

Synthesis, Characterization and Ethylene Oligomerization Studies of Nickel Complexes Bearing 2-Benzimidazolylpyridine Derivatives

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A series of nickel complexes ligated by 2-(2-benzimidazole)-6-methylpyridine, 2-(1-methyl-2-benzimidazole)-6-acetylpyridine, and 2-(1-methyl-2-benzimidazole)-6-(1-aryliminoethyl)pyridine was synthesized and examined by IR spectroscopic and elemental analysis. Their molecular structures were determined by single-crystal X-ray diffraction analysis. On activation with diethylaluminum chloride (Et₂AlCl), all the nickel complexes exhibited good catalytic activities for ethylene oligomerization, and the nickel(II) complexes bearing 2-(1-methyl-2-benzimidazole)-6-(1-aryliminoethyl)pyridines showed good activities up to $5.87 \times 10^5 \text{ g mol}^{-1}(\text{Ni}) \text{ h}^{-1} \text{ atm}^{-1}$. The various reaction parameters were investigated in detail, and the results revealed that both the steric and electronic effects of ligands strongly affect the catalytic activities of their nickel complexes as well as different coordination style.

1. Introduction

The oligomerization of ethylene is currently the major industrial process for the production of linear α -olefins, which are important reactants used in the preparation of detergents, lubricants, plasticizers, oil field chemicals, and monomers for copolymerization. Current industrial processes employ catalysts including either alkylaluminum compounds or a combination of alkylaluminum compounds and early transition metal compounds or nickel(II) complexes and bidentate monoanionic [P,O] ligands (the SHOP process).¹ In the past decade, late-transition metal complexes as homogeneous catalysts toward ethylene activation have attracted great attention in both academic and industrial research.² In contrast to early-transition metal complexes, late-transition metal complexes were less investigated because of the competition of β -hydrogen elimination with chain propagation, and the discovery of diimino cationic nickel complexes as effective catalysts for ethylene oligomerization and polymerization renewed interest in designing new late-transition metal complexes as catalysts.³ The important progress of ethylene activation promoted by nickel complexes is reflected by recent review articles.² Owing to fundamental research points from an organometallic chemistry perspective, the recent major

challenges of nickel complexes as catalysts toward ethylene oligomerization and/or polymerization include their coordination modes, catalytic activities, and selectivity toward α -olefins along with controlled molecular weights of products (oligomers and polymers). The nickel complexes are commonly four-coordinated nickel dihalides containing bidentate ligands such as P[^]O,^{1,4} P[^]N,⁵ N[^]N,^{3,6} and N[^]O.⁷ Intensive research, however, has shown moderate to high catalytic activities for conversion of ethylene by the five-coordinated nickel halides incorporating tridentate ligands of N[^]N[^]O,⁸ N[^]P[^]N,⁹ P[^]N[^]P[^]O,¹⁰ P[^]N[^]N,^{6n,10} and N[^]N[^]N.¹¹ Some of the nickel catalytic systems are worthy of further investigation and are promising for both industrial and academic development.

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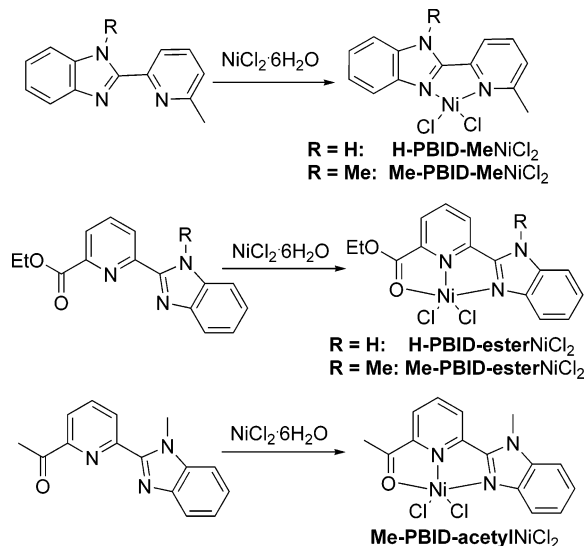
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Scheme 1. Reaction of NiCl₂·6H₂O with 2-(Benzimidazolyl)pyridine Derivatives



In our group, catalytic systems ligated by tridentate 2,9-bis(imino)-1,10-phenanthroline derivatives have been reported,^{11a} in which the nickel complexes showed better activities than their iron and cobalt analogues. Furthermore, the nickel complexes ligated by 2-imino-1,10-phenanthroline derivatives exhibited even higher activity for ethylene oligomerization, up to 10^6 g mol⁻¹(Ni) h⁻¹ atm⁻¹.^{11d} Their catalytic activity and product distributions were somehow controlled through changing the steric and electronic properties of the ligand backbones. Inspired by the above promising results, our subsequent exploration involves tridentate N[^]N[^]N ligands in new types of metal complexes as catalysts for ethylene oligomerization and polymerization. Very recently, a new family of iron(II) and cobalt(II) complexes bearing 2-(2-benzimidazole)pyridine derivatives was found to form highly active catalysts for ethylene oligomerization and polymerization upon activation with methylaluminoxane (MAO) or modified methylaluminoxane (MMAO),

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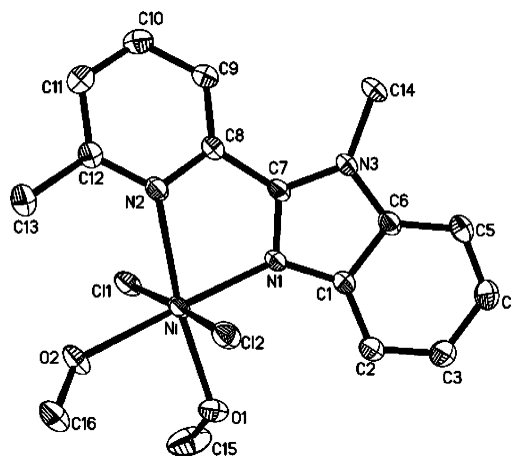


Figure 1. Molecular structure of Me-PBID-MeNiCl₂. Thermal ellipsoids are shown at 30% probability. Hydrogen atoms have been omitted for clarity.

and α -olefins were produced with high selectivity.¹² Subsequently, to distinguish them from former nickel catalysts, their nickel analogues as a new series of catalysts for ethylene activation were also synthesized by reactions of nickel halides with the synthesized 2-benzimidazolylpyridine derivatives. In the presence of diethylaluminum chloride (Et₂AlCl) as cocatalyst, all the nickel complexes showed good catalytic activities toward ethylene oligomerization, and the N[^]N[^]N nickel complexes (L¹NiCl₂–L⁵NiCl₂) showed high activities of ethylene oligomerization up to 5.87×10^5 g mol⁻¹(Ni) h⁻¹ atm⁻¹. Herein, the synthesis and characterization of these nickel complexes are reported with their catalytic properties for ethylene activation investigated under various reaction conditions.

