Nickel(II) Complexes Chelated by 2-Arylimino-6-benzoxazolylpyridine: Syntheses, Characterization, and Ethylene Oligomerization

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2-(2-Benzoxazolyl)-6-(1-(arylimino)-ethyl)pyridines (**L**) were designed as ligands, and their nickel complexes $LNiX_2$ (X = Cl, **1a**−**7a**; X = Br, **1b**−**7b**) were formed. All ligands were fully characterized by NMR, FT-IR spectra, and elemental analyses, while the nickel complexes were examined by FT-IR spectra and elemental analyses. The molecular structures of nickel complexes were established by single-crystal X-ray diffraction. Complex **6a** possesses coordination number 6 by coordination of one ligand, two moles of methanol, and one chloride anion, whereas complexes **1b** and **5b** possess coordination number 5 with distinct distortions, for **1b** toward trigonal-bipyramidal geometry and for **5b** toward square-pyramidal geometry. The nickel complex **1a** was evaluated in the catalytic oligomerization of ethylene with different alkylaluminums as cocatalysts, and diethylaluminum chloride (Et_2AlCl) proved to be the most effective. Upon activation with Et_2AlCl, all nickel complexes showed outstanding thermal stability and good catalytic activity toward ethylene dimerization with high selectivity for α-C_4.

1. Introduction

In the past dozen years we have witnessed great progress in the use of late-transition metal complexes as catalysts for reactions of ethylene in both academic and industrial research.[1,2] The SHOP process employing nickel complexes as catalysts has been commercialized,[3] and it was recognized by the Brookhart group that diimine nickel complexes have high activities toward ethylene in catalytic reactions.[4] The progress of ethylene activation by nickel complexes was summarized in recent review articles.[2] As far as efficient catalytic systems are concerned, four-coordinate nickel dihalides bearing chelating P^P,[5] N^O,[6,7] P^N,[8,9] and N^N[10,11] bidentate ligands have been commonly considered. The discovery of the catalytic activity of bis(arylimino)pyridyl Fe(II) and Co(II) dihalides by Brookhart[12] and Gibson[13] generated enthusiasm for designing pentacoordinate nickel(II) complexes incorporating O^N^N,[14] N^P^N,[15] P^N^N,[16] and N^N^N[17,18] tridentate ligands, which

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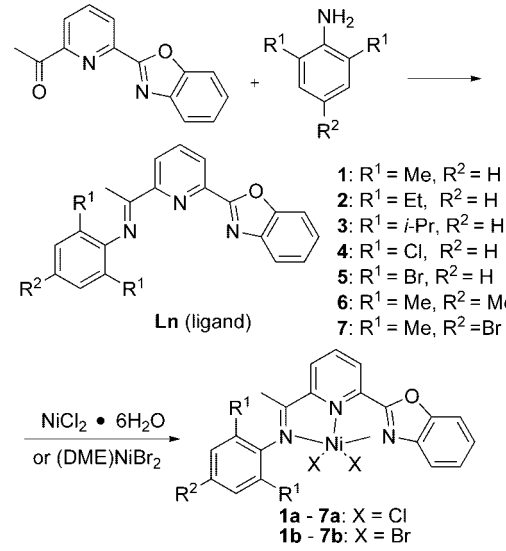
display good to high activity in ethylene oligomerization and polymerization. In exploring alternative tridentate ligands bearing benzene-fused heterocycles for nickel complexes in ethylene reactivity,,[18b,c] metal complexes ligated by 2-(2-benzimidazole)-6-(1-aryliminoethyl)pyridines showed high catalytic activity toward ethylene oligomerization.[19] However, for 2,6-bis(2-benzimidazolyl)pyridine, only its chromium(III) complexes were synthesized and showed high activity for ethylene oligomerization and polymerization.[20] Specifically it would be interesting to replace the benzimidazole with other N-heterocycles. With this in mind, 2-quinoxalinyl-6-aryliminopyridines were designed, and the good catalytic activities of their complexes were confirmed for ethylene oligomerization.[21] In fact, the latter model did not show catalytic activity as high as those containing 2-(2-benzimidazole)-6-(1-aryliminoethyl)pyridines.[19] Since the benzoxazole is considered a replacement for benzimidazole, new models of 2-benzoxazolylpyridine nickel(II) complexes[22] were synthesized and found to present high activity toward ethylene oligomerization. In extension, the N^N^N tridentate nickel(II) complexes bearing 2-(2-benzoxazole)-6-(1-aryliminoethyl) pyridine were synthesized and fully characterized. Upon activation with Et_2AlCl, all nickel complexes showed good catalytic activity toward ethylene dimerization with high selectivity for α-C_4. The influence of reaction parameters and the nature of the complexes on catalytic activities were investigated in detail. Herein the syntheses and characterization of organic compounds and their nickel complexes are reported and discussed along with the catalytic behavior of nickel complexes toward ethylene oligomerization.

Scheme 1. Synthetic Procedure



2. Results and Discussion

2.1. Syntheses and Characterization of the Ligands and Complexes. Following the synthetic procedure for 2-(2-benzimidazolyl)-6-acetylpyridine starting from the reaction of 2,6-lutidine with *o*-phenylenediamine,[19a] 2-(2-benzoxazolyl)-6-acetylpyridine was synthesized in acceptable yield via a modified reaction with *o*-aminophenol instead of *o*-phenylenediamine. The reaction of 2-(2-benzoxazolyl)-6-acetylpyridine with anilines forms 2-(2-benzoxazolyl)-6-(1-aryliminoethyl)pyridines (Scheme 1), and the product yields depended on the aniline substituents. Better yields were achieved with electron-donating substituents, whereas electron-withdrawing substituents gave lower yields. All ligand identities were confirmed by FT-IR and ^1H and ^{13}C NMR spectroscopy as well as by elemental analyses.

The nickel complexes were prepared by mixing $NiCl_2 \cdot 6H_2O$/(DME)$NiBr_2$ with 1 equiv of the corresponding ligand in ethanol/tetrahydrofuran (THF), stirring at room temperature for 12 h (Scheme 1). The resultant nickel complexes precipitated from their reaction solution and were collected by filtration, washed with diethyl ether, and dried under vacuum. All nickel complexes were isolated as air-stable gray powders in moderate to high yields and characterized by FT-IR spectra and elemental analyses, which were in agreement with the formula (L)NiX_2 (L = ligand).

