of different alkylaluminium reagents was investigated by employing complex Ni4 pre-catalyst in order to find the most suitable co-catalyst. However, as low activity was observed at atmospheric pressure, further explorations were carried out at 10 atm ethylene pressure. The function of co-catalyst is not only the alkylation of nickel halide complex, but also to allow for the formation of the active species in the presence of 'detrimental' impurities such as moisture and oxygen. Given this, a minimum amount of MAO/MMAO is required, and this is commonly higher than the required minimum needed when using diethylaluminum chloride (Et₂AlCl) or ethylaluminum sesquichloride (Et₃Al₂Cl₃, EASC) as co-catalyst. The evaluation results are tabulated in Table 2 with co-catalysts such as Et₂AlCl, MAO, MMAO and EASC. It is clear to see that the most suitable co-catalyst is EASC, and when activated with EASC, the catalytic system employing Ni4 achieved the highest productivity at 10 atm ethylene pressure. Thus, the cocatalyst EASC was selected for all further investigations.

2.3.2. Effects of the molar ratio of Al/Ni and the reaction temperature

Over the range 200–700 molar ratio of EASC/**Ni4** (Table 3, entries 1–7) under 10 atm ethylene at room temperature, the highest activity was observed with an Al/Ni ratio of 500:1, indicating that the active species required an optimum amount of alkylaluminium reagent, but that either lower or higher ratios were detrimental to these optimum conditions. On increasing the Al/Ni molar ratio, more

Table 2		
Selection	of suitable co-catalyst based on Ni4	1 ^a

Entry	Co-cat.	Al/Ni	T(°C)	Activity ^b	Oligomerization distribution (%) ^c		
					C₄/∑C	$C_6 / \sum C$	α-C ₄
1	Et ₂ AlCl	200	25	0.99	57.5	42.5	100
2	Et ₂ AlCl	300	25	2.28	79	21	97.5
3	MAO	1000	25	0.36	100	0	92.7
4	MMAO	1000	25	4.29	98.5	1.5	98.5
5	MMAO	1500	25	5.33	99.1	0.9	99.1
6	EASC	200	25	6.72	98.6	1.4	98.0

 $^{a}\,$ Conditions: 5 μmol Ni4, 100 mL toluene, 10 atm ethylene, 30 min.

^b 10⁴ g mol⁻¹ (Ni) h⁻¹

^c Determined by GC and $\sum C$ signifies the total amounts of oligomers.

hexenes are produced (entries 1–6, Table 3); it is possible to have active nickel species with a bi-dentate manner of ligands due to the possible coordination of the excessive amount of aluminum with one of the imino-nitrogen [61]. In addition, it was found that the activity for ethylene oligomerization initially increased with the optimum ratio of Al/Ni 500 (entries 1–6, Table 3), and good selectivity for 1-butene was observed (87.1–98.6%; the exception was run 11 at 45.9%, see Table 3). The activity observed for ethylene oligomerization decreased greatly when the ratio was 700, but with higher selectivity for hexenes. Given this, further experiments were performed at the molar ratio of Al/Ni 500:1.

On increasing the reaction temperature from 25 to 100 °C, the trend for oligomerisation activity is the same as that for the influence of the molar ratio of Al/Ni (entries 3 and 7–11, Table 3). This could be due to the deactivation of the active species and lower ethylene solubility [62] at higher temperature. In light of the observations, the best activity was observed at 40 °C (entry 8, Table 3). This phenomenon is different from that usually observed for nickel(II) complexes bearing 2-benzimidazolylpyridine [63] and N-(2-(1H-benzoimidazol-2-yl)quinolin-8-yl)benzamide [64], which perform best (highest activity) at 20 °C. Interestingly, the distribution of oligomers and α -olefin selectivity were far less affected by the Al/Ni molar ratio; however, when the reaction temperature was increased to 100 °C, the amount of butenes was drastically reduced to 45.9% with the lower selectivity of α -C4 (54.2%) and higher hexenes (54.1%). This elevation in temperature had an influence on the oligomerization activity, which could be