2. Results and Discussion

2.1. Synthesis and Characterization of Nickel Complexes Bearing Various 6-Substituted 2-Benzimidazolylpyridines.

As observed in our previous work on nickel complexes containing bidentate or tridentate ligands for ethylene activation,^{6b–j,10,11f,13} the nickel complexes based on the 6-substituted 2-benzimidazolylpyridine derivatives, 2-(1-R'-2-benzimidazole)-6-R''-pyridine (R' = H and R'' = Me: **H-PBID-Me**; R' = R'' = Me: **Me-PBID-Me**; R' = H and R'' = carboethoxyl: **H-PBID-ester**; R' = Me and R'' = carboethoxyl: **Me-PBID-ester**; R' = Me and R'' = acetyl: **Me-PBID-acetyl**) were synthesized in proper yields by equimolar reactions of the synthesized 2-benzimidazolylpyridine derivatives with NiCl₂·6H₂O in ethanol (Scheme 1).

These complexes were characterized by IR spectroscopic and elemental analysis. They showed high stability in both solution and solid state. Compared with the IR spectrometry of the free organic ligands, the C=N_{pyridine} and C=O absorption bands of the complexes were shifted to lower frequencies, indicating strong coordination effects. The unambiguous molecular structures of complexes **Me-PBID-MeNiCl₂**, **Me-PBID-esterNiCl₂**, and **Me-PBID-acetylNiCl₂** were confirmed by single-crystal X-ray diffraction analysis. Their molecular structures are shown in Figures 1–3, and selected bond lengths and angles are collected in Table 1.

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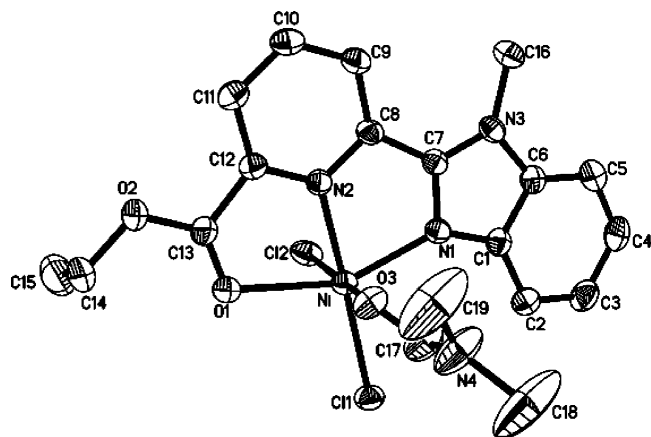


Figure 2. Molecular structure of **Me-PBID-esterNiCl₂**. Thermal ellipsoids are shown at 30% probability. Hydrogen atoms and one EtOH molecule have been omitted for clarity.

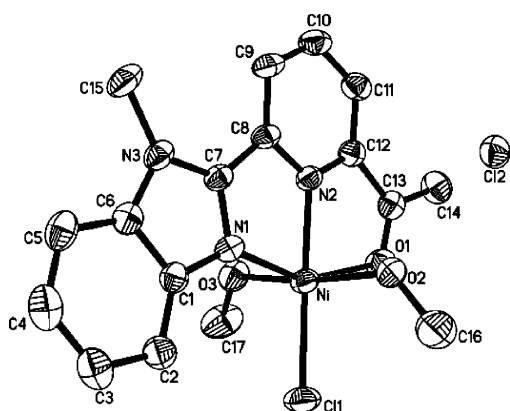


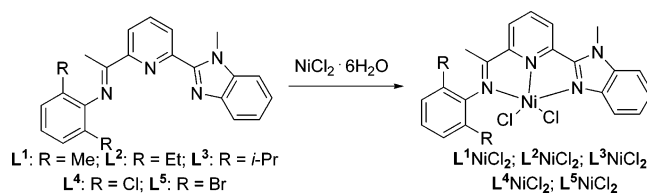
Figure 3. Molecular structure of **Me-PBID-acetylNiCl₂**. Thermal ellipsoids are shown at 30% probability. Hydrogen atoms have been omitted for clarity.

Table 1. Selected Bond Lengths and Angles for Complexes **Me-PBID-MeNiCl₂**, **Me-PBID-esterNiCl₂**, and **Me-PBID-acetylNiCl₂**

	Me-PBID-MeNiCl₂	Me-PBID-esterNiCl₂	Me-PBID-acetylNiCl₂
Bond Lengths (Å)			
Ni–N1	2.0571(2)	2.065(2)	2.051(3)
Ni–N2	2.2144(2)	2.045(2)	2.027(3)
Ni–Cl1	2.3880(6)	2.3196(7)	2.2887(1)
Ni–Cl2	2.3841(6)	2.3890(8)	
N1–C1	1.378(3)	1.373(3)	1.389(4)
N1–C7	1.323(2)	1.340(3)	1.333(4)
N2–C8	1.357(2)	1.341(3)	1.339(4)
N2–C12	1.341(3)	1.327(4)	1.334(4)
C7–C8	1.469(3)	1.473(4)	1.473(4)
Ni–O1	2.1198(2)	2.305(2)	2.243(2)
Bond Angles (deg)			
N2–Ni–N1	78.35(6)	78.28(8)	78.71(1)
N2–Ni–Cl1	85.00(5)	173.72(6)	176.14(8)
N1–Ni–Cl1	95.23(5)	104.52(6)	104.74(8)
Cl1–Ni–Cl2	174.46(2)	96.05(3)	
N1–Ni–Cl2	89.75(5)	92.81(7)	
N2–Ni–Cl2	93.66(5)	89.38(6)	
N2–Ni–O1	170.96(6)	74.55(8)	74.54(1)
N1–Ni–O1	93.10(6)	152.73(8)	153.24(1)

Crystals of complex **Me-PBID-MeNiCl₂** (Figure 1) were grown from a methanol solution layered with diethyl ether. The nickel center coordinates with two methanol molecules, and the coordinate geometry around the metal center could be described as a distorted octahedron. Perhaps due to higher basicity of benzimidazole, the bond length of Ni–N₂_{pyridine} (2.2144(2) Å)

Scheme 2. Synthesis of Nickel Complexes with 2-(1-Methyl-2-benzimidazole)-6-(1-aryliminoethyl)pyridines



is significantly longer than that of Ni–N₁_{benzimidazole} (2.0571(2) Å). It is noteworthy that the benzimidazole ring and phenyl ring are not strictly coplanar, with a dihedral angle of 24.3°.

