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Synthesis, characterization and ethylene oligomerization behavior of 2-(chloro-substituted-1*H*-benzoimidazol-2-yl)-6-(1-aryliminoethyl)pyridylnickel dihalides

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ABSTRACT

A series of 2-(chloro-substituted-1*H*-benzoimidazol-2-yl)-6-(1-aryliminoethyl)pyridines (**L1**–**L6**) was synthesized and fully characterized. They reacted with $NiCl_2$ or (DME)$NiBr_2$ to form the corresponding N^N^N tridentate nickel dichlorides (**C1**–**C6**) or dibromides (**C7**–**C12**). All nickel complexes were characterized by elemental analysis and infrared spectroscopy, while the X-ray diffraction study reveals the distorted octahedral geometry of representative nickel dichloride complex **C3** and nickel dibromide complex **C7**. All nickel complexes, activated with either $Et_3Al_2Cl_3$ or Et_2AlCl, showed good activities in ethylene oligomerization, and notably remarkably high selectivity of α-olefins was achieved in the presence of $Et_3Al_2Cl_3$. The chloro-substituted ligands enhanced the activities of complexes in ethylene polymerization.

1. Introduction

The consumption of α-olefins annually is about 6 million tons [1]. In the preparation by ethylene oligomerization, one of most important processes employs neutral Ni(II) complexes bearing bidentate monoanionic ligands [2–4], a system that has been commercialized since the 1980s [5,6]. Recently, cationic diimino-nickel complexes have been found to be active as procatalysts in ethylene polymerization and oligomerization [7]. Extensive investigations for new procatalysts of various late-transition metal complexes have been conducted [8], and nickel complexes bearing bidentate [9–19] or tridentate ligands [20–24] have been the focus of much research. Beyond our efforts for iron procatalysts in ethylene reactivity [25,26], some nickel procatalysts were also investigated and possessed good activities [27–31]. More recently, the metal complexes ligated by 2-(benzimidazol-2-yl)-6-(1-aryliminoethyl)pyridines have been explored [32–38], and the metal complexes ligated by 2-(1-alkylbenzimidazol-2-yl)-6-(1-aryl-iminoethyl)pyridines (model **A**, Scheme 1) [32–35] possessed lower activity than their analogs bearing 2-(1*H*-benzimidazol-2-yl)-6-(1-aryliminoethyl)pyridines (model **B**, Scheme 1) [36–38]. Extensive work was conducted on substituting the phenyl group of the benzimidazoles, and nickel complexes bearing 6-(methyl-substituted-1*H*-benzoimidazol-2-yl)-2-iminopyridines were studied in ethylene oligomerization (model **C**, Scheme 1) [39]. According to our previous observations, late-transition metal procatalysts containing ligands of electron-withdrawing substituents possessed better catalytic activities [40–43]. With this in our mind, the series of 6-(chloro-substituted-1*H*-benzoimidazol-2-yl)-2-iminopyridines (Scheme 1) was deemed a worthy target (Scheme 1), and the catalytic behavior of corresponding nickel complexes are interesting and compared with their analogs [33,34,37–39].

Employing the previous synthetic procedure [36,44], the 6-(chloro-substituted-1*H*-benzoimidazol-2-yl)-2-acetylpyridine is synthesized with two isomers in the 3:2 ratio of the major 6-(6-chloro-1*H*-benzoimidazol-2-yl)-2-acetylpyridine and the minor 6-(5-chloro-1*H*-benzoimidazol-2-yl)-2-acetylpyridine. Further condensation reactions with anilines produced the corresponding ligands, which when reacted with nickel halides formed the title complexes. All organic compounds and nickel complexes were fully characterized, including the single-crystal X-ray diffraction analysis of complexes **C3** and **C7**. In the presence of Et_2AlCl or $Et_3Al_2Cl_3$ as cocatalyst, all nickel procatalysts showed good activities in ethylene oligomerization. The influences on their catalytic activities and the selectivity of producing α-olefins have been investigated in detail according to the nature of ligands, the Al/Ni molar ratio and reaction temperature. Herein, the syntheses and characterization of the title complexes are reported with their catalytic performance in ethylene oligomerization.

2. Experimental

All experimental manipulations were performed at nitrogen atmosphere using standard Schlenk techniques. Toluene was

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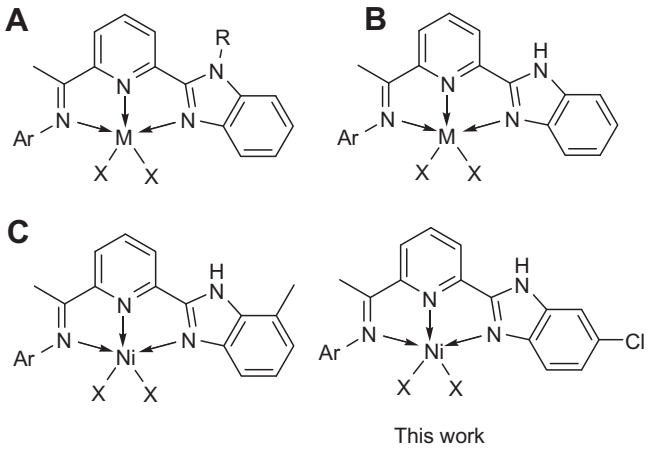


Scheme 1. Metal complexes ligated by 6-(benzoimidazol-2-yl)-2-iminopyridines.

refluxed over sodium-benzophenone and distilled under nitrogen prior to use. Diethylaluminum chloride (Et_2AlCl, 1.7 M in toluene) and ethylaluminum sesquichloride ($Et_3Al_2Cl_3$, 1.7 M in toluene) was purchased from Ablemarle Chemicals. ^1H 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 microanalyzer. 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 percentage.