Table 3

Ethylene catalytic activity with Ni1-Ni5/EASC system.^a

Entry	Cat.	Al/Ni	t (min)	T (°C)	Activity ^b	Oligomerization distribution (%) ^c		
						$C_4/\sum C$	$C_6/\sum C$	α-C ₄
1	Ni4	200	30	25	6.72	98.6	1.4	98.0
2	Ni4	400	30	25	7.65	97.1	2.9	96.5
3	Ni4	500	30	25	8.24	96.1	3.9	99.1
4	Ni4	550	30	25	3.99	95.2	4.8	98.4
5	Ni4	600	30	25	2.45	94.8	5.2	97.3
6	Ni4	700	30	25	0.49	87.1	12.9	95.9
7	Ni4	500	30	30	8.74	95.6	4.4	96.9
8	Ni4	500	30	40	13.3	95.4	4.6	95.8
9	Ni4	500	30	50	12.6	95.0	5.0	95.6
10	Ni4	500	30	80	11.7	95.0	5.0	90.0
11	Ni4	500	30	100	9.15	45.9	54.1	54.2
12	Ni4	500	15	40	23.7	95.5	4.5	95.7
13	Ni4	500	60	40	7.5	95.2	4.8	94.9
14	Ni1	500	30	40	17.0	95.5	4.5	97.2
15	Ni2	500	30	40	14.6	97.8	2.2	94.2
16	Ni3	500	30	40	7.4	95.1	4.9	94.5
17	Ni5	500	30	40	2.8	93.4	6.6	97.2

 $^a\,$ Conditions: 5 $\mu mol~\text{Ni},$ 100 mL toluene, 10 atm ethylene.

^b 10⁴ g mol⁻¹ (Ni) h⁻

 $^{\rm c}\,$ Determined by GC and $\sum C$ signifies the total amounts of oligomers.

attributed to the isomerization or the faster chain transfer at higher temperature.

2.3.3. Lifetime of the active species

For any catalyst, one of the most important factors is to maintain activity over a prolonged period in order to be feasible for industrial applications. Therefore, using EASC as co-catalyst, the nickel complex **Ni4** and an Al/Ni molar ratio of 500 at 40 °C, the effect of the reaction time on the catalytic activity was investigated over 60 min. On extending the reaction time from 15 min to 60 min, the oligomerization activity decreased (entries12 and 13, Table 3). Similar phenomena were also observed for ethylene oligomerization using nickel(II) catalysts bearing N-((pyridin-2-yl)methyl-ene) quinolin-8-amine [65] and (pyrazol-1-ylmethyl)pyridine [66].

2.3.4. Effect of the ligand environment

In order to investigate the catalytic behavior of these tridentate nickel(II) dibromide complexes on variation of the substituents on the ligands, the activity and distribution of ethylene oligomerization were investigated using **Ni1–Ni5**. Using the optimized reaction conditions (entry 8, Table 3), all the title nickel(II) dibromide pre-catalysts(**Ni1–Ni5**) exhibited catalytic activity toward ethylene oligomerization (Table 3). According to the data in Table 3, the variation of the ligand environment, caused by changing the substituents on the aryl ring linked to the imino-nitrogen atom, had a great influence on the catalytic behavior of the (**Ni1–Ni5**)/EASC system for ethylene reactivity. The order decreased through **Ni1** [2,6-di(Me)] > **Ni2**[2,6-di(Et)] > **Ni3**[2,6-di(i-Pr)] and **Ni4**[2,4,6-tri(Me)] > **Ni5**[2,6-di(Et)–4-Me], which is the same order as observed for nickel(II) catalysts ligated by 2-(benzoimidazol-2-yl)-6-(1-aryliminoethyl)pyridines [67].

2.4. Ethylene activation behavior of the N^N^N coordinated nickel(II) dichloride complexes

Similar to the nickel(II) dibromide complexes, the Al/Ni molar ratio, the reaction temperature, time and the nature of the complexes have been shown to have an influence on the activities, distribution of oligomers and the α -olefin selectivity. Using the optimized oligomerization reaction temperature for the nickel(II) dibromide complexes, viz 40 °C, the ethylene activation behavior of the chloride Ni6/EASC system was investigated (entries 1-6 in Table 4). The optimum Al/Ni ratio, 300, was found by increasing the molar ratio of Al/Ni from 100 to 500, and with this molar ratio fixed, the influence of the reaction temperature was investigated (entries 7–11 in Table 4). It was found that the highest activity was observed at 40 °C, which is the same as the observation by its bromide analog. Thus, using EASC as co-catalyst, the best performance for ethylene oligomerization activity was obtained with Ni6/EASC at 40 °C and with the Al/Ni molar ratio of 300 (entry 3 in Table 4) under 10 atm. In addition, the catalytic activity of Ni6 was increased greatly to 2.5 \times $10^{6}~g~mol^{-1}$ (Ni) $h^{-1}\!$, when 20 equiv. of PPh_3 was added into the catalytic system, while the selectivity for α -C₄ was dramatically decreased (entry 4 in Table 4). This may be attributed to the protecting of the auxiliary PPh₃ for the active species during the catalytic reaction, and inducing isomerization along with β -hydrogen elimination; this phenomena was consistent with previous results [68–74].