In the FT-IR spectra, the C=N stretching frequencies shifted to lower values between 1610 and 1616 cm^{-1} with weaker intensity compared with those of the corresponding free ligands. Such features are consistent with the existence of coordination between the imino nitrogen atom and the nickel center. The molecular structures of the representative complexes **6a**, **1b**, and **5b** were unambiguously confirmed by single-crystal X-ray diffraction studies.

2.2. Crystal Structures. Single crystals of **6a**, **1b**, and **5b** were grown by diffusing a diethyl ether layer into their methanol solutions. Their molecular structures are shown in Figures 1, 2, and 3, respectively, along with selected bond lengths and angles.

Complex **6a** possesses distorted octahedral coordination geometry around the Ni center, as shown in Figure 1, which

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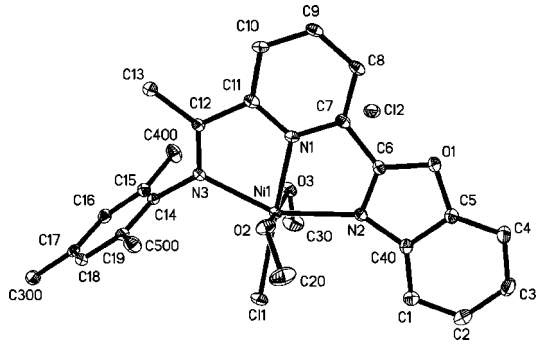

Figure 1. Molecular structure of complex **6a**. Thermal ellipsoids are shown at 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) are as follows: Ni(1)−N(1), 2.020(3); Ni(1)−N(2), 2.151(3); Ni(1)−N(3), 2.153(3); Ni(1)−Cl(1), 2.3043(1); Ni(1)−O(2) 2.111(3); Ni(1)−O(3), 2.109(3); N(2)−C(6), 1.311(4); O(1)−C(6), 1.365(4); N(3)−C(12), 1.291(4); N(1)−Ni(1)−N(2),77.49(1);N(2)−Ni(1)−N(3),154.21(1);N(1)−Ni(1)−N(3), 76.84(1); N(1)−Ni(1)−Cl(1), 176.61(8); N(2)−Ni(1)−Cl(1), 100.65(8); N(3)−Ni(1)−Cl(1), 105.12(8); N(1)−Ni(1)−O(2), 84.25(1); N(1)−Ni(1)−O(3), 87.42(1); O(3)−Ni(1)−O(2), 171.46(1); N(2)−Ni(1)−O(3),87.61(1);N(2)−Ni(1)−O(2),88.75(1);N(3)−Ni(1)−O(2), 91.10(1); N(3)−Ni(1)−O(3), 88.82(1); O(3)−Ni(1)−Cl(1), 95.35(7); O(2)−Ni(1)−Cl(1), 92.91(7).

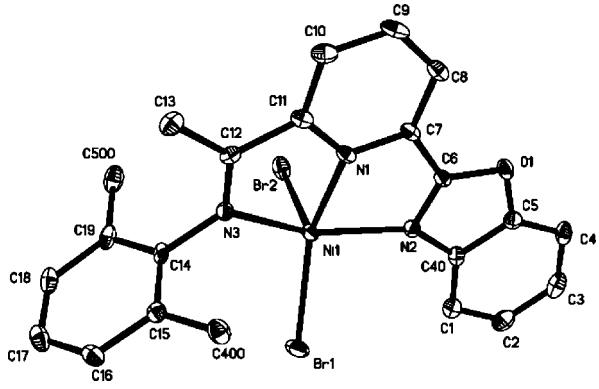

Figure 2. Molecular structure of complex **1b**. Thermal ellipsoids are shown at 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) are as follows: Ni(1)−N(1), 2.000(4); Ni(1)−N(2), 2.149(4); Ni(1)−N(3), 2.139(4); Ni(1)−Br(1), 2.3623(1); Ni(1)−Br(2), 2.4277(1); N(2)−C(6), 1.291(6); O(1)−C(6), 1.360(6); N(3)−C(12), 1.281(6); N(1)−Ni(1)−N(2), 77.31(2); N(2)−Ni(1)−N(3), 152.29(2); N(1)−Ni(1)−N(3), 76.73(2); N(1)−Ni(1)−Br(1), 147.80(1); N(2)−Ni(1)−Br(1), 96.61(1); N(3)−Ni(1)−Br(1), 100.17(1); N(1)−Ni(1)−Br(2), 95.29(1); N(2)−Ni(1)−Br(2), 91.10(1); N(3)−Ni(1)−Br(2), 100.76(1); Br(1)−Ni(1)−Br(2), 116.59(4).

also gives selected bond lengths and angles. The octahedral geometry around the Ni center is formed by three N atoms of the ligand, two O atoms of coordinated methanol solvent, and one Cl atom. The other Cl atom has been displaced from its coordinated site and is found as a free Cl^- anion. The Ni atom deviates by 0.0200 Å out of the N(1)−N(2)−N(3) plane, while the chlorine atom Cl(1) is almost coplanar with a deviation of 0.0411 Å. Two O atoms of coordinated methanol solvent (O(2) and O(3)) occupy the axial positions and with the nickel core form an angle of 171.46(1)°. The O atoms are nearly perpendicular to the equatorial plane with a dihedral angle of 90.3°. The benzoxazole ring is almost coplanar with the pyridine ring (0.9°). Its coordination geometry is similar to that observed in nickel dichloride complexes ligated by 2-(1-methyl-2-benzimidazolyl)-6-acetylpyridine[19b] and *N*-(1-(pyridin-2-yl)ethylidene-)quinolin-8-amine.[18d]

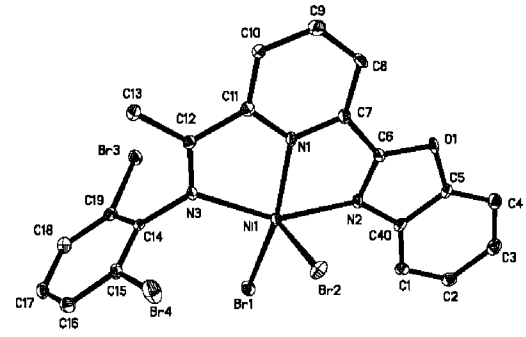

Figure 3. Molecular structure of **5b**. Thermal ellipsoids are shown at 30% probability. Hydrogen atoms and solvent are omitted for clarity. Selected bond lengths (Å) and angles (deg) are as follows: Ni(1)−N(1), 2.003(4); Ni(1)−N(2), 2.128(4); Ni(1)−N(3), 2.135(4); Ni(1)−Br(1), 2.3791(9); Ni(1)−Br(2), 2.4535(1); N(2)−C(6), 1.312(6);O(1)−C(6),1.356(5);N(3)−C(12),1.293(6);N(1)−Ni(1)−N(2), 77.81(2); N(2)−Ni(1)−N(3), 152.28(2); N(1)−Ni(1)−N(3), 76.66(2); N(1)−Ni(1)−Br(1), 159.33(1); N(2)−Ni(1)−Br(1), 100.48(1); N(3)−Ni(1)−Br(1),99.59(1);N(1)−Ni(1)−Br(2),92.20(1);N(2)−Ni(1)−Br(2), 91.43(1); N(3)−Ni(1)−Br(2), 100.14(1); Br(1)−Ni(1)−Br(2), 108.46(4).