2.1. Preparation of the organic compounds and nickel complexes

2.1.1. Preparation of 6-(chloro-substituted-1H-benzoimidazol-2-yl)-2-acetylpyridine

According to the synthetic procedure of 6-(1*H*-benzoimidazol-2-yl)-2-acetylpyridine [36], a mixture of diethyl 2,6-bis(β-keto-carboxylate)pyridine [44] (9.27 g, 0.030 mol), 1.5 equivalent molar 4-chlorinebenzene-1,2-diamine (5.49 g, 0.045 mol), and a catalytic amount of *p*-toluenesulfonic acid in the 80 mL solution of toluene and isopropyl alcohol (3:1, v/v) was refluxed for 14 h. A mixture of 20 mL of acetic acid and 5 mL of concentrated HCl was added and continued to reflux for additional 6 h. The resultant solution was cooled to room temperature, and then a 20% KOH solution was added to neutralize the solution to the pH value between 9 and 10. The aqueous phase was extracted with ethyl acetate (20 mL × 3), all organic extracts were combined and dried over anhydrous Na_2SO_4. After drying and purification by column chromatography (alumina column 3/1 petroleum ether/ethyl acetate), the product is obtained as white solids (2.19 g, 27.0% isolated yield) with the ratio of 3:2 for 6-(6-chloro-1*H*-benzoimidazol-2-yl)-2-acetylpyridine and 6-(5-chloro-1*H*-benzoimidazol-2-yl)-2-acetylpyridine. For combined isomers solids: Mp: 186–188 °C. IR (KBr, cm^{-1}): 3398s, 3081w, 3004w, 1692vs, 1454s, 1410s, 1301s, 1207s, 1054s, 922s, 824m. *Anal.* Calc. for $C_{14}H_{10}ClN_3O$ (271.70): C, 61.89; H, 3.71; N, 15.47. Found: C, 62.00; H, 3.75; N, 15.32%. 6-(6-Chloro-1*H*-benzoimidazol-2-yl)pyridine-2-acetylpyridine: δ_H (400 MHz, $CDCl_3$, TMS): 10.37 (s, 1H, N*H*), 8.57 (d, *J* 7.7, 1H, Py), 8.12 (d, *J* 7.7, 1H, Py), 8.02 (t, *J* 7.7, 1H, Py), 7.77 (d, *J* 8.5, 1H, Ph), 7.58 (s, 1H, Ph), 7.31 (t, *J* 8.1, 1H, Ph), 2.84 (s, 3H, C*H*$_3$). δ_C (100 MHz, $CDCl_3$, TMS): 199.1, 156.2, 152.1, 148.6, 146.9, 138.0, 129.8, 128.1, 123.4, 122.7, 112.1, 25.9, 17.4. 6-(5-Chloro-1*H*-benzoimidazol-2-yl)pyridine-2-acetylpyridine: δ_H (400 MHz, $CDCl_3$, TMS): 10.40 (s, 1H, N*H*), 8.57 (d, *J* 7.7, 1H, Py), 8.12 (d, *J* 7.7, 1H, Py), 8.02 (t, *J* 7.7, 1H, Py), 7.84 (s, 1H, Ph), 7.50 (d, *J* 8.5, 1H, Ph), 7.31 (t, *J* 8.1, 1H, Ph), 2.84 (s, 3H, C*H*$_3$). δ_C (100 MHz, $CDCl_3$, TMS): 199.1, 166.5, 153.2, 151.7, 148.6, 145.3, 138.0, 128.4, 128.1, 125.4, 123.8, 122.7, 111.5, 18.0.

2.1.2. Synthesis of 2-(chloro-substituted-1H-benzoimidazol-2-yl)-6-(1-aryliminoethyl)pyridines (**L1**–**L6**)

*2.1.2.1. 6-[1-(2,6-Dimethylphenylimino)ethyl]-2-(6-chloro-1H-benzoimidazol-2-yl)pyridine and 6-[1-(2,6-dimethylphenylimio)ethyl]-2-(5-chloro-1H-benzoimidazol-2-yl)pyridine (**L1**).* A solution of precursor compounds (0.82 g, 3.0 mmol), 2,6-dimethylaniline (0.54 g, 4.50 mmol), and a catalytic amount of *p*-toluenesulfonic acid dissolved in toluene (25 mL) was refluxed for 24 h. After solvent evaporation, the crude product was purified by column chromatography on basic Al_2O_3 with petroleum ether/ethyl acetate (v/v) 8:1 as eluent to afford the product as a light yellow powder in 81.3% (0.91 g) yield and with the ratio of 3:2. For combined isomers solids: Mp: 173–174 °C. IR (KBr, cm^{-1}): 3454w, 3083m, 2968w, 1665vs, 1571m, 1463s, 1433s, 1314s, 1226s, 824s, 789s, 761m. *Anal.* Calc. for $C_{22}H_{19}ClN_4$ (374.87): C, 70.49; H, 5.11; N, 14.95. Found: C, 70.27; H, 5.19; N, 14.68%. 6-[1-(2,6-Dimethylphenylimino)ethyl]-2-(6-chloro-*1H*-benzoimidazol-2-yl)pyridine: δ_H (400 MHz, $CDCl_3$, TMS): 10.54 (s, 1H, N*H*), 8.50 (d, *J* 7.8, 1H, Py), 8.45 (d, *J* 7.8, 1H, Py), 8.00 (t, *J* 7.8, 1H, Py), 7.77 (d, *J* 8.6, 1H, Ph), 7.56 (s, 1H, Ph), 7.28–7.30 (m, 1H, Ph), 7.10 (d, *J* 7.4, 2H, Ph), 6.97 (t, *J* 7.5, 1H, Ph), 2.29 (s, 3H, C*H*$_3$), 2.06 (s, 6H, C*H*$_3$). δ_C (100 MHz, $CDCl_3$, TMS): 166.3, 155.9, 151.6, 148.5, 147.0, 143.2, 137.9, 134.5, 129.7, 128.1, 125.4, 123.7, 123.4, 122.8, 122.6, 121.0, 119.9, 111.4, 18.0, 16.7. (6-[1-(2,6-Dimethylphenylimino)ethyl]-2-(5-chloro-*1H*-benzoimidazol-2-yl)pyridine: δ_H (400 MHz, $CDCl_3$, TMS): 10.57 (s, 1H, N*H*), 8.50 (d, *J* 7.8, 1H, Py), 8.45 (d, *J* 7.8, 1H, Py), 8.00 (t, *J* 7.8, 1H, Py), 7.77 (d, *J* 8.6, 1H, Ph), 7.84 (s, 1H, Ph), 7.48 (d, *J* 8.6, 1H, Ph), 7.28–7.30 (m, 1H, Ph), 7.10 (d, *J* 7.4, 2H, Ph), 6.97 (t, *J* 7.5, 1H, Ph), 2.29(s, 3H, C*H*$_3$), 2.06 (s, 6H, C*H*$_3$). δ_C (100 MHz, $CDCl_3$, TMS): 166.3, 155.9, 151.9, 148.5, 147.0, 145.4, 137.9, 132.5, 128.5, 128.1, 125.4, 124.6, 123.4, 122.9, 122.6, 121.0, 119.9, 112.1, 18.0, 16.7.

*2.1.2.2. 6-[1-(2,6-Diethylphenylimino)ethyl]-2-(6-chloro-1H-benzoimidazol-2-yl)pyridine and 6-[1-(2,6-diethylphenylimino)ethyl]-2-(5-chloro-1H-benzoimidazol-2-yl)pyridine (**L2**).* Using the same procedure as for the synthesis of **L1**, **L2** was obtained as a light yellow powder in 82.3% (1.0 g) yield and with the ratio of 3:2. For combined isomers solids: Mp: 114–117 °C. IR (KBr, cm^{-1}): 3423w, 3062w, 2964m, 1646vs, 1569m, 1459s, 1416s, 1300s, 925m, 807m, 738m. *Anal.* Calc. for $C_{24}H_{23}ClN_4$ (402.92): C, 71.54; H, 5.75; N, 13.91. Found: C, 71.25; H, 5.91; N, 13.61%. 6-[1-(2,6-Diethylphenylimino)ethyl]-2-(6-chloro-*1H*-benzoimidazol-2-yl)pyridine: δ_H (400 MHz, $CDCl_3$, TMS): 10.48 (s, 1H, N*H*), 8.50(d, *J* 7.7, 1H, Py), 8.45 (d, *J* 7.8, 1H, Py), 7.99 (t, *J* 7.8, 1H, Py), 7.77 (d, *J* 8.6, 1H, Ph), 7.55 (s, 1H, Ph), 7.28–7.30 (m, 1H, Ph), 7.13–7.15 (m, 2H, Ph), 7.06(t, *J* 7.3, 1H, Ph), 2.34–2.47(m, 4H, C*H*$_2$), 2.30 (s, 3H, C*H*$_3$), 1.15 (t, *J* 7.4, 6H, C*H*$_3$). δ_C (100 MHz, $CDCl_3$, TMS): 166.1, 156.1, 151.7, 147.5, 146.9, 142.9, 137.9, 134.6, 131.1, 128.4, 126.1, 123.6, 122.7, 122.5, 120.7, 111.5, 24.6, 16.8, 13.8. 6-[1-(2,6-Diethylphenylimino)ethyl]-2-(5-chloro-1*H*-benzoimidazol-2-yl) pyridine: δ_H (400 MHz, $CDCl_3$, TMS): 10.50 (s, 1H, N*H*), 8.50(d, *J* 7.7, 1H, Py), 8.45 (d, *J* 7.8, 1H, Py), 7.99 (t, *J* 7.8, 1H, Py), 7.84(s, 1H, Ph), 7.47 (d, *J* 8.5, 1H, Ph), 7.28–7.30 (m, 1H, Ph), 7.13–7.15 (m, 2H, Ph), 7.06 (t, *J* 7.3, 1H, Ph), 2.34–2.47(m, 4H, C*H*$_2$), 2.30 (s, 3H, C*H*$_3$), 1.15 (t, *J* 7.4, 6H, C*H*$_3$). δ_C (100 MHz, $CDCl_3$, TMS): 166.1, 156.1, 152.1, 147.5, 146.9, 137.9, 132.6, 131.1, 129.7, 126.1, 124.5, 123.6, 122.6, 119.6, 112.2, 24.6, 16.8, 13.8.