Finally, the oligomerization behavior of the nickel(II) dichloride complexes were investigated using EASC at 40 °C and an Al/Ni molar ratio of 300 under 10 atm ethylene (entries 3 and 12–15, Table 4). Compared with the behavior for the nickel(II) dibromide complexes **Ni1–Ni5**, the dichloride complexes exhibited much higher catalytic activities with a similar order as their bromide analogs, **Ni9** > **Ni10** and **Ni6** > **Ni7** > **Ni8**. Presumably the higher

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lable 4			
Ethylene catal	ytic activity with	Ni6-Ni10/E	ASC system. ^a

Entry	Complex	Al/Ni	<i>t</i> (min)	T (°C)	Activity ^b	Oligomer distribution (%)		ition ^c
						$C_4/\sum C$	$C_6/\sum C$	α-C ₄
1	Ni6	100	30	40	0.718	95.9	4.1	92.2
2	Ni6	200	30	40	4.12	95.7	4.3	90.1
3	Ni6	300	30	40	4.2	95.8	4.2	89.7
4 ^d	Ni6	300	30	40	24.8	93.7	6.3	36.1
5	Ni6	400	30	40	3.24	95.8	4.2	92.8
6	Ni6	500	30	40	2.78	97.3	2.7	93.4
7	Ni6	300	30	25	1.56	97.1	2.9	96.5
8	Ni6	300	30	30	2.3	96.4	3.6	93.2
9	Ni6	300	30	50	4.18	95.4	4.6	88.1
10	Ni6	300	30	60	4.11	93.0	7.0	83.5
11	Ni6	300	30	80	2.01	90.2	9.8	92.3
12	Ni7	300	30	40	2.67	95.4	4.6	95.8
13	Ni8	300	30	40	1.01	95.0	5.0	87.1
14	Ni9	300	30	40	2.03	95.9	4.1	93.9
15	Ni10	300	30	40	1.58	95.8	4.2	92.5
16	Ni6	300	15	40	7.9	94.6	5.4	91.7
17	Ni6	300	60	40	2.3	95.2	4.8	93.1

^a Conditions: 5 µmol **Ni**, 100 mL toluene, 10 atm ethylene, 30 min.

^b 10⁵ g mol⁻¹ (Ni) h⁻¹

^c Determined by GC and \sum C signifies the total amounts of oligomers.

^d 20 equiv. of PPh₃.

chloride activity is associated with higher net charge of the metal center [75–77]. We note however that the reverse trend was observed for the family of 8-(1-aryliminoethylene)quinalinyl nickel dihalide complexes due to the better solubility of the bromide complexes [51].

Table 5

Crystal data and structure refinement details for Ni4, Ni5 and Ni6.