Complex **1b** was confirmed as nickel dibromide bearing the tridentate ligand 2,6-dimethyl-*N*-(1-(6-(benzo[*d*]oxazol-2-yl)pyridin-2-yl)ethylidene)benzenamine (Figure 2). The nickel center is five-coordinated in an essentially distorted trigonal-bipyramidal manner. N(1) and two bromine atoms form the equatorial coordination plane, and the nickel center slightly deviates from the equatorial plane by 0.025 Å. The other two nitrogen atoms (N(2) and N(3)) occupy the axial positions and with the nickel core form an angle of 152.29(2)° while simultaneously making a dihedral angle of 97.5° with the equatorial plane. The 2,6-dimethylphenyl group is oriented almost orthogonally to the coordination plane with a dihedral angle of 94.7°. In the molecular structure, the N(2)−C(6) bond distance is 1.291(6) Å, which is shorter than C(6)−O(1) at 1.360(6) Å and is clearly a C═N double bond. This coordination geometry is essentially similar to those commonly observed in nickel complexes coordinated with 2-(benzimidazolyl)-6-(1-(arylimino)ethyl)pyridines.[19b,d]

In contrast to complexes **6a** and **1b**, the coordination geometry of complex **5b** (Figure 3) can be best described as a distorted square pyramid with the basal plane composed by N(1), N(2), N(3), and Br(1) (Figure 3). The nickel atom deviates from the plane formed by N(1), N(2), and N(3) by 0.0862 Å, while the bromine atom Br(1) is almost coplanar with a deviation of 0.0502 Å. The other bromine atom, Br(2), deviates 0.8332 Å from the basal plane at the apex of the pyramid. The plane of the chelating ring Ni(1)−N(2)−C(6)−C(7)−N(1)−C(11)−C(12)−N(3) is nearly perpendicular to the imino-aryl ring (89.1°). The dihedral angle between the imino-aryl ring and the pyridine ring is 88.2°. The Ni−N bond lengths display the trend Ni(1)−N(3) > Ni(1)−N(2) > Ni(1)−N(1), which was similarly observed in nickel(II) complexes bearing 2-(benzimidazolyl)-6-(1-(arylimino)ethyl)pyridines.[19b,d] The two Ni−Br bond lengths are significantly different from each other, which is also seen in **1b**. The N(2)−C(6) bond distance is 1.312(6) Å, shorter than C(6)−O(1) of 1.356(5) Å, displaying clear C═N double bond character. Compared with the structure of **1b**, the repulsion of three lone electron pairs on bromine would make it come close to a structure similar to **1b**.

2.3. Ethylene Oligomerization. When complex **1a** was activated with methylaluminoxane (MAO) or its modified form

Table 1. Selection of a Suitable Cocatalyst Based on 1a[a]

				oligomer distribution (%)[c]		
entry	cocat.	Al/Ni	activity[b]	$C_4/\sum C$	α-C_4	$C_6/\sum C$
1	Et_2AlCl	200	3.12	100	100	0
2	MAO	1000	0.21	98.5	93.7	1.5
3	MMAO	1000	0.04	100	100	0

[a] Reaction conditions: 5 μmol of Ni; 20 °C; 30 min; 10 atm of ethylene; 100 mL of toluene. [b] Activity, 10^5 g mol^{-1}(Ni) h^{-1}. [c] Determined by GC.

Table 2. Ethylene Oligomerization of the 3a/Et_2AlCl System[a]

				oligomer distribution (%)[c]		
entry	Al/Ni	T (°C)	activity[b]	$C_4/\sum C$	α-C_4	$C_6/\sum C$
1	100	20	0.67	98.8	100	1.2
2	200	20	3.43	97.0	97.1	3.0
3	300	20	3.14	97.5	96.4	2.5
4	400	20	2.97	97.9	95.9	2.1
5	600	20	1.44	100	93.8	0
6	200	30	5.52	96.2	89.8	3.8
7	200	40	6.77	96.3	88.1	3.7
8	200	50	14.5	94.6	77.9	5.4
9	200	60	9.49	93.5	77.5	6.5
10	200	70	3.87	100	69.1	0
11[d]	200	50	71.9	94.5	8.30	5.5

[a] Conditions: 5 μmol of Ni; 30 min; 10 atm of ethylene; 100 mL of toluene. [b] Activity, 10^5 g mol^{-1}(Ni) h^{-1}. [c] Determined by GC. [d] 20 equiv of PPh_3 as auxiliary ligand. $\sum C$ denotes the total amount of oligomers.

MMAO for ethylene oligomerization, the catalytic systems showed low activities on the order of 10^4 g mol^{-1}(Ni) h^{-1}. However, when diethylaluminum chloride (Et_2AlCl) was used as the activator, the catalytic activity was an order of magnitude higher (Table 1).

On the basis of these results with complex **1a**, Et_2AlCl was selected as a practical activator for further investigation. All nickel complexes would mainly dimerize ethylene with good selectivity for α-C_4 along with minor amounts of trimers (see below). Compared with a typical good nickel catalyst for ethylene dimerization, such as $(Cy_3P)_2NiCl_2$,[23] the described catalytic nickel systems showed much higher selectivities for α-C_4.

2.3.1. Effects of the Ratio of Et_2AlCl and Temperature on Catalytic Behavior. The influence of the reaction parameters on the catalytic activities, including the molar ratio of Et_2AlCl to nickel complex and reaction temperature, was investigated with complex **3a**. The detailed results are summarized in Table 2. Both the ratio of activator to nickel complex and the reaction temperature significantly affected the catalytic activity, whereas there is no obvious influence on the distribution of oligomers produced.