*2.1.2.3. 6-[1-(2,6-Diisopropylphenylimino)ethyl]-2-(6-chloro-1H-benzoimidazol-2-yl)pyridine and 6-[1-(2,6-diisopropylphenylimino)ethyl] -2-(5-chloro-1H-benzoimidazol-2-yl)pyridine (**L3**).* Using the same procedures for the synthesis of **L1**, **L3** was obtained as a light yellow powder in 87.4% (1.13 g) yield and with the ratio of 3:2. For combined isomers solids: Mp: 135–139 °C. IR (KBr, cm^{-1}): 3449w, 3064w, 1646vs, 1583s, 1569s, 1533w, 1424m, 1316s, 1157m, 1057m, 928s, 812m, 736m. *Anal.* Calc. for $C_{26}H_{27}ClN_4$ (430.97): C 72.46, H 6.31, N 13.00. Found: C, 72.61; H, 6.59; N, 12.75%. 6-[1-(2,6-Diisopropylphenylimino)ethyl]-2-(6-chloro-1*H*-benzoimidazol-2-yl)pyridine: δ_H (400 MHz, $CDCl_3$, TMS): 10.51 (s, 1H, N*H*), 8.50 (d, *J* 7.6, 1H, Py), 8.45 (d, *J* 7.8, 1H, Py), 8.00 (t, *J* 7.7, 1H, Py), 7.77 (d, *J* 8.6, 1H, Ph), 7.55 (s, 1H, Ph), 7.28–7.30 (m, 1H, Ph), 7.18–7.20 (m, 2H, Ph), 7.13–7.15 (m, 1H, Ph), 2.72–2.78 (m, 2H, C*H*), 2.32 (s, 3H, CH_3), 1.17 (d, *J* 6.6, 12H, CH_3). δ_C (100 MHz, $CDCl_3$, TMS): 166.1, 156.0, 151.7, 146.9, 146.2, 143.0, 137.9, 135.7, 134.6, 129.7, 124.6, 123.9, 123.1, 122.7, 122.7, 122.5, 119.7, 111.4, 28.3, 23.2, 22.8. 6-[1-(2,6-Diisopropylphenylimino)ethyl]-2-(5-chloro-1*H*-benzoimidazol-2-yl)pyridine: δ_H (400 MHz, $CDCl_3$, TMS): 10.53 (s, 1H, N*H*), 8.50 (d, *J* 7.6, 1H, Py), 8.45 (d, *J* 7.8, 1H, Py), 8.00 (t, *J* 7.7, 1H, Py), 7.84 (s, 1H, Ph), 7.47 (d, *J* 8.5, 1H, Ph), 7.28–7.30 (m, 1H, Ph), 7.18–7.20 (m, 2H, Ph), 7.13–7.15 (m, 1H, Ph), 2.72–2.78 (m, 2H, C*H*), 2.32 (s, 3H, CH_3), 1.17 (d, *J* 6.6, 12H, CH_3). δ_C (100 MHz, $CDCl_3$, TMS): 166.1, 156.0, 152.0, 146.8, 146.2, 145.2, 137.9, 135.7, 132.5, 128.4, 123.9, 123.7, 123.1, 122.8, 122.6, 120.7, 112.2, 28.3, 23.2, 22.8.

*2.1.2.4. 6-[1-(2,4,6-Trimethylphenylimino)ethyl]-2-(6-chloro-1H-benzoimidaz ol-2-yl)pyridine and 6-[1-(2,4,6-trimethylphenylimino)ethyl]-2-(5-chlo ro-1H-benzoimidazol-2-yl)pyridine (**L4**).* Using the same procedure as for the synthesis of **L1**, **L4** was obtained as a light yellow powder in 66.7% (0.78 g) yield and with the ratio of 3:2. For combined isomers solids: Mp: 200 °C. IR (KBr, cm^{-1}): 3460m, 2918m, 1647vs, 1568s, 1465m, 1428m, 1324s, 1125m, 854s, 824m, 753s. *Anal.* Calc. for $C_{23}H_{21}ClN_4$ (388.89): C, 71.03; H, 5.44; N, 14.41. Found: C, 71.09; H, 5.50; N, 14.31%. 6-[1-(2,4,6-Trimethyl-phenylimino)ethyl]-2-(6-chloro-1*H*-benzoimidazol-2-yl) pyrindine: δ_H (400 MHz, $CDCl_3$, TMS): 10.60 (s, 1H, N*H*), 8.49 (d, *J* 7.7, 1H, Py), 8.41 (d, *J* 7.9, 1H, Py), 7.98 (t, *J* 7.8, 1H, Py), 7.76 (d, *J* 8.7, 1H, Ph), 7.55 (s, 1H, Ph), 7.28–7.30 (m, 1H, Ph), 6.91(s, 2H, Ph), 2.30 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.02 (s, 6H, CH_3). δ_C (100 MHz, $CDCl_3$, TMS): 166.6, 156.2, 151.7, 147.0, 146.0, 143.1, 137.9, 132.6, 128.5, 125.2, 123.7, 122.8, 122.6, 119.8, 111.5, 20.9, 17.9, 16.6. 6-[1-(2,4,6-Trimethylphenylimino)ethyl]-2-(5-chloro-1*H*-benzoimidazol-2-yl)pyridine: δ_H (400 MHz, $CDCl_3$, TMS): 10.63 (s, 1H, N*H*), 8.49 (d, *J* 7.7, 1H, Py), 8.41 (d, *J* 7.9, 1H, Py), 7.98 (t, *J* 7.8, 1H, Py), 7.84(s, 1H, Ph), 7.47(d, *J* 8.4, 1H, Ph), 7.28–7.30 (m, 1H, Ph), 6.91(s, 2H, Ph), 2.30 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.02 (s, 6H, CH_3). δ_C (100 MHz, $CDCl_3$, TMS): 166.6, 156.2, 152.1, 146.9, 146.0, 145.3, 134.6, 132.6, 129.7, 128.7, 125.2, 124.6, 122.9, 122.6, 120.9, 112.3, 20.9, 17.9, 16.6.