Single crystals of **Me-PBID-esterNiCl₂** were obtained by diffusing the diethyl ether layer into its solution mixture of ethanol and DMF. The molecular structure of six-coordinated **Me-PBID-esterNiCl₂** can be described as a distorted octahedron geometry in which the nickel atom is surrounded by one ligand, two chlorides, and one DMF molecule through linkage by its oxygen atom (Figure 2). The ester-substituted pyridylbenzimidazole ligand coordinates the nickel center as a tridentate $N\wedge N\wedge O$ ligand. The plane of the benzimidazole ring is nearly oriented coplanar to the pyridine plane (8.0°). The distance between oxygen (O1) and the nickel atom is 2.305(2) Å, which is substantially shorter than the value observed in the 2-(ethylcarboxylato)-6-iminopyridylnickel(II) complexes (2.342(3)–2.402(5) Å).⁶¹ Compared with the nickel complex **Me-PBID-MeNiCl₂**, the Ni–N₂_{pyridine} bond is remarkably shorter, which might be attributed to the strong interaction between the nickel and carbonyl oxygen atom and formation of a five-membered chelate ring. Also, the distance between the nickel and the *trans*-disposed chloride is significantly shorter than the distance of the chloride in the *cis* position.

In the molecular structure of **Me-PBID-acetylNiCl₂** (Figure 3), the geometry around the nickel center can also be described as a distorted octahedron. The nickel atom is surrounded by one ligand, one chloride, and two methanol molecules. The pyridine ring was nearly coplanar with the benzimidazole ring, and the dihedral angle is 5.0°. The distance between oxygen (O1) and the nickel atom is 2.243(2) Å, and it is shorter than that in **Me-PBID-esterNiCl₂**, which indicates a much stronger interaction between these two atoms. In addition, the bond length of Ni–N₂ in **Me-PBID-acetylNiCl₂** is noticeably shorter than that in the former two nickel complexes. Furthermore, the distance of Ni–Cl1 is much shorter than *cis* Ni–Cl distances.

2.2. Synthesis and Characterization of the Nickel Complexes Containing 2-(1-Methyl-2-benzimidazole)-6-(1-aryliminoethyl)pyridines. The 2-(1-methyl-2-benzimidazole)-6-(1-aryliminoethyl)pyridines (**L¹–L⁵**) were prepared according to our reported procedures.¹² The nickel complexes (**L¹NiCl₂–L⁵NiCl₂**) were obtained by treating the ethanol solution of NiCl₂·6H₂O with the corresponding ligand (**L¹–L⁵**) at room temperature in satisfying yields (57%–88%) (Scheme 2). These complexes showed high stability in both solution and solid state and were identified by FT-IR and elemental analysis. The IR spectra of the ligands **L¹–L⁵** gave C=N_{imino} stretching frequencies in the range 1639 to 1650 cm^{–1},¹² while the C=N_{imino} stretching vibrations of the complexes **L¹NiCl₂–L⁵NiCl₂** shifted toward lower frequencies between 1594 and 1595 cm^{–1} with weak intensities. This indicates the effective coordination between the imino nitrogen atom and the nickel center.

Moreover, single crystals of complexes **L¹NiCl₂**, **L²NiCl₂**, and **L³NiCl₂** suitable for X-ray diffraction were individually obtained by slow diffusion of diethyl ether into their methanol solutions or their saturated solution in a methanol–DMF solvent

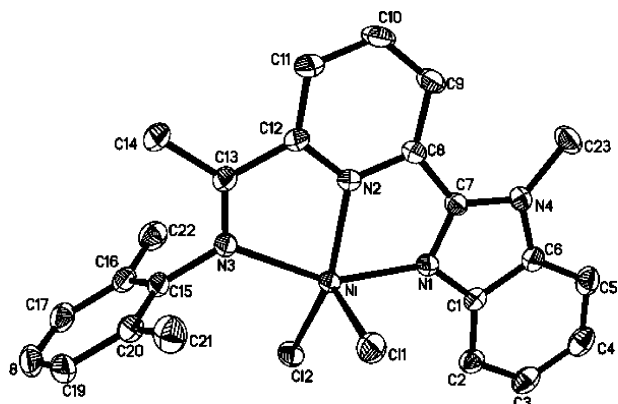


Figure 4. Molecular structure of L^1NiCl_2 . Thermal ellipsoids are shown at 30% probability. Hydrogen atoms and one DMF molecule have been omitted for clarity.

Table 2. Selected Bond Lengths and Angles for Complexes L^1NiCl_2 , L^2NiCl_2 , and L^3NiCl_2

	L^1NiCl_2	L^2NiCl_2	L^3NiCl_2
Bond Lengths (Å)			
Ni–N1	2.0701(2)	2.091(2)	2.1012(1)
Ni–N2	2.0100(1)	2.002(2)	2.0140(1)
Ni–N3	2.1809(2)	2.171(2)	2.1964(1)
Ni–Cl1	2.2954(6)	2.2516(9)	2.2815(5)
Ni–Cl2	2.2662(5)	2.2759(9)	2.2561(5)
N1–C1	1.379(2)	1.381(3)	1.379(2)
N1–C7	1.328(2)	1.320(4)	1.3234(2)
N2–C8	1.346(2)	1.351(4)	1.3435(2)
N2–C12	1.337(2)	1.335(3)	1.3328(2)
N3–C13	1.277(2)	1.284(4)	1.283(2)
N3–C15	1.438(2)	1.439(4)	1.4480(2)
Bond Angles (deg)			
N2–Ni–N1	77.78(6)	77.66(9)	77.27(5)
N2–Ni–N3	76.21(6)	76.42(9)	75.90(5)
N1–Ni–N3	152.60(6)	152.17(9)	150.50(5)
N2–Ni–Cl1	100.38(5)	150.06(8)	97.30(4)
N1–Ni–Cl1	94.34(5)	98.49(7)	95.80(4)
N3–Ni–Cl1	98.66(4)	98.90(7)	99.56(4)
Cl1–Ni–Cl2	110.17(2)	114.00(4)	108.02(2)
N1–Ni–Cl2	149.45(5)	95.93(7)	154.68(4)
N2–Ni–Cl2	99.31(4)	95.01(7)	99.33(4)
N3–Ni–Cl2	98.66(4)	97.54(7)	99.64(4)

mixture. An X-ray crystallographic study of the nickel complex L^1NiCl_2 revealed the coordination geometry around the metal center as a distorted trigonal bipyramid with the pyridyl nitrogen atom and the two chlorides forming an equatorial plane; the molecular structure is shown in Figure 4 with selected bond lengths and angles in Table 2. In the structure of L^1NiCl_2 , the nickel atom is nearly in the equatorial plane with equatorial angles ranging between $100.38(5)^\circ$ and $149.45(5)^\circ$, deviating from 120° . The two nitrogen atoms (N1 and N3) occupy the axial coordination sites with a bond angle of $152.60(6)^\circ$ for N1–Ni–N3. This benzimidazole ring and the pyridyl ring are nearly coplanar, with a dihedral angle of 2.9° . The dihedral angle between the phenyl ring and the plane of pyridine is 84.8° . The phenyl ring lies almost perpendicular to the plane formed by the coordinated nitrogen atoms (80.8°), which is similar to the 2-imino-1,10-phenanthrolyl nickel(II) complexes.^{11d} The two Ni–Cl bond lengths show a slight difference between the Ni–Cl(1) (2.2954(6) Å) and Ni–Cl(2) (2.2662(5) Å) bonds. Furthermore, the imino N(3)–C(13) bond in L^1NiCl_2 displays clear double-bond character (1.277(2) Å), and it is 0.015 Å longer than that in the free ligand L^1 .