	Ni4	2Ni5	Ni6
Empirical formula	C ₅₁ H ₄₇ Br ₂ N ₃ Ni	C106H101Br4N6Ni2	C ₅₀ H ₄₅ Cl ₂ N ₃ Ni
Fw	920.45	1895.99	817.50
T (K)	173(2)	293(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073 A
Cryst system	Monoclinic	Triclinic	Monoclinic
Space group	P2(1)/c	P-1	P2(1)/n
a (Å)	17.446(4)	13.329(3)	9.6228(19)
b (Å)	15.401(3)	16.784(3)	34.330(7)
<i>c</i> (Å)	18.774(4)	24.933(5)	13.403(3)
α (°)	90	81.55(3)	90
β(°)	105.01(3)	80.58(3)	106.87(3)
γ (°)	90	87.66(3)	90
$V(Å^3)$	4872.6(17)	5441.8(19)	4237.1(15)
Ζ	4	2	4
Dcalcd. (g cm ⁻³)	1.255	1.157	1.282
$\mu ({\rm mm^{-1}})$	2.072	1.857	0.622
F(000)	1888	1950	1712
Cryst size (mm)	$0.24 \times 0.21 \times 0.18$	$0.35\times0.28\times0.22$	$\textbf{0.20} \times \textbf{0.17} \times \textbf{0.10}$
θ range (°)	1.73–7.47	0.84-27.47	2.39-27.46
Limiting indices	$-22 \le h \le 16$	$-17 \le h \le 17$	$-12 \le h \le 7$
	$-19 \le k \le 13$	$-21 \le k \le 1$	$-44 \le k \le 26$
	$-24 \le l \le 24$	$-21 \le l \le 32$	$-17 \leq l \leq 16$
No. of rflns collected	21,375	46,060	18,586
No. unique rflns [R(int)]	11,019 (0.0663)	24,281 (0.0797)	9574 (0.0542)
Completeness to θ (%)	98.8%	97.4%	98.6%
Data/restraints/	11,019/0/514	24,281/0/1063	9574/0/505
Goodness of fit on F^2	1.038	1.030	1.104
Final <i>R</i> indices	R1 = 0.0737	R1 = 0.1019	R1 = 0.0863
$[I > 2\sigma(I)]$	wR2 = 0.1883	wR2 = 0.2774	wR2 = 0.2044
<i>R</i> indices (all data)	R1 = 0.1037	R1 = 0.1523	R1 = 0.1112
	wR2 = 0.2092	wR2 = 0.3145	wR2 = 0.2240
Largest diff peak and hole (e Å ⁻³)	0.477 and -0.721	0.849 and -1.183	0.481 and -0.472

For the dichloride catalysts, the reaction time played the same important role on the influence of the catalytic activity as for the nickel(II) dibromide complexes (entries 16 and 17, Table 4). For example, when the reaction time was extended from 15 min to 60 min, the oligomerization activity decreased.

3. Conclusion

A series of nickel(II) dibromide and dichloride catalysts bearing 2-[1-(2,6-dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(arylimino)ethyl]pyridyl were synthesized and fully characterized. With EASC as co-catalyst, these complexes could be easily activated and showed high activities for ethylene oligomerization with moderate to good selectivities for 1-butene (54.2–99.1%) at 10 atm ethylene pressure. However, the **Ni4**/EASC system exhibited different oligomerization behavior, and selectivity for hexenes, which substantially increased from 3.9% to 54.1%, when the reaction temperature was elevated from 25 °C to 100 °C. The catalytic activity for ethylene oligomerization and selectivity for butenes and hexenes could be easily controlled by altering the reaction conditions such as temperature and the molar ratio of Al/Ni.

4. Experiment

4.1. General considerations

All manipulations of air- and moisture-sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk techniques. Before use, toluene was refluxed over sodiumbenzophenone and distilled under nitrogen. Methylaluminoxane (MAO, 1.46 M solution in toluene) and modified methylaluminoxane(MMAO, 1.93 M in heptane, 3A) were purchased from Akzo Nobel Corp. Ethylaluminum sesquichloride (EASC, 0.87 M in toluene) and diethylaluminum chloride (Et₂AlCl, 0.5 M in toluene) were purchased from Acros Chemicals. High-purity ethylene was purchased from Beijing Yansan Petrochemical Company and used as received. Other reagents were purchased from Aldrich, Acros, or local suppliers. FT-IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer. Elemental analysis was carried out using a Flash EA 1112 microanalyzer. GC analyses were 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.

4.2. Synthesis of title nickel complexes

4.2.1. 2-[1-(2,6-Dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(2,6-dimethylphenylimino)ethyl]pyridine NiBr₂ (**Ni1**)

The complexes **Ni1–Ni5** were synthesized in the same manner by the reaction of (DME)NiBr₂ with the corresponding 2-[1-(2,6dibenzhydryl-4-methylphenylimino) ethyl]-6-[1-(arylimino)ethyl] pyridine ligands in dichloromethane.

A typical synthesis of complex **Ni1** is described as follows: the ligand **L1** (0.1374 g, 0.20 mmol) and (DME)NiBr₂ (0.0617 g, 0.20 mmol) were added to a Schlenk tube together with 5 mL of dichloromethane and then the reaction mixture was stirred for 8 h at room temperature. Diethylether (10 mL) was added in order to precipitate the complex when the reaction was finished, and then the precipitate was washed with diethylether (3×5 mL) and dried under vacuum to obtain a brown powder of **Ni1** in 75.06% (0.14 g) yield. Anal. Calcd for C₅₀H₄₅Br₂N₃Ni (906.41): C, 66.25; H, 5.00; N, 4.64. Found: C, 66.14; H, 5.22; N, 4.35. FT–IR (Diamond disk, cm⁻¹): 3024, 1976, 1588 (ν_{C} =N), 1494, 1445, 1371, 1262, 1217, 1078, 1030, 862, 803, 748, 702.