Initial experiments tested a Al/Ti molar ratio over the range 100−600 at 20 °C. The catalytic activity reached its optimum value of 3.43×10^5 g mol^{-1}(Ni) h^{-1} with a ratio of 200 (entry 2 in Table 2). Upon further increasing the Al/Ni ratio, a slight decrease of the catalytic activity was observed. Compared to the effect of the Al/Ni ratio, the reaction temperature had a dramatic impact on the catalytic activity and selectivity. Increasing the reaction temperature from 20 to 50 °C (entries 2 and 6−8 in Table 2) led to a significant increase in activity. The SHOP catalysts present higher activity at the appropriate temperature higher than room temperature;[24] however, nitrogen-multidentate coordinated cationic nickel(II) catalysts[17,18] usually present higher activity at room temperature than improved temperature. To the best of our knowledge, this catalyst exhibits best activity at 50 °C (entry 8 in Table 2) and represents a unique characteristic among all of the cationic nickel complexes used in ethylene oligomerization. This phenomenon might be attributed to the singular thermal stability of the catalysts formed. With an increase of reaction temperature, the catalytic reaction rate and the reversible β-H elimination rate both increase, which results in lower selectivity for α-C4 along with minor amounts of trimers. Complex **3a** exhibited an activity of 1.45×10^6 g mol^{-1}(Ni) h^{-1} at 50 °C with an Al/Ni molar ratio of 200 under 10 atm of ethylene. By further increasing the temperature from 50 to 70 °C, a decreased activity and lower α-C_4 selectivity were observed (entries 8−10 in Table 2).

Table 3. Oligomerization of Ethylene with 1a−7a/Et_2AlCl[a]

			oligomer distribution (%)[c]		
entry	complex	activity[b]	$C_4/\sum C$	α-C_4	$C_6/\sum C$
1	**1a**	3.69	98.0	93.6	2.0
2	**2a**	4.46	97.5	90.3	2.5
3	**3a**	14.5	94.6	77.9	5.4
4	**4a**	12.5	94.3	77.7	5.7
5	**5a**	5.43	97.3	89.4	2.7
6	**6a**	6.14	97.4	86.5	2.6
7	**7a**	10.4	97.8	89.2	2.2

[a] Conditions: 5 μmol of Ni; Et_2AlCl/Ni = 200; 50 °C; reaction time, 30 min; 10 atm of ethylene; 100 mL of toluene. [b] Activity, 10^5 g mol^{-1}(Ni) h^{-1}. [c] Determined by GC.

Including PPh_3 as an auxiliary ligand in the nickel catalyst system has led to great improvements in the catalytic activities and lifetimes.[7c,9e,17a,e,19b,25] The plausible role of PPh_3 is to stabilize the catalytically active species while being labile enough to provide a site for ethylene coordination.[3c8e] For complex **3a**, the addition of 20 equiv of PPh_3 resulted in increased catalytic activity, but a drastic decrease in the selectivity for α-butene was observed (entry 11 in Table 2).

2.3.2. Effect of the Nature of the Complexes on Their Catalytic Activities. The nature of the nickel complexes is dependent upon the ligands and the halide and affects their catalytic behavior in ethylene oligomerization. The nickel complexes would be better separated into two groups based upon the coordinated halide [(L)$NiCl_2$ (**1a**−**7a**) and (L)$NiBr_2$ (**1b**−**7b**)]. Employing the optimum reaction conditions selected by using complex **3a** (molar ratio of Et_2AlCl/Ni 200, temperature 50 °C and 10 atm ethylene), all nickel complexes displayed good to high catalytic activities. The results for the nickel chlorides (L)$NiCl_2$ (**1a**−**7a**) are collected in Table 3, and the results for the nickel bromides (L)$NiBr_2$ (**1b**−**7b**) in Table 4.

Comparing the two sets of data, the effect of the ligands on catalytic activities is clearly reflected. Since excessive amounts of Et_2AlCl were used in these catalytic systems, the function of halide anions of complexes should become very weak. However, the nickel chloride complexes (Table 3) generally showed higher catalytic activities than their bromide analogues (Table 4). The bonding strength of the Al−Cl is higher than that of the Al−Br; therefore the trend for the chloride anion to

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Table 4. Oligomerization of Ethylene with 1b−7b/Et_2AlCl[a]

			oligomer distribution (%)[c]		
entry	complex	activity[b]	$C_4/\sum C$	α-C_4	$C_6/\sum C$
1	**1b**	1.74	97.7	91.5	2.3
2	**2b**	3.48	95.1	90.6	4.9
3	**3b**	8.31	94.6	81.7	5.4
4	**4b**	5.67	94.2	87.9	5.8
5	**5b**	4.03	95.6	90.3	4.4
6	**6b**	3.12	97.3	91.2	2.7
7	**7b**	6.24	98.8	90.2	1.2

[a] Conditions: 5 μmol of Ni; $Et_2AlCl/Ni = 200$; 50 °C; reaction time, 30 min; 10 atm of ethylene; 100 mL of toluene. [b] Activity, 10^5 g mol^{-1}(Ni) h^{-1}. [c] Determined by GC.

be lost is easier than that of the bromide anion in their nickel complexes, and then the net positive charge on the nickel center bearing two chloride anions is higher than the ones bearing two bromide anions. This results in higher catalytic activities for the nickel complexes bearing two chloride anions. These results also agree with our previous computational conclusion on the relationship of catalytic activity with the net charge of late-transition metal complexes.[26] We have also chosen to investigate how the nature of the substituents as well as the substitution pattern on the imino-phenyl group of the 2-(2-benzoxazolyl)-6-(1-aryliminoethyl)pyridine ligands affects the catalytic activity of the nickel complexes. With 2,6-dialkyl substituents (entries 1−3 in Table 3 and 1−3 in Table 4), the bulkier substituents led to increases in the catalytic activity of the nickel complexes. The active sites in the systems with less bulky substituents are exposed to not only ethylene but also other reactants (impurities), and this leads to the deactivation of the active species. In addition, the bulkier substituents increase the solubility of the complexes.