Similarly, its analogues, nickel complexes L^2NiCl_2 and L^3NiCl_2 (Figure 5 and Figure 6), also show a distorted trigonal-bipyramidal geometry. The nickel atom slightly resides 0.0045

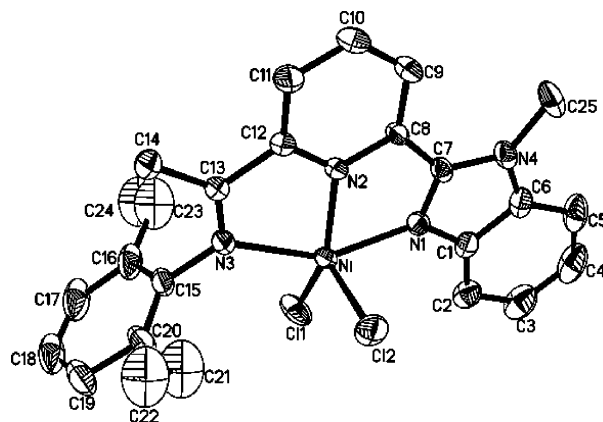


Figure 5. Molecular structure of L^2NiCl_2 . Thermal ellipsoids are shown at 30% probability. Hydrogen atoms have been omitted for clarity.

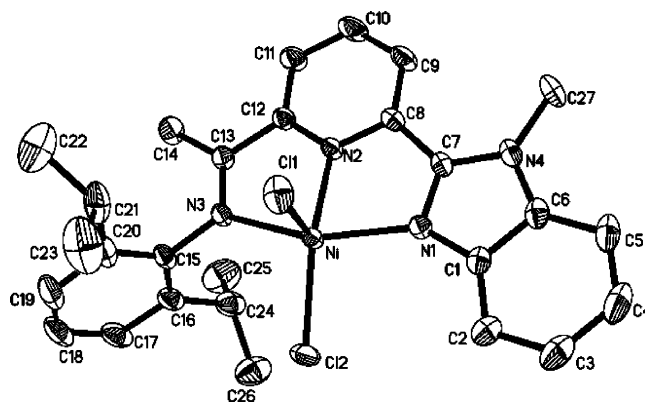


Figure 6. Molecular structure of L^3NiCl_2 . Thermal ellipsoids are shown at 30% probability. Hydrogen atoms have been omitted for clarity.

and 0.0052 Å out of the equatorial plane in L^2NiCl_2 and L^3NiCl_2 , respectively. The axial Ni–N bonds subtend an angle of $152.17(9)^\circ$ (L^2NiCl_2) and $150.50(5)^\circ$ (L^3NiCl_2) (N(1)–Ni–N(3)). The dihedral angles between the phenyl ring and the pyridyl plane are 85.6° (L^2NiCl_2) and 83.2° (L^3NiCl_2), respectively. The equatorial planes of these two complexes are nearly perpendicular to the benzimidazole ring, with dihedral angles of 91.6° in L^2NiCl_2 and 92.6° in L^3NiCl_2 . Similar to L^1NiCl_2 , the Ni–N(1) and Ni–N(3) bond lengths are noticeably longer than that of Ni–N(2). The imino N(3)–C(13) bond lengths are 1.284(4) Å (L^2NiCl_2) and 1.283(2) Å (L^3NiCl_2) with the typical character of a C=N double bond, but slightly longer than that of L^1NiCl_2 (1.277(2) Å). The difference is probably due to the less bulky methyl at the *ortho*-position of the phenyl ring in L^1NiCl_2 .

2.3. Ethylene Oligomerization. 2.3.1. Ethylene Oligomerization Promoted by $N\wedge N$ or $N\wedge N\wedge O$ Coordinated Nickel Complexes. Different functional groups and coordination environments of the complexes exert varied influences on their reactivity with ethylene. The above presented nickel complexes with bidentate $N\wedge N$ and tridentate $N\wedge N\wedge O$ ligands were investigated for their use in ethylene oligomerization in the presence of various organoaluminum cocatalysts. At ambient pressure of ethylene, these systems showed low catalytic activities. Therefore, 20 atm pressure of ethylene was employed for the catalytic reaction. Considerable catalytic activities of the nickel complexes were obtained with cocatalysts such as MAO, MMAO, and Et_2AlCl . As a matter of fact, the catalytic activities were not largely different in the systems with various

Table 3. Ethylene Oligomerization by Nickel Complexes Ligated with H-PBID-Me, Me-PBID-Me, H-PBID-ester, Me-PBID-ester, and Me-PBID-acetyl and Their Oligomer Distribution^a

entry	complex	cocat.	Al/Ni	activity ^b	oligomer distribution ^c	
					C ₄ /ΣC	C ₆ /ΣC
1	H-PBID-Me NiCl ₂	Et ₂ AlCl	200	3.15	95.5	4.5
2	H-PBID-Me NiCl ₂	MAO	1000	2.95	95.1	4.9
3	Me-PBID-Me NiCl ₂	Et ₂ AlCl	200	0.83	88.7	11.3
4	H-PBID-ester NiCl ₂	Et ₂ AlCl	500	0.88	44.6	55.4
5	H-PBID-ester NiCl ₂	Et ₂ AlCl	200	0.70	31.7	68.3
6	H-PBID-ester NiCl ₂	MAO	1000	1.04	47.3	52.7
7	H-PBID-ester NiCl ₂	MMAO	1000	1.15	74.4	25.6
8	Me-PBID-ester NiCl ₂	Et ₂ AlCl	200	0.29	72.6	27.4
9	Me-PBID-acetyl NiCl ₂	Et ₂ AlCl	200	0.73	61.5	38.5

^a Conditions: 5 μmol of catalyst; 30 min; toluene (100 mL); 20 atm; 20 °C. ^b 10⁴ g mol⁻¹(Ni) h⁻¹ atm⁻¹. ^c Determined by GC.

Table 4. Ethylene Oligomerization of the H-PBID-MeNiCl₂/Et₂AlCl System^a

entry	Al/Ni	P/atm	T/°C	activity ^b	oligomer distribution ^c	
					C ₄ /ΣC	C ₆ /ΣC
1	50	20	20	0.36	85.5	14.5
2	100	20	20	0.52	81.1	18.9
3	200	20	20	3.15	95.5	4.5
4	500	20	20	3.66	94.5	5.5
5	1000	20	20	11.2	93.8	6.2
6	500	30	20	4.13	93.1	6.9
7	500	10	20	1.85	89.8	10.2
8	500	20	40	0.86	85.8	14.2
9	500	20	60	0.64	84.6	15.4
10 ^d	500	30	20	1.65	89.8	10.2

^a Conditions: 5 μmol of catalyst; 30 min; toluene (100 mL). ^b 10⁴ g mol⁻¹(Ni) h⁻¹ atm⁻¹. ^c Determined by GC. ^d 10 equiv of PPh₃.

cocatalysts (Table 3). Et₂AlCl requires the smallest Al/Ni ratio and therefore is chosen for a detailed investigation.