*2.1.2.5. 6-[1-(2,6-Diethyl-4-methylphenylimino)ethyl]-2-(6-chloro-1H-benzoimidazol-2-yl)pyridine and 6-[1-(2,6-diethyl-4-methylphenylimino)ethyl]-2-(5-chloro-1H-benzoimidazol-2-yl)pyridine (**L5**).* Using the same procedure as for the synthesis of **L1**, **L5** was obtained as a light yellow powder in 67.3% yield and with the ratio of 3:2. For combined isomers solids: Mp: 159–160 °C. IR (KBr, cm^{-1}): 3448w, 2965m, 1645vs, 1569m, 1461s, 1415s, 1300s, 1124m, 925m, 859s, 738m. *Anal.* Calc. for $C_{25}H_{25}ClN_4$ (416.95): C, 72.02; H, 6.04; N, 13.44. Found: C, 72.09; H, 6.21; N, 13.15%. 6-[1-(2,6-Diethyl-4-methylphenylimino)ethyl]-2-(6-chloro-1*H*-benzoimidazol-2-yl) pyridine: δ_H (400 MHz, $CDCl_3$, TMS): 10.51(s, 1H, N*H*), 8.49 (d, *J* 7.5, 1H, Py), 8.42 (d, *J* 7.9, 1H, Py), 7.98 (t, *J* 7.8 Hz, 1H, Py), 7.77 (d, *J* 8.6, 1H, Ph), 7.55(s, 1H, Ph), 7.26–7.29 (m, 1H, Ph), 6.95 (s, 2H, Ph), 2.35–2.39 (m, 7H, CH_2, CH_3), 2.30 (s, 3H, CH_3), 1.14 (t, *J* 7.4, 6H, CH_3). δ_C (100 MHz, $CDCl_3$, TMS): 166.3, 156.3, 151.8, 146.9, 145.0, 142.9, 137.9, 134.7, 132.7, 131.0, 129.7, 126.8, 123.7, 122.7, 122.5, 120.6, 24.8, 21.0, 16.7, 13.9. 6-[1-(2,6-Diethyl-4-methylphenylimino)ethyl]-2-(5-chloro-1*H*-benzoimidazol-2-yl) pyridine: δ_H (400 MHz, $CDCl_3$, TMS): 10.54 (s, 1H, N*H*), 8.49 (d, *J* 7.5, 1H, Py), 8.42 (d, *J* 7.9, 1H, Py), 7.98 (t, *J* 7.8, 1H, Py), 7.84 (s, 1H, Ph), 7.47 (d, *J* 8.5, 1H, Ph), 7.26–7.29 (m, 1H, Ph), 6.95 (s, 2H, Ph), 2.35–2.39 (m, 7H, CH_2, CH_3), 2.30 (s, 3H, CH_3), 1.14 (t, 6H, *J* 7.4, CH_3). δ_C (100 MHz, $CDCl_3$, TMS): 166.3, 156.3, 152.2, 146.8, 145.3, 145.0, 137.9, 134.7, 132.7, 131.0, 128.4, 125.2, 126.8, 124.5, 122.8, 122.6, 119.6, 24.8, 21.0, 16.7, 13.9.

*2.1.2.6. 6-[1-(2,6-Dichlorophenylimino)ethyl]-2-(6-chloro-1H-benzoimidazol-2-yl)pyridine and 6-[1-(2,6-dichlorophenylimino)ethyl]-2-(6-chloro-1H-benzoimidazol-2-yl)pyridine (**L6**).* Using a similar procedure to that for the synthesis of **L1**, with silicic acid tetraethyl ester employed as solvent instead of toluene, **L6** was obtained as a white powder in 27.3% yield and with the ratio of 3:2. For combined isomers solids: Mp: 228–230 °C. IR (KBr, cm^{-1}): 3402m, 3082w, 1648vs, 1568m, 1460m, 1308s, 1222s, 925m, 789m, 738s. *Anal.* Calc. for $C_{20}H_{13}N_4Cl_3$ (415.7): C, 57.79; H, 3.15; N, 13.48. Found: C, 57.88; H, 3.19; N, 13.11%. 6-[1-(2,6-Dichlorophenylimino)ethyl]-2-(6-chloro-1*H*-benzoimidazol-2-yl)pyridine: δ_H (400 MHz, $CDCl_3$, TMS): 10.34 (s, 1H, N*H*), 8.53 (d, *J* 7.7, 1H, Py), 8.47 (d, *J* 7.8, 1H, Py), 8.02 (t, *J* 7.9, 1H, Py), 7.77 (d, *J* 8.9, 1H, Ph), 7.57 (s, 1H, Ph), 7.39 (d, *J* 8.0, 2H, Ph), 7.17–7.30 (m, 2H, Ph), 7.03 (t, *J* 7.9, 1H, Ph), 2.42 (s, 3H, CH_3). δ_C (100 MHz, $CDCl_3$, TMS): 170.4, 155.2, 151.2, 146.9, 145.3, 143.1, 138.0, 134.2, 129.7, 128.3, 124.6, 124.4, 123.6, 123.2, 119.9, 111.3, 17.8. 6-[1-(2,6-Dichlorophenylimino)ethyl]-2-(5-chloro-1*H*-benzoimidazol-2-yl)pyridine: δ_H (400 MHz, $CDCl_3$, TMS): 10.37 (s, 1H, N*H*), 8.53 (d, *J* 7.7, 1H, Py), 8.47 (d, *J* 7.8, 1H, Py), 8.02 (t, *J* 7.9, 1H, Py), 7.85 (s, 1H, Ph), 7.49 (d, *J* 8.9, 1H, Ph), 7.39 (d, *J* 8.0, 2H, Ph), 7.17–7.30 (m, 2H, Ph), 7.03 (t, *J* 7.9, 1H, Ph), 2.42 (s, 3H, CH_3). δ_C (100 MHz, $CDCl_3$, TMS): 170.4, 155.2, 151.6, 146.9, 145.3, 143.1, 138.1, 132.3, 128.4, 128.3, 124.6, 124.4, 123.3, 123.2, 121.0, 112.0, 17.8.

*2.1.3. Synthesis of tridentate nickel complexes **C1–C12***

Complexes **C1–C6** were prepared by the same synthetic procedures and obtained as a yellow powder. The synthetic procedure of nickel dichloride complex **C1** can be described as follows: to a mixture of ligand **L1** (0.131 g, 0.35 mmol) and $NiCl_2{\cdot}6H_2O$ (0.083 g, 0.35 mmol) was added freshly distilled ethanol (5 mL) at room temperature. The solution turned yellow immediately. The reaction mixture was stirred for 10 h, and the precipitate was collected by filtration and washed with diethyl ether, followed by drying in vacuum. The desired complex was obtained as a yellow powder in good yield (81.2%, 0.14 g). IR (KBr, cm^{-1}): 3269m, 2968w, 1596vs, 1482m, 1465m, 1416s, 1315s, 1212s, 1051s, 805s, 771m. *Anal.* Calc. for $C_{22}H_{19}Cl_3N_4Ni$ (504.47): C, 52.38; H, 3.80; N, 11.11. Found: C, 52.63; H, 3.57; N, 11.35%.

Data for **C2** Yield: 78.3% (0.15 g). IR (KBr, cm^{-1}): 3087w, 2979m, 1594vs, 1462m, 1407s, 1317s, 1054s, 928s, 816m, 799m, 748m. *Anal.* Calc. for $C_{24}H_{23}Cl_3NiN_4$(532.52): C, 54.13; H, 4.35; N, 10.52. Found: C, 53.97; H, 4.17; N, 10.72%.