4.2.2. 2-[1-(2,6-Dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(2,6-diethylphenylimino)ethyl]pyridine NiBr₂ (**Ni2**)

Obtained as brown powder in 59.8% (0.11 g) yield. Anal. Calcd. for $C_{52}H_{49}Br_2N_3Ni$ (931.47): C, 66.84; H, 5.29; N, 4.50. Found: C, 66.54; H, 5.31; N, 4.33. FT–IR (Diamond disk, cm⁻¹): 2967, 1975, 1584 (ν_C =N), 1494, 1447, 1371, 1260, 1215, 1077, 1031, 918, 864, 805, 769, 746, 702.

4.2.3. 2-[1-(2,6-Dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(2,6-diisopropylphenylimino)ethyl]pyridine NiBr₂ (**Ni3**)

Obtained as brown powder in 81.29% (0.16 g) yield. Anal. Calcd. for $C_{54}H_{53}Br_2N_3Ni$ (962.52): C, 67.38; H, 5.55; N, 4.37. Found: C, 67.28; H, 5.64; N, 4.25. FT–IR (Diamond disk, cm⁻¹): 3058, 2961, 2165, 2024, 1584 (ν_C =N), 1494, 1447, 1371, 1320, 1263, 1210, 1099, 1031, 795, 769, 746, 700.

4.2.4. 2-[1-(2,6-Dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(2,4,6-trimethylphenylimino)ethyl]pyridine NiBr₂ (**Ni4**)

Obtained as brown powder in 83.7% (0.23 g) yield. Anal. Calcd. for $C_{51}H_{47}Br_2N_3Ni$ (920.44): C, 66.55; H, 5.15; N, 4.57. Found: C, 66.35; H, 5.03; N, 4.62. FT-IR (Diamond disk, cm⁻¹): 3024, 2166, 2030, 1978, 1586 (ν_{C}), 1494, 1445, 1371, 1264, 1222, 1184, 1077, 1032, 859, 808, 747, 700.

4.2.5. 2-[1-(2,6-Dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(2,6-diethyl-4-methylphenylimino)ethyl]pyridine NiBr₂ (**Ni5**)

Obtained as brown powder in 63.6% (0.12 g) yield. Anal. Calcd. for $C_{53}H_{51}Br_2N_3Ni$ (948.49): C, 67.11; H, 5.42; N, 4.43. Found: C, 67.02; H, 5.54; N, 4.23. FT–IR (Diamond disk, cm⁻¹): 3023, 2964, 2030, 1978, 1584 (ν_{C} =N), 1494, 1446, 1371, 1263, 1219, 1078, 1031, 859, 813, 768, 747, 700.

4.2.6. 2-[1-(2,6-Dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(2,6-dimethylphenylimino)ethyl]pyridine NiCl₂ (**Ni6**)

The complexes **Ni6–Ni10** were synthesized in the same manner by the reaction of (DME)NiCl₂ with the corresponding 2-[1-(2,6dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(arylimino)ethyl] pyridine ligands in dichloromethane.

A typical synthesis of complex **Ni6** is described as follows: the ligand **L1** (0.1374 g, 0.20 mmol) and (DME)NiCl₂ (0.0617 g, 0.20 mmol) were added to a Schlenk tube together with 5 mL of dichloromethane and then the reaction mixture was stirred for 8 h at room temperature. Diethylether (10 mL) was added in order to precipitate the complex when the reaction was finished, and then the precipitate was washed with diethylether (3×5 mL) and dried under vacuum to obtain a reddish brown powder of Ni1 in 96.88% (0.16 g) yield. Anal. Calcd. for C₅₀H₄₅Cl₂N₃Ni (817.51): C, 73.46; H, 5.55; N, 5.14. Found: C, 73.21; H, 5.65; N, 5.03. FT–IR (Diamond disk, cm⁻¹): 3352, 2166, 1586 (ν_{C} =N), 1494, 1447, 1371, 1261, 1215, 1078, 1031, 860, 809, 768, 746, 699.