Comparing with the nickel complexes ligated by **Me-PBID-Me** as catalysts (entries 3 in Table 3), the catalytic systems of complexes **H-PBID-Me**NiCl₂ had relatively higher reactivity (entries 1 in Table 3), and the same phenomenon was also observed in the nickel complexes ligated by **H-PBID-ester** and **Me-PBID-ester** (entry 5 vs 8 in Table 3). These results can be attributed to the deprotonation of the N-H group to give anionic amide ligands when activated by a cocatalyst of organoaluminum to form N-Al species with increased catalytic activity.^{12,14,15} Furthermore, the nickel complexes **H-PBID-Me**NiCl₂ and **Me-PBID-Me**NiCl₂, containing N[^]N ligands, exhibited higher catalytic reactivity than their analogues containing N[^]N[^]O ligands **H-PBID-ester**, **Me-PBID-ester**, and **Me-PBID-acetyl**. When the nickel complexes with ester groups were used as catalysts, the C₆ proportion in the products was higher than the C₄ proportion and the C₆ proportion in the N[^]N catalyst hints to slower elimination or higher stability of the organometallic intermediate in the catalytic cycle. When it was activated by MMAO, the C₆ proportion decreased sharply because of the inhibition of the isobutyl group in the cocatalyst.

Different reaction temperature, amount of cocatalyst, and pressure of ethylene also affected their catalytic reactivity. Their influences were investigated in detail using the catalytic system of **H-PBID-Me**NiCl₂/Et₂AlCl, and the results are summarized in Table 4. The catalytic activity was increased when the Al/Ni molar ratio was varied from 50 to 1000. However, the optimum Al/Ni molar ratio was fixed at 500 considering the economy (entries 1–5 in Table 4). Elevating the reaction temperature from 20 °C to 60 °C resulted in decreased catalytic activity

Table 5. Ethylene Catalytic Activity with L¹NiCl₂ Using Different Cocatalyst^a

entry	cocat.	Al/Ni	activity ^b	oligomer distribution ^c	
				C ₄ /ΣC	C ₆ /ΣC
1	MAO	1000	6.50	95.2	4.8
2	MMAO	1000	1.82	93.3	6.7
3	Et ₂ AlCl	200	4.97	91.8	8.2

^a Conditions: 5 μmol of precatalyst, 30 atm of ethylene, 0.5 h, 100 mL of toluene. ^b 10⁴ g mol⁻¹(Ni) h⁻¹ atm⁻¹. ^c Determined by GC.

(entries 4, 8, and 9 in Table 4), which might be attributed to the instability of the active species or lower concentration of ethylene in the reaction solution. Commonly, lower catalytic activity was observed at lower pressure, and only butenes were produced at ethylene pressures lower than 10 atm (entries 4, 6, and 7 in Table 4). Previous studies reported that nickel catalysts incorporating PPh₃ into their catalytic systems resulted in higher activity.^{6i,7c,g,11d,16} Therefore, the oligomerization reaction with the **H-PBID-Me**NiCl₂/Et₂AlCl system was carried out in the presence of 10 equiv of PPh₃ (entry 10 of Table 4). However, a sharp decrease in catalytic activity was observed. The reason might be that the stronger Ni–P bond in this system prevented the coordination of ethylene on the active metal center.

2.3.2. Ethylene Oligomerization Behavior of the N[^]N[^]N Coordinated Nickel Complexes. The influences of various cocatalysts on the ethylene activation were evaluated with the catalytic systems formed from L¹NiCl₂ in the presence of methylaluminoxane (MAO), modified methylaluminoxane (MMAO), or Et₂AlCl. Because of the low reactivity at ambient pressure of ethylene, it was difficult to evaluate the influence of cocatalyst; hence an elevated pressure of ethylene at 30 atm was used. The optimum conditions were determined for various cocatalysts in different molar ratios to L¹NiCl₂. The results compiled in Table 5 indicate that the L¹NiCl₂/MAO or Et₂AlCl systems showed remarkable and similar catalytic activity on the order of 10⁵ g mol⁻¹(Ni) h⁻¹ atm⁻¹. However, the Al/Ni ratio is only 200 for Et₂AlCl; therefore, it would be better to use Et₂AlCl on the basis of economical consideration.

On fixing the Al/Ni ratio of Et₂AlCl at 200, all nickel complexes ligated by 2-(1-methyl-2-benzimidazole)-6-(1-aryliminoethyl)pyridines were examined for ethylene oligomerization with changing pressure of ethylene and reaction temperature. The results are summarized in Table 6.

2.3.2.1. Effect of Ligand Environment. According to Table 6 (entries 1–5), the oligomerization activities decreased in the order L³NiCl₂ > L²NiCl₂ > L¹NiCl₂ with decreasing size of the alkyl substituents on the aryl group, and likewise for L⁵-

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Table 6. Oligomerization of Ethylene with L¹NiCl₂–L⁵NiCl₂ and their Oligomer Distribution^a

entry	complex	P/atm	T/°C	activity ^b	oligomer distribution ^c		
					C ₄ /ΣC	C ₆ /ΣC	C ₈ /ΣC
1	L ¹ NiCl ₂	30	20	0.50	91.8	8.2	
2	L ² NiCl ₂	30	20	1.00	94.9	5.1	
3	L ³ NiCl ₂	30	20	1.18	95.1	4.9	
4	L ⁴ NiCl ₂	30	20	3.06	93.1	6.6	0.3
5	L ⁵ NiCl ₂	30	20	3.40	94.3	5.5	0.2
6	L ⁴ NiCl ₂	10	20	2.82	92.4	7.6	
7	L ⁴ NiCl ₂	20	20	1.66	91.8	8.2	
8	L ⁴ NiCl ₂	30	40	5.87	89.5	9.6	0.9
9	L ⁴ NiCl ₂	30	60	4.00	82.4	16.4	1.2
10	L ⁴ NiCl ₂	30	80	0.29	74.6	21.3	4.1
11 ^d	L ³ NiCl ₂	30	20	13.7	85.3	14.5	0.2
12 ^d	L ⁴ NiCl ₂	30	20	18.8	88.6	10.8	0.6

^a Conditions: 5 μmol of precatalyst; 0.5 h; 100 mL of toluene; cocat.: 200 equiv of Et₂AlCl. ^b 10⁵ g mol⁻¹(Ni) h⁻¹ atm⁻¹. ^c Determined by GC. ^d 10 equiv of PPh₃.