Data for **C3** Yield: 81.7% (0.16 g). IR (KBr, cm^{-1}): 3406m, 3021w, 2961s, 1597vs, 1462m, 1434m, 1318s, 1057m, 824s, 792s, 751s. *Anal.* Calc. for $C_{26}H_{27}Cl_3NiN_4$ (560.57): C, 55.71; H, 4.85; N, 9.99. Found: C, 55.82; H, 4.61; N, 10.21%.

Data for **C4** Yield: 83.2% (0.15 g). IR (KBr, cm^{-1}): 3308m, 2981w, 1595vs, 1483m, 1415s, 1316s, 1218s, 933m, 815s, 784m. *Anal.* Calc. for $C_{23}H_{21}Cl_3NiN_4$ (518.49): C, 53.28; H, 4.08; N, 10.81. Found: C, 53.47; H, 4.10; N, 10.62%.

Data for **C5** Yield: 80.7% (0.15 g). IR (KBr, cm^{-1}): 3398s, 2968m, 1599vs, 1487w, 1413s, 1315s, 858s, 813s, 749m. *Anal.* Calc. for $C_{25}H_{25}Cl_3NiN_4$ (546.55): C, 54.94; H, 4.61; N, 10.25. Found: C, 55.04; H, 4.28; N, 10.35%.

Table 1
Crystal data and structure refinement for [L3NiCl·CH_3OH·DMF]Cl (**C3**) and [L1NiBr·2CH_3OH]Br (**C7**).

	[L3NiCl·CH_3OH·DMF]Cl (**C3**)	[L1NiBr·2CH_3OH]Br (**C7**)
Empirical formula	$C_{31}H_{42}Cl_3N_5NiO_3$	$C_{24}H_{26}Br_2ClN_4NiO_2$
Formula weight	697.76	656.43
Temperature (K)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$c2/c$
a (Å)	8.8411(18)	30.367(9)
b (Å)	14.298(3)	13.586(3)
c (Å)	14.727(3)	14.519(3)
α (°)	103.57(3)	90
β (°)	99.01(3)	116.18(4)
γ (°)	105.72(3)	90
V (Å^3)	1693.0(6)	5376(2)
Z, D_{calc} (g cm^{-3})	2, 1.367	8, 1.622
μ (mm^{-1})	0.848	3.822
F(0 0 0)	732	2631
Crystal size (mm)	0.25 × 0.08 × 0.05	0.20 × 0.10 × 0.08
θ Range (°)	1.79–27.48	1.49–27.44
Limiting indices	$-11 \leqslant h \leqslant 11$ $-18 \leqslant k \leqslant 18$ $-19 \leqslant l \leqslant 19$	$-39 \leqslant h \leqslant 39$ $-11 \leqslant k \leqslant 17$ $-13 \leqslant l \leqslant 18$
Reflections collected	22981	21398
Independent reflections	7759 [$R_{(int)}$ = 0.0573]	6129 [$R_{(int)}$ = 0.1212]
Number of parameters	409	317
Completeness to θ (%)	99.9	99.8
Goodness of fit on F^2	1.078	1.245
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0761 wR_2 = 0.1925	R_1 = 0.1288 wR_2 = 0.2427
R indices (all data)	R_1 = 0.0834 wR_2 = 0.1984	R_1 = 0.1521 wR_2 = 0.2542
Maximum/minimum $\Delta\rho$[a] (e Å^{-3})	3.773 and −1.556	1.171 and −0.869

Data for **C6** Yield: 62.9% (0.12 g). IR (KBr, cm^{-1}): 3369s, 3068w, 1600vs, 1485m, 1436m, 1317s, 1059m, 934m, 814m. *Anal.* Calc. for $C_{20}H_{13}Cl_5NiN_4$ (545.30): C, 44.05; H, 2.40; N, 10.27. Found: C, 44.27; H, 2.43; N, 10.03%.

Complexes **C7**–**C12** were synthesized by the reaction of (DME)·$NiBr_2$ with the corresponding ligands in tetrahydrofuran (THF). A typical synthetic procedure for nickel dibromide complex **C7** is as follows: to a mixture of ligand **L1** (0.131 g, 0.35 mmol) and (DME)·$NiBr_2$ (0.107 g, 0.35 mmol) was added tetrahydrofuran (5 mL) at room temperature, and the mixture was stirred for 12 h. The precipitate was collected by filtration which was washed with ether and dried in vacuo. The complex **C7** was obtained as yellow powder with isolate yield: 89.3% (0.19 g). IR (KBr, cm^{-1}): 3326s, 3069w, 1592vs, 1485w, 1412s, 1315s, 1126m, 933m, 805s. *Anal.* Calc. for $C_{22}H_{19}ClBr_2NiN_4$ (593.37): C, 44.53; H, 3.23; N, 9.44. Found: C, 44.51; H, 2.99; N, 9.53%.

Data for **C8** Yield: 87.1% (0.19 g). IR (KBr, cm^{-1}): 3360m, 2935s, 1599vs, 1487m, 1413vs, 1316s, 1184w, 868w, 796s. *Anal.* Calc. for $C_{24}H_{23}ClBr_2NiN_4$ (621.42): C, 46.39; H, 3.73; N, 9.02. Found: C, 46.65; H, 3.57; N, 9.18%.

Data for **C9** Yield: 89.4% (0.20 g). IR (KBr, cm^{-1}): 3378s, 2961m, 1593vs, 1464m, 1321s, 1178w, 814m, 792s. *Anal.* Calc. for $C_{26}H_{27}ClBr_2NiN_4$ (649.47): C, 48.08; H, 4.19; N, 8.63. Found: C, 48.25; H, 4.01; N, 8.65%.

Data for **C10** Yield: 90.0% (0.19 g). IR (KBr, cm^{-1}): 3372s, 3059w, 1593vs, 1485m, 1412s, 1316s, 1218m, 853m, 816s. *Anal.* Calc. for $C_{23}H_{21}ClBr_2NiN_4$ (607.39): C, 45.48; H, 3.48; N, 9.22. Found: C, 45.37; H, 3.38; N, 9.25%.

Data for **C11** Yield: 81.3% (0.18 g). IR (KBr, cm^{-1}): 3323s, 2937w, 1595vs, 1458s, 1417m, 1415s, 1314s, 1214m, 932m, 813s, 747w. *Anal.* Calc. for $C_{25}H_{25}ClBr_2NiN_4$ (635.45): C, 47.25; H, 3.97; N, 8.82. Found: C, 47.38; H, 4.03; N, 8.57%.

Data for **C12** Yield: 70.7% (0.16 g). IR (KBr, cm^{-1}): 3309s, 2936w, 1599vs, 1436s, 1414s, 1316m, 933m, 814m, 785m. *Anal.* Calc. for $C_{20}H_{13}Cl_3Br_2NiN_4$ (634.2): C, 37.88; H, 2.07; N, 8.83. Found: C, 38.13; H, 2.27; N, 8.65%.

2.2. X-ray crystallographic studies

The crystals of [**L3**NiCl·CH_3OH·DMF]Cl (**C3**) was obtained by laying diethyl ether on the solution of mixed solvents of methanol and dimethyl formamide (DMF) at room temperature and [**L1**NiBr·2CH_3OH]Br (**C7**) was obtained by laying diethyl ether on a methanol solution at room temperature. With graphite-monochromated Mo Ka radiation (λ = 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 [45]. Details of the X-ray structure determinations and refinements are provided in Table 1.