The catalytic activities of complexes with 2,6-dihalo-substituted imino-phenyl groups (entries 4, 5 in Tables 3 and 4) are comparable, but better activities for the chloro-substituted complexes were observed. Though the halogen atoms are far from the nickel atom, the net charge of active species would still be partly affected, and the more positive the net charge of nickel is, the more active the species.[26] Surely, we could not figure out that the less steric hindrance of chlorine than bromine could provide more appropriate space for ethylene to insert and result in better activity. The complexes bearing 2,6-dihalo-substituted imino-phenyl groups did not show better activities than complexes bearing 2,6-diisopropyl substituents. A possible reason could be the better solubility of complexes bearing 2,6-diisopropyl substituents. In the same manner, by placing a substituent at the 4-position of the aryl ring, it is possible to increase the solubility of the nickel complex. This would explain the higher catalytic activities of complexes **6a** and **6b** containing a methyl group at the 4-position (entry 6 in Tables 3 and 4) and **7a** and **7b** with a bromo group at the 4-position of aryl group (entry 7 in Tables 3 and 4), when compared to their 2,6-dimethyl analogues **1a** and **1b** (entry 1 in Tables 3 and 4). Moreover, complexes **7a** and **7b** showed the highest activity.

The mechanism of ethylene oligomerization and polymerization by traditional Brookhart-type Ni(II) and Pd(II) diimine catalysts and tridentate bis(imino)pyridine Fe(II) and Co(II) catalysts has been extensively studied by using density functional theory (DFT),[27] integrated molecular orbital−molecular mechanics (IMOMM) method,[28] low-temperature ^{1}H NMR spectroscopy,[4a,29] and in situ UV−vis spectroscopy.[30] An alkylated nickel active species was isolated as an intermediate in the related nickel catalytic system.[7c] Tridentate Ni(II) catalysts used for ethylene activation have been reported,[14−18] and the distribution of products was determined by rates of chain propagation and chain transfer rates. In our system, the nickel catalyst precursors showed high activity and selectivity in forming C4, and a similar phenomenon has been observed in other N^N^N tridentate nickel(II) complexes.[17,18] According to the mechanism proposed by Braunstein,[14] the formation of various hexenes could be inferred by reincorporation of butene. That the title catalysts showed high selectivity for forming α-C_4 might be attributed to the fact that rates of chain transfer are much higher than chain propagation rates.

Compared with nickel complexes bearing 2-benzimidazole-6-(1-aryliminoethyl)pyridines,[19b,d] the title complexes containing a 2-benzoxazole substituent present much higher catalytic activities as well as better thermal stability. The benzoxazole substituent on the ligand backbone is helpful in increasing the net charge on the metal center, thus having a positive impact on the catalytic activity and the stability of the active center. All nickel complexes show good activity even at relatively high temperatures. These results also are in line with the computational conclusions on the relationship of catalytic activity to the net charge of the metal center in late-transition metal complexes, in that the stronger the electron-donating ability of the ligand, the lower the net charge on the metal, which results in lower catalytic activities.[26]

3. Conclusions

A series of nickel(II) complexes bearing 2-benzoxazolyl-6-(1-aryliminoethyl)pyridines has been synthesized and fully characterized. Upon treatment with Et_2AlCl, these nickel (II) complexes showed high catalytic activities of up to 1.45×10^6 g mol^{-1}(Ni) h^{-1} at 50 °C, which is a higher activity and due to better thermostability compared to the related cationic nickel catalysts.[19b,d,21b] The nickel chloride catalyst showed better activity than the bromide analogues. The R-substituents on the *N*-aryl ring influenced the catalytic activities. The bulkier the alkyl substituents the ligand has, the higher catalytic activity the complex shows; complexes with additional substituents at the 4-position of the aryl group had even higher activity. When PPh_3 was employed as an auxiliary ligand, the catalytic activity increased to up to 7.19×10^6 g mol^{-1}(Ni) h^{-1}.

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. 2-(2-Benzoxazole)-6-acetylpyridine was prepared using a modified procedure according to the literature.[19a] Toluene was refluxed over sodium-benzophe-

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none 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, 3A) were purchased from Akzo Nobel Corp. Diethylaluminum chloride (Et_2AlCl_2, 1.7 M in toluene) was purchased from Acros Chemicals. Other reagents were purchased from Aldrich or Acros Chemicals. ^1H and ^{13}C NMR spectra were recorded on a Bruker DMX 300 or 400 MHz instrument at ambient temperature using TMS as an internal standard. FT-IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer. Elemental analyses were 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. The yields of oligomers were 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 α-C_4 was defined as (amount of α-C_4)/(total amounts of C_4) in percent.

4.2. Syntheses and Characterization. 2,6-Dimethyl-*N*-(1-(6-(benzo[*d*]oxazol-2-yl)pyridin-2-yl)ethylidene)benzenamine (L1). A solution of 2-(2-benzoxazole)-6-acetylpyridine (0.95 g, 4 mmol), 2,6-dimethylaniline (0.67 g, 4.8 mmol), and a catalytic amount of *p*-toluenesulfonic acid in toluene (50 mL) was refluxed for 24 h. After solvent evaporation, the crude product was purified with petroleum ether/ethyl acetate (v/v = 20:1) on an alumina column. The second part to elute was collected and concentrated to give a yellow powder (0.70 g, 51% yield). Mp: 136−137 °C. FT-IR (KBr disk, cm^{-1}): 3069, 1644 ($\nu_{C=N}$), 1581, 1552, 1453, 1365, 1245, 1208, 1155, 1110, 1092, 1075, 823, 762. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 8.56 (d, 1H, J = 7.9, Py, H_m), 8.45 (d, 1H, J = 7.7, Py, H_m), 8.02 (t, 1H, J = 7.9, Py, H_p), 7.88−7.86 (m, 1H, Ar *H*), 7.70−7.68 (m, 1H, Ar *H*), 7.45−7.39 (m, 2H, Ar *H*), 7.09 (d, 2H, J = 7.5, Ar *H*), 6.96 (t, 1H, J = 7.4, Ar *H*), 2.36 (s, 3H, CH_3), 2.06 (s, 6H, 2 × CH_3). ^{13}C NMR (300 MHz, $CDCl_3$, TMS): δ 167.0, 156.9, 151.1, 148.6, 145.2, 141.9, 137.4, 128.0, 126.0, 125.3, 124.9, 124.7, 123.2, 120.8, 111.2, 18.0, 16.7. Anal. Calcd for $C_{22}H_{19}N_3O$ (341.41): C, 77.40; H, 5.61; N, 12.31. Found: C, 77.21; H, 5.64; N, 12.42.