NiCl₂ > L⁴NiCl₂ with decreasing size of halide substituents. The catalytic activity for L⁵NiCl₂ is up to 3.40 × 10⁵ g mol⁻¹(Ni) h⁻¹ atm⁻¹. The lower activity for less bulky substituents can be explained by the exposure of the active sites of the catalyst to not only ethylene but also other reactive species, and the latter actually led to the deactivation of the active species. Indeed, Gibson has proved that the catalytic intermediates formed from the precursors containing pyridyldiimine ligands are more easily deactivated through the interaction with alkylaluminum reagents if they lack sufficient steric bulk in the aryl ring.¹⁷ In our experiments, the major products are C₄ and the minor products are C₆ by using L³NiCl₂, L²NiCl₂, or L¹NiCl₂, while the catalytic systems of L⁴NiCl₂ and L⁵NiCl₂ also produced a very small amount of C₈. When the nickel complexes contain halides as the electron-withdrawing substituents on the aryl ring, the reactivity is much higher than with alkyl substituents (entries 4 and 5 show higher activities than entries 1–3). The electron-withdrawing groups at the *ortho*-position of the aryl rings make the central metal more positive, so the ethylene can easily coordinate to nickel species, which finally led to higher catalytic activity.

2.3.2.2. Effects of Ethylene Pressure and Reaction Temperature. Oligomerization experiments with L⁴NiCl₂ catalysts were conducted under different pressures of ethylene as shown in Table 6. It is observed that the catalytic activities were improved with increasing ethylene pressure, attributable to the higher monomer concentration around active nickel centers at higher pressure. In addition, at 10 or 20 atm of ethylene, there is no C₈ in the oligomer products, and the higher monomer concentration speeds up not only the ethylene reactivity (coordination and insertion) but also the rate of alkyl-chain propagation.

As the ethylene oligomerization is a highly exothermic reaction, the reaction temperature significantly affects the catalytic activity. To estimate this influence, the catalytic system of L⁴NiCl₂ with 200 equiv of Et₂AlCl at 30 atm of ethylene was investigated with varied reaction temperature (entries 4 and 8–10 in Table 6). Increasing the temperature from 20 to 80 °C, the optimum catalytic activity was shown at 40 °C. At 80 °C, its catalytic activity was 1/20 of that at 40 °C because of the lower stability of nickel active species with lower coordination rate of ethylene. Interestingly, on raising the temperature from 40 to 80 °C, increased C₆ and C₈ oligomer

Table 7. Influence of Different Al/Ni ratios on Complex L⁴NiCl₂/Et₂AlCl Catalytic Activity^a

entry	Al/Ni	activity ^b	oligomer distribution ^c		
			C ₄ /ΣC	C ₆ /ΣC	C ₈ /ΣC
1	5	0.25	87.0	13.0	
2	10	0.53	92.4	7.6	
3	50	1.54	92.8	7.2	
4	100	3.80	92.5	7.0	0.5
5	200	3.06	93.1	6.6	0.3
6	300	2.17	93.7	6.3	
7	500	1.91	92.5	7.5	
8	1000	0.80	92.8	7.2	

^a Conditions: 5 μmol of precatalyst; 30 atm of ethylene; 20 °C; 0.5 h; 100 mL of toluene. ^b 10⁵ g mol⁻¹(Ni) h⁻¹ atm⁻¹. ^c Determined by GC.

proportions were recorded, implying that the rate of chain propagation increases more rapidly than that of β-hydrogen elimination.

2.3.2.3. Effects of Auxiliary Ligand. The influence of auxiliary ligand on the nickel catalyst was also investigated for this system. Upon the addition of 10 equiv of PPh₃ to the catalytic system, the reactivity was strongly increased. It became about 5 times higher than that without PPh₃. Moreover, larger amounts of C₆ and C₈ are observed (entries 11 and 12 in Table 6). This phenomenon was attributed to the fact that the active nickel species are coordinated with auxiliary PPh₃ on the vacant coordination sites when lacking ethylene monomers. This prevents deactivation by impurities of active reactants in the catalytic species, while the incoming molecules of ethylene easily replace PPh₃ for further reactions. This is consistent with previous observations,^{11d,e,g,15b} and a series of active species containing PPh₃ was once isolated in our group.^{7g}

2.3.2.4. Effects of Al/Ni Molar Ratio. The influence of different molar ratios of Et₂AlCl to nickel complexes on ethylene activation was investigated in detail with L⁴NiCl₂. When the Al/Ni molar ratio was varied from 5 to 1000, the oligomerization activities initially increased and then decreased (Table 7). Increasing the Al/Ni molar ratio from 5 to 100 led to a predominantly increased reactivity up to 3.80 × 10⁵ g mol⁻¹(Ni) h⁻¹ atm⁻¹, indicating that L⁴NiCl₂ can be easily activated. On increasing the Al/Ni ratio further from 100 to 1000, the activity gradually decreased. A small amount of C₈ was found in the oligomers when the catalytic activity is at the high stage. In addition, employing a very small amount of Et₂AlCl such as with an Al/Ni ratio of 5 or 10, the ethylene oligomerization with this catalyst system is still promising, with an activity of about 10⁴ g mol⁻¹(Ni) h⁻¹ atm⁻¹.

3. Conclusion

A series of nickel complexes ligated by 2-(2-benzimidazole)-6-methylpyridine, 2-(1-methyl-2-benzimidazole)-6-acetylpyridine, and 2-(1-methyl-2-benzimidazole)-6-(1-aryliminoethyl)pyridine was synthesized and characterized carefully. The X-ray crystallographic studies on all 2-(1-methyl-2-benzimidazole)-6-(1-aryliminoethyl)pyridylnickel chlorides revealed a distorted trigonal-bipyramidal geometry, while other nickel complexes displayed a distorted octahedral coordination geometry with incorporation of solvent molecules. These complexes could be easily activated and exhibited good to high activities for ethylene oligomerization in the presence of Et₂AlCl as cocatalyst, even though the amount of cocatalyst was very small and the main products were dimers and trimers of ethylene. The complexes ligated by tridentate N[^]N[^]N ligands, 2-(1-methyl-2-benzimidazole)-6-(1-aryliminoethyl)pyridines, more favored the inser-

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Table 8. Crystal Data and Structure Refinement for Compounds