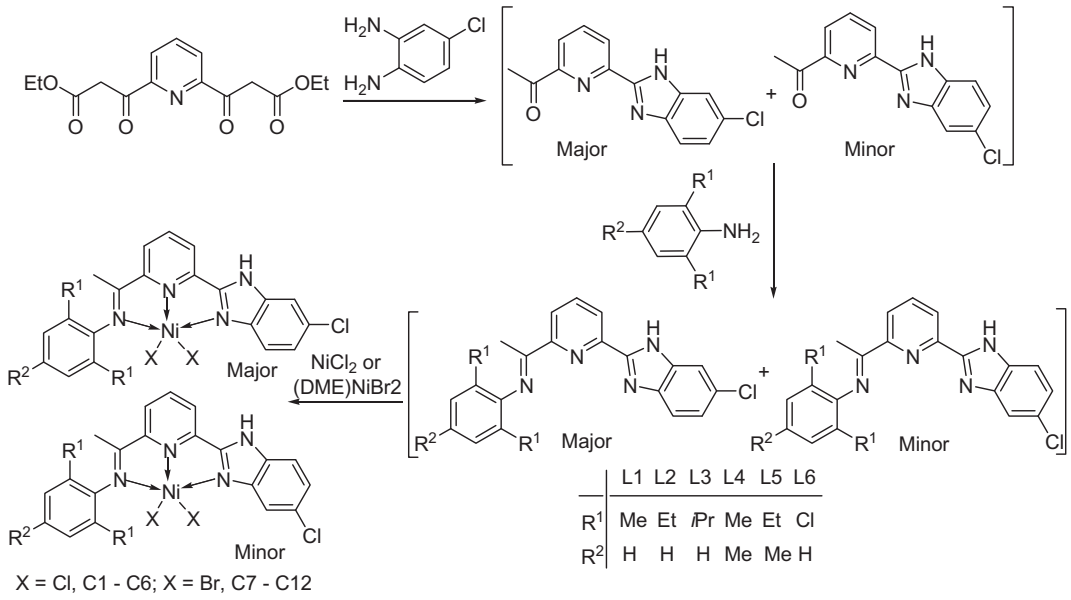
2.3. Procedure for ethylene oligomerization

Ethylene oligomerizations at 10 atm ethylene pressures were carried out in a 500 mL stainless steel autoclave equipped with a mechanical stirrer and a temperature controller. Toluene, the desired amount of cocatalyst, and a toluene solution of the catalytic precursor (the total volume was 100 mL) were added to the reactor in this order under an ethylene atmosphere. When the desired reaction temperature was reached, the ethylene pressure was increased to 10 atm, and maintained at this level by constant feeding of ethylene. After desired reaction time, the reaction was stopped by cooling the reactor on an ice bath before the excess pressure was released. A small amount of the reaction solution was collected, the reaction was terminated by the addition of 5% aqueous hydrogen chloride, and then this mixture was analyzed by gas chromatography (GC) to determine the distribution of oligomers obtained. The remaining reaction solution was quenched with HCl-acidified ethanol (5%).

3. Results and discussion

3.1. Synthesis and characterization of2-(chloro-substituted-1H-benzoimidazol-2-yl)-6-(1-arylimino ethyl)pyridines and their nickel complexes

The 6-(chloro-substituted-1*H*-benzoimidazol-2-yl)-2-acetylpyridine was synthesized by the condensation reaction of 4-chloro-1,2-diaminobenzene with 2,6-bis(β-keto-carboxylate)pyridine [39,44] according to our previous procedure [36]. The resultant mixture contained two isomers in the molar ratios of 3:2 with major 6-(6-chloro-*1H*-benzoimidazol-2-yl)-2-acetylpyridine and minor 6-(5-chloro-*1H*-benzoimidazol-2-yl)-2-acetylpyridine according to the ^{1}H NMR spectrum. Further condensation reaction of 6-(chloro-1*H*-benzoimidazol-2-yl)-2-acetylpyridine with aniline derivatives gave the corresponding compounds, 2-(chloro-*1H*-benzo-imidazol-2-yl)-6-(1-aryliminoethyl)pyridines (**L1**–**L6**), which also have two isomers with the same molar ratios as the acetylpyridine substance. According to their ^{1}H NMR spectra, there was no difference for products in the early and late eluting fractions on column chromatography, which indicated fast isomerization of the two isomers in each producing mixture. The stoichiometric



Scheme 2. Synthesis of nickel complexes.

reactions with $NiCl_2{\cdot}6H_2O$ in ethanol gave their dichloronickel complexes (**C1**–**C6**), and with (DME)·$NiBr_2$ in tetrahydrofuran (THF) gave dibromonickel complexes (**C7**–**C12**) (Scheme 2). All nickel dihalide complexes were air-stable yellow solids. Compared with the IR spectra of the free ligands, the C=N stretching vibrations in complexes **C1**–**C12** were shifted to lower frequencies in the range 1590–1560 cm^{-1}, indicating an effective coordination interaction between the imino nitrogen atom and the nickel center.

Crystals of **C3** suitable for single-crystal X-ray diffraction were obtained by slowly diffusing diethyl ether into its solution of mixed solvents of dimethyl formamide (DMF) and methanol solutions, meanwhile the crystals of **C7** suitable for single-crystal X-ray diffraction were obtained by laying diethyl ether on its methanol solution. The single-crystal X-ray diffraction study indicated two isomers of each nickel complex, in which the major isomer contained its ligands with substituted chlorine far away from the nickel center (Scheme 2). In our previous paper [39], 2-(7-methyl-1*H*-benzoimidazol-2-yl)-6-(1-aryliminoethyl)pyridylnickel dihalides were only obtained in the reaction of nickel halides with the isomeric mixture of 2-(7-methyl-1*H*-benzoimidazol-2-yl)-6-(1-aryliminoethyl)pyridines and 2-(4-methyl-1*H*-benzoimidazol-2-yl)-6-(1-aryliminoethyl)pyridines, which was isomerized due to the methyl steric hindrance in coordinating with nickel. In current system, the chloro-substituent of ligands is one more carbon away from the coordination nitrogen and as a consequence exerts a smaller bulky effect on nickel.

The two isomers of complex **C3** show a disorder of the chlorine atom in its solid state the major position having the chlorine far away from nickel center. In its structure, there were two coordinated molecules of dimethyl formamide (DMF) and methanol solvents around nickel to form a cationic ion, meanwhile a free chloride was observed. The molecular structure of [**L3**NiCl·CH_3OH·DMF]Cl is shown in Fig. 1, and the selected bond lengths and angles are collected in Table 2. The nickel atom deviates by 0.0442 Å from the plane containing N(2), N(3), and N(4). The Cl(2) deviates by 0.2718 Å from the plane of N(2), N(3) and N(4). The basal plane composed by N(2), N(3) and N(4) is almost coplanar to the pyridyl ring with a dihedral angle of 4.7°, the pyridyl ring and the benzimidazole ring are also nearly coplanar with a dihedral angle of 5.2°. The dihedral angles between the phenyl plane with the benzimidazole ring and of the phenyl plane with the pyridine ring are 87.2° and 91.3°, respectively. The spherical coordinated cationic nickel center is far from the anionic Cl(1) and is thus considered non-bonding. The disorder phenomena of Cl(3), caused with two isomers of the ligand, is reflected with the high spurious peak (3.773 e Å).