2,6-Diethyl-*N*-(1-(6-(benzo[*d*]oxazol-2-yl)pyridin-2-yl)ethylidene)benzenamine (L2). Using the same procedure as for the synthesis of **L1**, **L2** was obtained as a yellow powder in 69% yield. Mp: 123−124 °C. FT-IR (KBr disk, cm^{-1}): 2966, 1651 ($\nu_{C=N}$), 1584, 1569, 1551, 1455, 1403, 1364, 1326, 1244, 1200, 1156, 1115, 1074, 855, 752. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 8.55 (d, 1H, J = 7.9, Py, H_m), 8.45 (d, 1H, J = 7.8, Py, H_m), 8.01 (t, 1H, J = 7.9, Py, H_p), 7.87−7.85 (m, 1H, Ar *H*), 7.72−7.66 (m, 1H, Ar *H*), 7.46−7.38 (m, 2H, Ar *H*), 7.13 (d, 2H, J = 7.6, Ar *H*), 7.08−6.96 (m, 1H, Ar *H*), 2.42 (q, 2H, J = 7.8, CH_2), 2.37 (s, 3H, CH_3), 2.34 (q, 2H, CH_2), 1.15 (t, 6H, J = 6.5, 2 × CH_3). ^{13}C NMR (400 MHz, $CDCl_3$, TMS): δ 166.2, 161.1, 156.4, 150.6, 147.2, 144.7, 141.4, 137.0, 130.6, 127.1, 125.5, 124.5, 124.2, 123.1, 122.6, 120.3, 117.8, 110.7, 24.2, 16.6, 13.3. Anal. Calcd for $C_{24}H_{23}N_3O$ (369.46): C, 78.02; H, 6.27; N, 11.37. Found: C, 77.82; H, 6.24; N, 11.43.

2,6-Diisopropyl-*N*-(1-(6-(benzo[*d*]oxazol-2-yl)pyridin-2-yl)-ethylidene)benzenamine (L3). Using the same procedure as for the synthesis of **L1**, **L3** was obtained as a yellow powder in 50% yield. Mp: 159−160 °C. FT-IR (KBr disk, cm^{-1}): 2964, 1651 ($\nu_{C=N}$), 1586, 1550, 1456, 1366, 1324, 1242, 1190, 1116, 1076, 766, 751, 670. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 8.56 (d, 1H, J = 7.9, Py, H_m), 8.45 (d, 1H, J = 7.8, Py, H_m), 8.01 (t, 1H, J = 7.9, Py, H_p), 7.89−7.86 (m, 1H, Ar *H*), 7.70−7.67 (m, 1H, Ar *H*), 7.46−7.38 (m, 2H, Ar *H*), 7.21−7.18 (m, 2H, Ar *H*), 7.14−7.09 (m, 1H, Ar *H*), 2.81−2.74 (m, 2H, 2 × CH), 2.40 (s, 3H, CH_3), 1.18−1.15 (m, 12H, 4 × CH_3). ^{13}C NMR (400 MHz, $CDCl_3$, TMS): δ 166.7, 161.5, 156.8, 151.0, 146.2, 145.1, 141.8, 137.5, 135.7, 126.0, 124.9, 124.7, 123.7, 123.2, 123.0, 120.7, 111.2, 28.3, 23.2, 22.9, 17.3. Anal. Calcd for $C_{26}H_{27}N_3O$ (397.51): C, 78.56; H, 6.85; N, 10.57. Found: C, 78.32; H, 6.67; N, 10.54.

2,6-Dichloro-*N*-(1-(6-(benzo[*d*]oxazol-2-yl)pyridin-2-yl)ethylidene)benzenamine (L4). A solution of 2-(2-benzoxazole)-6-acetylpyridine (0.72 g, 3 mmol), 2,6-dichoroaniline (0.64 g, 3.9 mmol), and a catalytic amount of *p*-toluenesulfonic acid in tetraethyl silicate in toluene solvent (3 mL) was refluxed for 24 h. After solvent evaporation, the crude product was purified with petroleum ether/ethyl acetate (v/v = 20:1) on an alumina column. The second part to elute was collected and concentrated to give a white powder in 12.0% yield. Mp: 170−171 °C. FT-IR (KBr disk, cm^{-1}): 3066, 1646 ($\nu_{C=N}$), 1585, 1550, 1454, 1434, 1367, 1245, 1225, 1155, 1116, 1077, 786, 767, 745. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 8.56 (d, 1H, J = 7.8, Py, H_m), 8.48 (d, 1H, J = 7.7, Py, H_m), 8.03 (t, 1H, J = 7.8, Py, H_p), 7.89−7.86 (m, 1H, Ar *H*), 7.70−7.68 (m, 1H, Ar *H*), 7.46−7.40 (m, 2H, Ar *H*), 7.37 (d, 2H, J = 8.0, Ar *H*), 7.02 (t, 1H, J = 8.0, Ar *H*), 2.48 (s, 3H, CH_3). ^{13}C NMR (300 MHz, $CDCl_3$, TMS): δ 170.5, 160.7, 155.4, 150.4, 144.8, 144.6, 141.2, 137.0, 127.6, 125.4, 124.6, 124.3, 123.9, 123.8, 123.2, 120.1, 110.5, 17.1. Anal. Calcd for $C_{20}H_{13}Cl_2N_3O$ (382.24): C, 62.84; H, 3.43; N, 10.99. Found: C, 62.72; H, 3.44; N, 11.02.

2,6-Dibromo-*N*-(1-(6-(benzo[*d*]oxazol-2-yl)pyridin-2-yl)ethylidene)benzenamine (L5). Using the same procedure as for the synthesis of **L4**, **L5** was obtained as a white powder in 43% yield. Mp: 169−170 °C. FT-IR (KBr disk, cm^{-1}): 3063, 1647 ($\nu_{C=N}$), 1583, 1549, 1454, 1432, 1402, 1368, 1243, 1223, 1153, 1120, 1093, 1076, 853, 762. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 8.58 (d, 1H, J = 7.8, Py, H_m), 8.49 (d, 1H, J = 7.8, Py, H_m), 8.04 (t, 1H, J = 7.8, Py, H_p), 7.89−7.87 (m, 1H, Ar *H*), 7.71−7.68 (m, 1H, Ar *H*), 7.59 (d, 2H, J = 8.1, Ar *H*), 7.46−7.40 (m, 2H, Ar *H*), 6.88 (t, 1H, J = 8.0, Ar *H*), 2.47 (s, 3H, CH_3). ^{13}C NMR (400 MHz, $CDCl_3$, TMS): δ 171.1, 161.5, 156.1, 151.2, 148.1, 145.5, 142.0, 137.8, 132.1, 126.2, 125.6, 125.4, 125.1, 124.0, 120.9, 113.6, 111.3, 18.0. Anal. Calcd for $C_{20}H_{13}Br_2N_3O$ (471.14): C, 50.99; H, 2.78; N, 8.92. Found: C, 50.84; H, 2.84; N, 8.69.