	Me-PBID-Me-NiCl ₂	Me-PBID-ester-NiCl ₂	Me-PBID-acetyl-NiCl ₂	L ¹ NiCl ₂	L ² NiCl ₂	L ³ NiCl ₂
empirical formula	C ₁₆ H ₂₁ Cl ₂ N ₃ NiO ₂	C ₂₁ H ₂₈ Cl ₂ N ₄ NiO ₄	C ₁₇ H ₂₁ Cl ₂ N ₃ NiO ₃	C ₂₆ H ₂₉ Cl ₂ N ₅ NiO	C ₂₅ H ₂₆ Cl ₂ N ₄ Ni	C ₂₇ H ₃₀ Cl ₂ N ₄ Ni
fw	416.97	530.08	444.98	557.13	512.11	540.16
cryst color	green	green	green	brown	brown	brown
temp (K)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	triclinic	triclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2(1)/c$	$P1$	$P2(1)/c$	$P2(1)/c$
<i>a</i> (Å)	9.9010(2)	8.0306(2)	7.8096(4)	8.6398(3)	9.5439(3)	9.6969(2)
<i>b</i> (Å)	10.8544(2)	12.5947(3)	12.9994(8)	12.7231(4)	13.9544(4)	14.9381(3)
<i>c</i> (Å)	11.0362(2)	13.3400(3)	19.3219(1)	12.8188(4)	18.5858(6)	18.2266(4)
α (deg)	62.3650(1)	71.778(2)	90	70.6870(1)	90.0	90.0
β (deg)	69.4580(1)	86.4870(1)	93.425(3)	80.1010(1)	94.433(2)	91.9400(1)
γ (deg)	63.2600(1)	86.6650(1)	90	86.3540(1)	90.0	90.0
volume (Å ³)	923.10(3)	1278.09(5)	1958.06(2)	1309.98(7)	2467.84(1)	2638.67(1)
<i>Z</i>	2	2	4	2	4	4
<i>D</i> _{calc} (g cm ⁻³)	1.500	1.377	1.509	1.412	1.378	1.360
μ (mm ⁻¹)	1.353	1.000	1.285	0.973	1.022	0.960
<i>F</i> (000)	432	552	920	580	1064	1128
cryst size (mm)	0.42 × 0.32 × 0.10	0.35 × 0.25 × 0.14	0.35 × 0.24 × 0.13	0.30 × 0.10 × 0.05	0.30 × 0.20 × 0.10	0.35 × 0.10 × 0.05
θ range (deg)	2.12–28.37	1.61–28.30	1.89–28.30	1.70–28.34	1.83–28.33	1.76–28.31
limiting indices	–13 ≤ <i>h</i> ≤ 10, –14 ≤ <i>k</i> ≤ 14, –14 ≤ <i>l</i> ≤ 14	–10 ≤ <i>h</i> ≤ 10, –16 ≤ <i>k</i> ≤ 16, –17 ≤ <i>l</i> ≤ 16	–9 ≤ <i>h</i> ≤ 10, –17 ≤ <i>k</i> ≤ 17, –25 ≤ <i>l</i> ≤ 25	–11 ≤ <i>h</i> ≤ 7, –16 ≤ <i>k</i> ≤ 16, –17 ≤ <i>l</i> ≤ 16	–12 ≤ <i>h</i> ≤ 12, –18 ≤ <i>k</i> ≤ 18, –23 ≤ <i>l</i> ≤ 24	–12 ≤ <i>h</i> ≤ 12, –19 ≤ <i>k</i> ≤ 19, –23 ≤ <i>l</i> ≤ 24
no. of reflns collected	14 501	19 074	20 918	16 294	21 881	26 953
no. of unique reflns	4582	6290	4833	6436	6135	6520
completeness to θ (%)	99.2 ($\theta=28.37^\circ$)	98.9 ($\theta=28.30^\circ$)	99.2 ($\theta=28.30^\circ$)	98.6 ($\theta=28.34^\circ$)	99.6 ($\theta=28.33^\circ$)	99.4 ($\theta=28.31^\circ$)
absorp corr	empirical	empirical	empirical	empirical	empirical	empirical
no. of params	225	289	243	316	271	307
goodness-of-fit on <i>F</i> ²	1.123	0.961	0.818	1.108	1.088	1.034
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0333, w <i>R</i> 2 = 0.0990	<i>R</i> 1 = 0.0435, w <i>R</i> 2 = 0.1232	<i>R</i> 1 = 0.0415, w <i>R</i> 2 = 0.0881	<i>R</i> 1 = 0.0344, w <i>R</i> 2 = 0.1004	<i>R</i> 1 = 0.0522, w <i>R</i> 2 = 0.1594	<i>R</i> 1 = 0.0305, w <i>R</i> 2 = 0.0875
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0450, w <i>R</i> 2 = 0.1028	<i>R</i> 1 = 0.0767, w <i>R</i> 2 = 0.1406	<i>R</i> 1 = 0.1429, w <i>R</i> 2 = 0.1084	<i>R</i> 1 = 0.0441, w <i>R</i> 2 = 0.1046	<i>R</i> 1 = 0.0721, w <i>R</i> 2 = 0.1713	<i>R</i> 1 = 0.0416, w <i>R</i> 2 = 0.0930
largest diff peak and hole (e Å ⁻³)	0.455 and –0.390	0.545 and –0.460	0.289 and –0.333	0.408 and –0.351	1.087 and –1.389	0.292 and –0.311

tion of ethylene and led to better catalytic activities than those bearing bidentate $N\wedge N$ or tridentate $N\wedge N\wedge O$ ligands. In the tridentate $N\wedge N\wedge N$ catalytic system, the complexes containing large steric substituents or electron-withdrawing groups on the *N*-aryl ring had higher ethylene insertion activity, and especially the electronic effect was very obvious. Good activities ($5.87 \times 10^5 \text{ g mol}^{-1}(\text{Ni}) \text{ h}^{-1} \text{ atm}^{-1}$) were observed at higher pressures of ethylene, with optimum conditions of the Al/Ni molar ratio and reaction temperature. In addition, the catalytic system containing the auxiliary ligand PPh_3 showed better catalytic activities toward ethylene oligomerization because of the protection of the phosphine group.

4. Experimental Section

4.1. General Considerations. All manipulations of air- and moisture-sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk techniques. Toluene was refluxed over sodium-benzophenone and distilled under argon prior to use. Methylaluminoxane (MAO, a 1.46 M solution in toluene) and modified methylaluminoxane (MMAO, 1.93 M in heptane) were purchased from Akzo Nobel Corp. Diethylaluminum chloride (Et_2AlCl , 1.7 M in toluene) was purchased from Acros Chemicals. Other reagents were purchased from Aldrich or Acros Chemicals. 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 Carlo Erba

Strumentazione gas chromatograph equipped with a flame ionization detector and a 30 m (0.25 mm i.d., 0.25 μm film thickness) DM-1 silica capillary 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. All the organic compounds used as ligands for the nickel complexes were prepared by employing our developed procedure.¹²

4.2. Synthesis of Nickel Complexes. General Procedure: A solution of the ligand in ethanol was added dropwise to an equimolar amount (1 mmol) of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in ethanol solution. Immediately, the color of the solution changed and some precipitate formed. The reaction mixture was stirred at room temperature for 6 h, then diluted with diethyl ether. The resulting precipitate was collected, washed with diethyl ether, and dried in vacuum. All of the complexes were prepared in high yield in this manner.