Similar coordination was observed in the molecular structure of complex **C7**, shown in Fig. 2. The axial plane (O(1)–Ni(1)–O(2)) is nearly perpendicular to the equatorial plane which is formed by N(2), N(3) and N(4) with a dihedral angle of 88.9°. Comparison with the above [**L3**NiCl·CH_3OH·DMF]Cl, the N–Ni lengths of [**L1**NiBr·$2CH_3OH$]Br are a little shorter.

In summary, both complexes possessed a six-coordinated geometry at the nickel center with two additional molecules of coordinated solvents. The likely disorder of chlorine on the phenyl of the benzimidazole was caused by two isomers of the ligands. All complexes for elemental analysis and for further catalytic screening were dried for 4 h under vacuum before experimental processes.

3.2. Ethylene oligomerization

Though there are two isomers of individual nickel complexes, the similar catalytic activities are assumed because the chloro-substituent is far from nickel and has little steric influence.

3.2.1. Ethylene activation in the presence of Et_2AlCl

When procatalyst **C4** was activated with diethylaluminum chloride (Et_2AlCl) at 1 atm ethylene pressure, there was low activity observed. Increasing the ethylene pressure up to 10 atm, good activity was achieved. The reaction parameters, such as molar ratio of Et_2AlCl to nickel and the reaction temperature, were varied for the optimum condition. The catalytic activity improved with increasing Al/Ni ratio from 300 up to 500 (Entries 1–3, Table 3), however, lower activity was observed on further increasing the Al/Ni ratio to 600 or 700 (Entries 4–5, Table 3). Using a reaction temperature within 30–70 °C (Entries 3, 6–9, Table 3), the highest activity is obtained at 50 °C (Entry 3, Table 3). Comparison with the analog procatalysts performing the best activities at ambient reaction temperature [33–38], the current system shows good activity at a higher temperature 50 °C, which is an important practical issue for oligomerization at higher reaction temperature. The

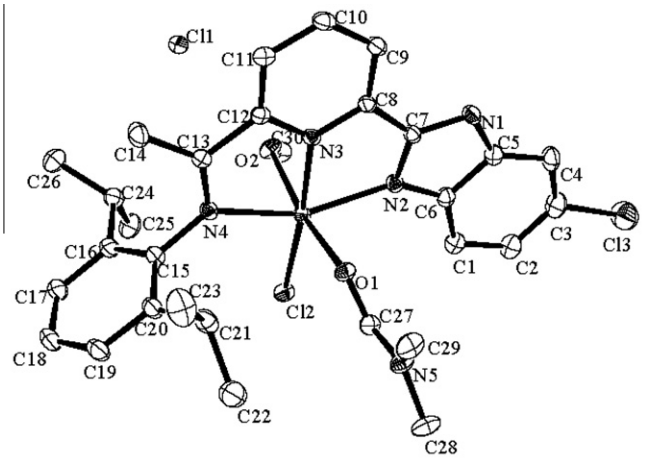


Fig. 1. ORTEP structure of [**L3**NiCl·CH_3OH·DMF]Cl (**C3**). Thermal ellipsoids are shown at 30% probability level. Hydrogen atoms have been omitted for clarity.

Table 2
Selected bond lengths and angles for complexes **C3** and **C7**.

	[L3NiCl·CH_3OH·DMF]Cl (**C3**)	[L1NiBr·2CH_3OH]Br (**C7**)
Bond lengths (Å)		
Ni–N2	2.146(3)	2.127(9)
Ni–N3	2.026(3)	2.038(9)
Ni–N4	2.244(3)	2.182(10)
Ni–X	2.2926(14)	2.4199(18)
N1–C7	1.348(5)	1.384(14)
N2–C7	1.326(5)	1.321(14)
N4–C13	1.282(5)	1.296(14)
Ni–O1	2.068(3)	2.180(8)
Ni–O2	2.128(3)	2.126(8)
Bond angles (°)		
N2–Ni–N3	78.16(13)	78.2(4)
N2–Ni–N4	153.45(13)	153.7(4)
N3–Ni–N4	75.34(13)	75.8(4)
N2–Ni–X	104.68(10)	102.1(3)
N3–Ni–X	174.74(9)	174.1(2)
N4–Ni–X	101.87(10)	104.1(3)
O1–Ni–O2	171.44(12)	170.8(3)

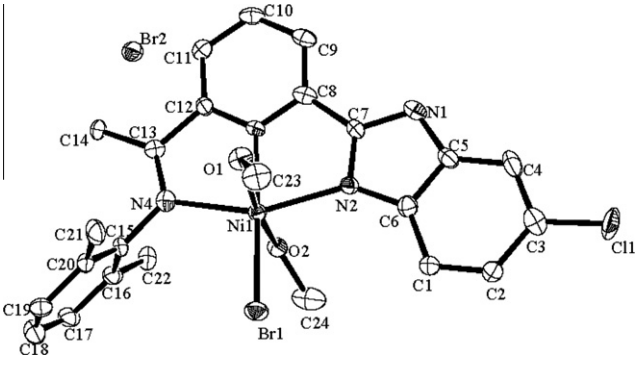


Fig. 2. ORTEP molecular structure of [L1NiBr·2CH_3OH]Br (**C7**). Thermal ellipsoids are shown at 30% probability level. Hydrogen atoms have been omitted for clarity.

advantage of maintaining good activity at reasonable reaction temperature is due to the effect of the chlorine substituent on phenyl group of benzimidazole. The lifetime of the active species was investigated (Entries 3, 10–14, Table 3), the values of the activities gradually decreased with prolonged reaction time, indicating no initial stage required, and the oligomerization terminated after 40 min (Entries 12–14, Table 3). As a consequence, further investigations of nickel complexes were carried out with the optimum condition at Al/Ni ratio 500 at 50 °C within 30 min.

On the bases of different halides, the title procatalysts could be separated into two groups, dichlorides **C1**–**C6** and dibromides **C7**–**C12**. All chlorides procatalysts **C1**–**C6** (Entries 3, 15–19, Table 3), and the bromides analogs **C7**–**C12** (Entries 20–25, Table 3) showed high activities. It was found that the higher catalytic activity was observed with bromide procatalysts over chloride analogs [34,37,38], possibly due to solubility of metal bromide in organic solvents which is usually better than that of chloride analogs. In this work, the complexes showed better activities, the possible cause is the significant electronic influence by the chloro-substituted phenyl group of the benzoimidazoles. In addition, it was confirmed the optimum reaction temperature at 50 °C by procatalyst **C10** (Entries 23, 26–27, Table 3).

As shown for other nickel analogs procatalysts [34–38], the less bulky ligands (varying different substituents of the imino N-aryl rings) enhance catalyst activities of the corresponding nickel complexes with the activity order as **C1** > **C2** > **C3** (Entries 15–17, Table 3) and **C7** > **C8** > **C9** (Entries 20–22, Table 3). However, the 2,4,6-trimethyl-substituted procatalysts **C4** and **C10** showed the highest catalytic activity in each set of complexes (Entries 3 and 23, Table 3). Regarding nickel analogs [34,37,38], two exceptions are procatalysts **C6** (Entry 19, Table 3) and **C12** (Entry 25, Table 3) bearing the ligand containing 2,6-dichlorophenyl which showed higher catalytic activities than some of their analogs of ligands having dialkylphenyl (e.g. **C6** > **C5** > **C3** and **C12** > **C11** > **C8** > **C9**). This observation is consistent with our simulation results [39], where there is a turnover point between the catalytic activities and the net-charge of the metal active species in catalytic system.