2,4,6-Trimethyl-*N*-(1-(6-(benzo[*d*]oxazol-2-yl)pyridin-2-yl)-ethylidene)benzenamine (L6). Using the same procedure as for the synthesis of **L1**, **L6** was obtained as a yellow powder in 57% yield. Mp: 150−151 °C. FT-IR (KBr disk, cm^{-1}): 3069, 1645($\nu_{C=N}$), 1550, 1479, 1453, 1364, 1245, 1215, 1146, 1116, 1074, 850, 822, 744. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 8.55 (d, 1H, J = 7.9, Py, H_m), 8.44 (d, 1H, J = 7.6, Py, H_m), 8.00 (t, 1H, J = 7.8, Py, H_p), 7.88−7.86 (m, 1H, Ar *H*), 7.70−7.68 (m, 1H, Ar *H*), 7.46−7.39 (m, 2H, Ar *H*), 6.91 (s, 2H, Ar *H*), 2.35 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.02 (s, 6H, 2 × CH_3). ^{13}C NMR (400 MHz, $CDCl_3$, TMS): δ 167.3, 161.7, 157.2, 151.2, 146.2, 145.3, 142.0, 137.6, 132.5, 129.0, 128.8, 126.1, 125.3, 125.1, 124.8, 123.3, 120.9, 111.3, 20.9, 18.0, 16.8. Anal. Calcd for $C_{23}H_{21}N_3O$ (355.43): C, 77.72; H, 5.96; N, 11.82. Found: C, 77.64; H, 6.02; N, 11.88.

4-Bromo-2,6-dimethyl-*N*-(1-(6-(benzo[*d*]oxazol-2-yl)pyridin-2-yl)ethylidene)benzenamine (L7). Using the same procedure as for the synthesis of **L1**, **L7** was obtained as a yellow powder in 56% yield. Mp: 170−171 °C. FT-IR (KBr disk, cm^{-1}): 2924, 1642 ($\nu_{C=N}$), 1583, 1554, 1453, 1365, 1244, 1207, 1154, 1108, 1074, 835, 744. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 8.52 (d, 1H, J = 7.9, Py, H_m), 8.45 (d, 1H, J = 7.6, Py, H_m), 8.01 (t, 1H, J = 7.8, Py, H_p), 7.88−7.86 (m, 1H, Ar *H*), 7.70−7.67 (m, 1H, Ar *H*), 7.46−7.39 (m, 2H, Ar *H*), 7.23 (s, 2H, Ar *H*), 2.35 (s, 3H, CH_3), 2.02 (s, 6H, 2 × CH_3). ^{13}C NMR (400 MHz, $CDCl_3$, TMS): δ 167.9, 161.6, 156.7, 151.2, 147.8, 145.4, 142.0, 137.6, 130.7 × 3, 127.8 × 2, 126.2, 125.0, 123.3, 120.9, 115.9, 111.3, 17.9 × 2, 17.0. Anal. Calcd for $C_{22}H_{18}BrN_3O$ (420.30): C, 62.87; H, 4.32; N, 10.00. Found: C, 62.47; H, 4.54; N, 10.38.

4.3. Synthesis of Nickel Complexes. General Procedure: A solution of $NiCl_2 \cdot 6H_2O$ in ethanol or $(DME)NiBr_2$ in THF was added dropwise to a solution of the corresponding ligand in ethanol

(THF). The reaction mixture was stirred at room temperature for 12 h, forming a precipitate. The resulting precipitate was collected, washed with diethyl ether, and dried under vacuum. All of the complexes were prepared in high yield in this manner.

1a: gray powder in 84% yield. FT-IR (KBr disk, cm^{-1}): 2916, 1615 ($\nu_{C=N}$), 1595, 1544, 1449, 1377, 1280, 1216, 1173, 1101, 1029, 812, 792, 768. Anal. Calcd for $C_{22}H_{19}Cl_2N_3NiO$ (471.01): C, 56.10; H, 4.07; N, 8.92. Found: C, 55.75; H, 3.98; N, 8.70.

2a: gray powder in 70% yield. FT-IR (KBr disk; cm^{-1}): 2972, 1611 ($\nu_{C=N}$), 1594, 1571, 1544, 1449, 1377, 1278, 1211, 1195, 1104, 1028, 814, 788, 769, 750. Anal. Calcd for $C_{24}H_{23}Cl_2N_3NiO$ (499.06): C, 57.76; H, 4.65; N, 8.42. Found: C, 57.36; H, 4.71; N, 8.27.

3a: gray powder in 62% yield. FT-IR (KBr disk; cm^{-1}): 3066, 2962, 2869, 1613 ($\nu_{C=N}$), 1594, 1544, 1449, 1377, 1278, 1210, 1193, 1102, 1027, 817, 788, 769, 746. Anal. Calcd for $C_{26}H_{27}Cl_2N_3NiO$ (527.11): C, 59.24; H, 5.16; N, 7.97. Found: C, 59.53; H, 5.23; N, 7.98.

4a: gray powder in 62% yield. FT-IR (KBr disk; cm^{-1}): 3051, 1617 ($\nu_{C=N}$), 1595, 1544, 1439, 1378, 1280, 1234, 1176, 1089, 1030, 814, 773. Anal. Calcd for $C_{20}H_{13}Cl_4N_3NiO$ (511.84): C, 46.93; H, 2.56; N, 8.21. Found: C, 46.63; H, 2.45; N, 8.14.

5a: gray powder in 76% yield. FT-IR (KBr disk; cm^{-1}): 3046, 1616 ($\nu_{C=N}$), 1595, 1546, 1431, 1377, 1279, 1230, 1177, 1089, 1029, 773, 730. Anal. Calcd for $C_{20}H_{13}Br_2Cl_2N_3NiO$ (600.74): C, 39.99; H, 2.18; N, 6.99. Found: C, 39.73; H, 2.25; N, 6.93.