4.2.7. 2-[1-(2,6-Dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(2,6-diethylphenylimino)ethyl]pyridine NiCl₂ (**Ni7**)

Obtained as reddish brown powder in 64.65% (0.16 g) yield. Anal. Calcd. for $C_{52}H_{49}Cl_2N_3Ni$ (845.56): C, 73.86; H, 5.84; N, 4.97. Found: C, 73.65; H, 5.54; N, 5.07. FT–IR (Diamond disk, cm⁻¹): 2914, 2164, 2030, 1978, 1583 ($\nu_C =_N$), 1495, 1446, 1373, 1318, 1256, 1216, 1080, 1032, 866, 809, 772, 747, 704.

4.2.8. 2-[1-(2,6-Dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(2,6-diisopropylphenyl imino)ethyl]pyridine NiCl₂ (**Ni8**)

Obtained as reddish brown powder in 94.36% (0.16 g) yield. Anal. Calcd. for C₅₄H₅₃Cl₂N₃Ni (873.62): C, 74.24; H, 6.11; N, 8.12. Found: C, 74.03; H, 6.22; N, 8.09. FT–IR (Diamond disk, cm⁻¹): 3355, 2961, 2166, 2028, 1621, 1586 (ν_{C} =_N), 1494, 1447, 1371, 1321, 1263, 1211, 1100, 1032, 861, 795, 769, 746, 700.

4.2.9. 2-[1-(2,6-Dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(2,4,6-trimethylphenylimino)ethyl]pyridine NiCl₂ (**Ni9**)

Obtained as reddish brown powder in 93.86% (0.16 g) yield. Anal. Calcd. for C₅₁H₄₇Cl₂N₃Ni (831.54): C, 73.66; H, 5.70; N, 5.05. Found: C, 73.34; H, 5.85; N, 4.96. FT–IR (Diamond disk, cm⁻¹): 3022, 2166, 1977, 1587 (ν_{C} =_N), 1494, 1447, 1371, 1262, 1223, 1079, 1032, 856, 813, 748, 701.

4.2.10. 2-[1-(2,6-Dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(2,6-diethyl-4-methylphenylimino)ethyl]pyridine NiCl₂ (**Ni10**)

Obtained as reddish brown powder in 89.58% (0.15 g) yield. Anal. Calcd. for $C_{53}H_{51}Cl_2N_3Ni$ (948.49): C, 67.11; H, 5.42; N, 4.43. Found: C, 66.98; H, 5.31; N, 4.57. FT–IR (Diamond disk, cm⁻¹): 3372, 3023, 2964, 2165, 2027, 1584 (ν_C =N), 1494, 1449, 1371, 1261, 1219, 1079, 1031, 858, 818, 768, 746, 700.

4.3. X-ray crystallographic studies

X-ray diffraction studies of single-crystal of **Ni4**, **Ni5** and **Ni6** were obtained respectively by slow laying of diethylether on its dichloromethane solution at room temperature. With graphite-monochromated Mo K α radiation (k = 0.71073 Å) at 173(2) K, cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F^2 . All hydrogen atoms were placed in calculated positions. Using the SHELXL-97 package [78], structure solution and refinement were performed. Details of the X-ray structure determinations and refinements are provided in Table 5.

4.4. General procedure for ethylene activation

A 250 mL stainless steel autoclave, equipped with a mechanical stirrer and a temperature controller, was used to perform the reaction of ethylene oligomerization at 10 atm ethylene pressure. Firstly, when the requisite temperature was attained, the complex (5 µmol) was dissolved in 50 mL toluene in a Schlenk tube then injected into the autoclave, which was full of ethylene. Secondly, the require amount of co-catalyst (MAO, MMAO, EASC and Et₂AlCl) and the residual toluene were added continuously by syringe under an ethylene atmosphere (the total volume of toluene was 100 mL). The system was then stirred strongly for the desired time under corresponding pressure of ethylene. On completion, nearly 1 mL of the reaction solution was collected to be analyzed by gas chromatography (GC) to determine the distribution of oligomers obtained after terminating the reaction. The leftover solution was quenched with HCl-acidified ethanol (5%), and the precipitated polyethylene was filtered, washed with ethanol, dried under vacuum at 60 °C and weighed.

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Appendix A. Supplementary material

CCDC 852859, 852860, and 852861 contain the supplementary crystallographic data for the complexes **Ni4**, **Ni5** and **Ni6**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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