3.2.2. Ethylene activation in the presence of ethylaluminum sesquichloride ($Et_3Al_2Cl_3$)

In addition, ethylaluminum sesquichloride ($Et_3Al_2Cl_3$) was used as the cocatalyst; the ethylene dimerization was predominant with some trimerization (Table 4). The procatalyst **C10** was routinely studied in finding the optimum condition of Al/Ni molar ratio and reaction temperature. As observed in using Et_2AlCl as cocatalyst, the best activity was achieved at 50 °C but using slightly higher Al/Ni molar ratio 600 than for the system with $Et_3Al_2Cl_3$. In the catalytic systems with $Et_3Al_2Cl_3$, all procatalysts displayed higher catalytic activities, surprisingly the selectivity of α-olefin was quite high (>99%). The high selectivity for α-olefin is a quite unique property in nickel catalytic systems, because a high proportion of inert olefins are obtained due to chain-immigration and β-hydrogen elimination on active nickel species. Comparing data by the title procatalysts, there is no significant difference between catalytic systems of chlorides and bromides.

The catalytic behavior of all the nickel procatalysts with $Et_3Al_2Cl_3$, as affected by the substituents of the imino N-aryl rings, is similar as their counterpart systems with Et_2AlCl. The activities were in the order **C1** (with substituent of dimethyl) > **C2** (with diethyl) > **C3** (with diisopropyl) (Entries 10–12, Table 4) and **C7** (with substituent of dimethyl) > **C8** (with diethyl) > **C9** (with diisopropyl) (Entries 16–18, Table 4). In addition, complexes **C6** and **C12** (Entries 15 and 20, Table 4) bearing the 2,6-dichlorophenyl group maintained good activity as for the analog complexes containing 2,6-dialkylphenyl.

4. Conclusions

A series of new nickel procatalysts ligated by 2-(chloro-substituted-1*H*-benzoimidazol-2-yl)-6-(1-aryliminoethyl)pyridines were synthesized and fully characterized. Using the Et_2AlCl as activators, the catalytic activity of 2.6×10^6 g mol^{-1} Ni h^{-1} was reached in

Table 3
Ethylene catalytic activity with nickel complexes using Et_2AlCl.[a]

Entry	Precatalyst	Al/Ni	T (°C)	t (min)	Activity[c]	Oligomer distribution[b]		
						C4/ΣC	C6/ΣC	α-Olefin (%)
1	**C4**	300	50	30	5.4	96.0	4.0	93.1
2	**C4**	400	50	30	20.3	91.8	8.2	60.1
3	**C4**	500	50	30	25.9	89.2	10.8	64.4
4	**C4**	600	50	30	19.1	90.9	9.1	60.3
5	**C4**	700	50	30	13.3	92.9	7.1	73.3
6	**C4**	500	30	30	4.5	97.1	2.9	41.2
7	**C4**	500	40	30	10.1	95.7	4.3	80.9
8	**C4**	500	60	30	9.4	90.7	9.3	72.4
9	**C4**	500	70	30	5.8	94.4	5.6	82.3
10	**C4**	500	50	10	42.8	87.8	12.2	63.2
11	**C4**	500	50	20	34.2	88.6	11.4	65.3
12	**C4**	500	50	40	19.8	89.4	10.6	64.1
13	**C4**	500	50	50	15.9	89.4	10.6	65.3
14	**C4**	500	50	60	13.2	89.4	10.6	65.5
15	**C1**	500	50	30	18.2	93.4	6.6	70.6
16	**C2**	500	50	30	15.7	95.3	4.7	95.4
17	**C3**	500	50	30	12.3	92.5	7.5	70.7
18	**C5**	500	50	30	12.5	91.6	8.4	68.2
19	**C6**	500	50	30	14.6	92.0	8.0	64.0
20	**C7**	500	50	30	13.1	92.2	7.8	74.5
21	**C8**	500	50	30	9.3	93.6	6.4	75.1
22	**C9**	500	50	30	8.6	91.6	8.4	71.8
23	**C10**	500	50	30	17.1	90.0	10.0	65.6
24	**C11**	500	50	30	9.5	93.3	6.7	72.8
25	**C12**	500	50	30	12.4	91.8	8.2	67.4
26	**C10**	500	40	30	8.8	98.6	1.4	61.9
27	**C10**	500	60	30	5.7	93.6	6.4	72.7

[a] Reaction condition: 5 μmol; Et_2AlCl; 10 atm ethylene; 100 mL toluene.
[b] Determined by GC.
[c] 10^5 g mol^{-1} Ni h^{-1}.

Table 4
Ethylene catalytic activity with nickel complexes using $Et_3Al_2Cl_3$.[a]

Entry	Precatalyst	Al/Ni	T (°C)	Activity[c]	Oligomer distribution[b]		
					C4/ΣC	C6/ΣC	α-Olefin (%)
1	**C10**	200	20	7.1	91.4	8.6	>99
2	**C10**	400	20	7.7	90.8	9.2	>99
3	**C10**	600	20	8.8	89.7	10.3	>99
4	**C10**	800	20	7.5	75.1	24.9	>99
5	**C10**	1000	20	6.7	88.6	11.4	>99
6	**C10**	600	40	10.7	80.4	19.6	>99
7	**C10**	600	50	13.5	79.0	21.0	>99
8	**C10**	600	60	9.4	80.1	19.9	>99
9	**C10**	600	80	5.5	83.1	16.9	>99
10	**C1**	600	50	7.1	79.3	20.7	>99
11	**C2**	600	50	5.2	77.7	22.3	>99
12	**C3**	600	50	2.2	84.9	15.1	>99
13	**C4**	600	50	8.2	84.6	15.4	>99
14	**C5**	600	50	6.5	83.4	16.6	>99
15	**C6**	600	50	6.3	82.5	17.5	>99
16	**C7**	600	50	6.5	79.0	21.0	>99
17	**C8**	600	50	5.8	84.5	15.5	>99
18	**C9**	600	50	3.1	81.7	18.3	>99
19	**C11**	600	50	8.6	83.5	16.5	>99
20	**C12**	600	50	8.2	84.2	15.8	>99

[a] Reaction condition: 5 μmol; 30 min, $Et_3Al_2Cl_3$; 10 atm ethylene; 100 mL toluene.
[b] Determined by GC.
[c] 10^6g mol^{-1} Ni h^{-1}.

ethylene oligomerization. When activated by $Et_3Al_2Cl_3$, all nickel procatalysts exhibited higher activities for ethylene oligomerization with up to 1.35×10^7 g mol^{-1} Ni h^{-1} and high selectivity of α-olefins (>99%). In practice, the activities of procatalysts could be improved by modifying ligands through fine-tuning of substituents far from the nickel center. The title nickel procatalysts bearing chloro-modified ligands performed higher activities at elevated reaction temperature 50 °C, compared with analogs' procatalysts with optimum temperature at room temperature [34,37,38].

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Appendix A. Supplementary material

CCDC 763875 and 763876 contain the supplementary crystallographic data for complexes **C3** and **C7**, 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.2011.01.054.

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