4.2.1. Preparation of the Nickel Complexes with Precursor Compounds. 2-(2-Benzimidazole)-6-methylpyridine NiCl_2 (H-PBID-MeNiCl₂): yellow powder, 91% yield. IR (KBr; cm^{-1}): 3396, 3061, 1609, 1577, 1477, 1460, 1322, 1251, 1040, 806, 748. Anal. Calcd for $\text{C}_{13}\text{H}_{11}\text{Cl}_2\text{N}_3\text{Ni}$: C, 46.08; H, 3.27; N, 12.40. Found: C, 45.74; H, 2.99; N, 12.61.

2-(1-Methyl-2-benzimidazole)-6-methylpyridine NiCl_2 (Me-PBID-MeNiCl₂): yellow powder, 97% yield. IR (KBr; cm^{-1}): 3346, 2926, 1605, 1477, 1491, 1442, 1384, 1336, 1160, 1102, 801, 755. Anal. Calcd for $\text{C}_{14}\text{H}_{13}\text{Cl}_2\text{N}_3\text{Ni}$: C, 47.65; H, 3.71; N, 11.91. Found: C, 47.29; H, 3.83; N, 11.58.

2-Carboethoxy-6-(2-benzimidazolyl)pyridine NiCl₂ (H-PBID-esterNiCl₂): green powder, 77% yield. IR (KBr; cm⁻¹): 2977, 1694, 1605, 1469, 1422, 1375, 1329, 1275, 1157, 1007, 856, 837, 765. Anal. Calcd for C₁₅H₁₃Cl₂N₃NiO₂: C, 45.39; H, 3.30; N, 10.59. Found: C, 45.24; H, 3.47; N, 10.40.

2-Carboethoxy-6-(1-methyl-2-benzimidazolyl)pyridine NiCl₂ (Me-PBID-esterNiCl₂): green powder, 98% yield. IR (KBr; cm⁻¹): 3302, 1684, 1600, 1487, 1408, 1380, 1332, 1285, 1157, 1013, 825, 758. Anal. Calcd for C₁₆H₁₅Cl₂N₃NiO₂: C, 46.77; H, 3.68; N, 10.23. Found: C, 47.11; H, 3.29; N, 10.12.

2-(1-Methyl-2-benzimidazole)-6-acetylpyridine NiCl₂ (Me-PBID-acetylNiCl₂): green powder, 84% yield. IR (KBr; cm⁻¹): 3207, 1666, 1570, 1488, 1423, 1404, 1335, 1277, 1251, 1189, 1089, 814, 758. Anal. Calcd for C₁₅H₁₃Cl₂N₃NiO: C, 47.30; H, 3.44; N, 11.03. Found: C, 47.51; H, 3.31; N, 11.08.

4.2.2. Preparation of the Title Nickel Complexes. Data for these complexes are as follows.

L¹NiCl₂: yellow powder, 57% yield. IR (KBr; cm⁻¹): 1595 ($\nu_{C=N}$); 1490; 1402; 1368; 1334; 1307; 1282; 1258; 1212; 1157; 1098; 796; 752. Anal. Calcd for C₂₃H₂₂Cl₂N₄Ni: C, 57.07; H, 4.58; N, 11.57. Found: C, 56.77; H, 4.83; N, 11.22.

L²NiCl₂: yellow powder, 87% yield. IR (KBr; cm⁻¹): 1595 ($\nu_{C=N}$); 1489; 1446; 1404; 1370; 1330; 1283; 1257; 1203; 1164; 1091; 1030; 794; 758. Anal. Calcd for C₂₅H₂₆Cl₂N₄Ni: C, 58.63; H, 5.12; N, 10.94. Found: C, 58.55; H, 5.01; N, 10.68.

L³NiCl₂: yellow powder, 88% yield. IR (KBr; cm⁻¹): 1595 ($\nu_{C=N}$); 1490; 1461; 1424; 1404; 1370; 1329; 1306; 1283; 1255; 1201; 1105; 1028; 794; 760. Anal. Calcd for C₂₇H₃₀Cl₂N₄Ni: C, 60.04; H, 5.60; N, 10.37. Found: C, 59.85; H, 5.75; N, 10.08.

L⁴NiCl₂: yellow powder, 73% yield. IR (KBr; cm⁻¹): 1595 ($\nu_{C=N}$); 1489; 1434; 1403; 1365; 1308; 1282; 1259; 1192; 1159; 1090; 1027; 867; 790; 748. Anal. Calcd for C₂₁H₁₆Cl₄N₄Ni: C, 48.05; H, 3.07; N, 10.67. Found: C, 47.86; H, 3.33; N, 10.46.

L⁵NiCl₂: yellow powder, 87% yield. IR (KBr; cm⁻¹): 3377; 3072; 1594 ($\nu_{C=N}$); 1488; 1431; 1368; 1281; 1259; 1228; 1188; 1159; 1025; 927; 816; 789; 748. Anal. Calcd for C₂₁H₁₆Cl₂Br₂-NiN₄: C, 41.09; H, 2.63; N, 9.13. Found: C, 40.72; H, 2.57; N, 9.07.

4.3. Procedure for Ethylene Oligomerization. Ethylene oligomerization was performed in a stainless steel autoclave (0.5 L capacity) equipped with a gas ballast through a solenoid valve for continuous feeding of ethylene at constant pressure. A 100 mL amount of toluene containing the catalyst precursor was transferred

to the fully dried reactor under a nitrogen atmosphere. The required amount of cocatalyst (MAO, MMAO, or Et₂AlCl) was then injected into the reactor via a syringe. At the reaction temperature, the reactor was sealed and pressurized to high ethylene pressure, and the ethylene pressure was maintained during feeding of ethylene. After the reaction mixture was stirred for the desired period, the pressure was released and a small amount of the reaction solution was collected, which was then analyzed by gas chromatography (GC) to determine the composition and mass distribution of the oligomers obtained. Then the residual reaction solution was quenched with 5% hydrochloric acid ethanol. The precipitated low molecular weight waxes were collected by filtration, washed with ethanol and water, and dried in a vacuum until constant weight.

4.4. X-ray Crystallographic Studies. Single-crystal X-ray diffraction studies for **Me-PBID-MeNiCl₂**, **Me-PBID-esterNiCl₂**, **Me-PBID-acetylNiCl₂**, **L¹NiCl₂**, **L²NiCl₂**, and **L³NiCl₂** were carried out on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). 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 non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package.¹⁸ Crystal data and processing parameters for **Me-PBID-MeNiCl₂**, **Me-PBID-esterNiCl₂**, **Me-PBID-acetylNiCl₂**, **L¹NiCl₂**, **L²NiCl₂**, and **L³NiCl₂** are summarized in Table 8.

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Supporting Information Available: X-ray crystallographic data (CIF) for **Me-PBID-MeNiCl₂**, **Me-PBID-esterNiCl₂**, **Me-PBID-acetylNiCl₂**, **L¹NiCl₂**, **L²NiCl₂**, and **L³NiCl₂**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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