6a: gray powder in 89.7% yield. FT-IR (KBr; cm^{-1}): 2917, 1611 ($\nu_{C=N}$), 1592, 1541, 1448, 1373, 1277, 1219, 1173, 1028, 815, 772, 745. Anal. Calcd for. $C_{23}H_{21}Cl_2NiN_3O$ (485.03): C, 56.95; H, 4.36; N, 8.66. Found: C, 56.77; H, 4.32; N, 8.57.

7a: gray powder in 83.3% yield. FT-IR (KBr disk, cm^{-1}): 2911, 1618 ($\nu_{C=N}$), 1595, 1548, 1453, 1374, 1276, 1211, 1023, 995, 865, 772. Anal. Calcd for $C_{22}H_{18}BrCl_2NiN_3O$ (549.90): C, 48.05; H, 3.30; N, 7.64. Found: C, 47.86; H, 3.43; N, 7.76.

1b: gray powder in 88% yield. FT-IR (KBr disk; cm^{-1}): 3410, 1614 ($\nu_{C=N}$), 1594, 1543, 1449, 1377, 1279, 1215, 1173, 1101, 1029, 814, 791, 765. Anal. Calcd for $C_{22}H_{19}Br_2N_3NiO$ (559.91): C, 47.19; H, 3.42; N, 7.50. Found: C, 46.89; H, 3.53; N, 7.10.

2b: gray powder in 88% yield. FT-IR (KBr disk; cm^{-1}): 2975, 1610 ($\nu_{C=N}$), 1594, 1571, 1543, 1448, 1378, 1278, 1211, 1194, 1172, 1103, 1028, 812, 788, 764, 750. Anal. Calcd for $C_{24}H_{23}Br_2N_3NiO$ (587.96): C, 49.03; H, 3.94; N, 7.15. Found: C, 48.96; H, 4.07; N, 6.98.

3b: gray powder in 86% yield. FT-IR (KBr disk; cm^{-1}): 2960, 1612 ($\nu_{C=N}$), 1594, 1543, 1448, 1378, 1278, 1209, 1193, 1103, 1028, 816, 788, 765. Anal. Calcd for $C_{26}H_{27}Br_2N_3NiO$ (616.01): C, 50.69; H, 4.42; N, 6.82. Found: C, 50.75; H, 4.68; N, 6.57.

4b: gray powder in 72% yield. FT-IR (KBr disk; cm^{-1}): 2904, 1616 ($\nu_{C=N}$), 1596, 1543, 1439, 1378, 1280, 1233, 1175, 1088, 1030, 855, 783, 770. Anal. Calcd for $C_{20}H_{13}Br_2Cl_2N_3NiO$ (600.74): C, 39.99; H, 2.18; N, 6.99. Found: C, 39.60; H, 2.33; N, 6.90.

5b: gray powder in 82% yield. FT-IR (KBr disk; cm^{-1}): 3060, 1612 ($\nu_{C=N}$), 1593, 1541, 1430, 1377, 1279, 1229, 1174, 1088, 1026, 854, 788, 758, 730. Anal. Calcd for $C_{20}H_{13}Br_4N_3NiO$ (689.65): C, 34.83; H, 1.90; N, 6.09. Found: C, 34.65; H, 1.92; N, 5.84.

6b: gray powder in 87.2% yield. FT-IR (KBr; cm^{-1}): 2918, 1610 ($\nu_{C=N}$), 1592, 1538, 1448, 1370, 1276, 1217, 1172, 1026, 814, 772, 744. Anal. Calcd for $C_{23}H_{21}Br_2NiN_3O$ (573.93): C, 48.13; H, 3.69; N, 7.32. Found: C, 48.24; H, 3.77; N, 7.42.

7b: gray powder in 85.1% yield. FT-IR (KBr disk, cm^{-1}): 2909, 1612 ($\nu_{C=N}$), 1593, 1540, 1450, 1379, 1279, 1212, 1030, 1002, 867, 760. Anal. Calcd for $C_{22}H_{18}Br_3NiN_3O$ (638.80): C, 41.36; H, 2.84; N, 6.58. Found: C, 41.62; H, 2.88; N, 6.74.

4.3. X-ray Crystallographic Studies. Single crystals of **6a**, **1b**, and **5b** suitable for X-ray diffraction studies were obtained by diffusing a diethyl ether layer into their methanol solutions. Single-crystal X-ray diffraction studies for **6a**, **1b**, and **5b** were carried out on a Rigaku RAXIS Rapid IP diffractometer with graphite-monochromated Mo Kα radiation (λ= 0.71073 Å). Cell parameters were obtained by global refinement of the positions of all collected

Table 5. Crystal Data and Structure Refinement Details for 1a, 1b, and 5b

	6a·$3CH_3OH$	**1b**	**5b**·CH_3OH
formula	$C_{23}H_{21}Cl_2N_3NiO \cdot 3CH_3OH$	$C_{22}H_{19}Br_2N_3NiO$	$C_{20}H_{13}Br_4N_3NiO \cdot CH_3OH$
fw	581.16	559.93	721.67
T (K)	173(2)	173(2)	173(2)
wavelength (Å)	0.71073	0.71073	0.71073
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2(1)/c$	$P\bar{1}$	$P2(1)/c$
a (Å)	9.984(2)	9.2389(2)	11.110(2)
b (Å)	12.774(3)	9.817(2)	15.427(3)
c (Å)	22.118(4)	11.656(2)	15.714(6)
α (deg)	90	91.31(3)	90
β (deg)	95.56(3)	98.99(3)	121.36(2)
γ (deg)	90	95.83(3)	90
V (Å^3)	2807.6(1)	4643.87(1)	2299.8(1)
Z	4	2	4
D_{calc} (Mg m^{-3})	1.375	1.791	2.084
μ (mm^{-1})	0.917	4.803	7.817
F(000)	1216	556	1392
cryst size (mm)	0.52 × 0.40 × 0.33	0.42 × 0.21 × 0.11	0.28 × 0.23 × 0.22
θ range (deg)	1.84 - 25.00	2.24 - 25.00	2.15 − 25.00
limiting indices	$-11 \le h \le 11$, $-15 \le k \le 15$, $-26 \le l \le 26$	$-10 \le h \le 10$, $-11 \le k \le 11$, $-13 \le l \le 13$	$-13 \le h \le 13$, $-18 \le k \le 18$, $-18 \le l \le 18$
no. of rflns collected	9471	6732	7498
no. of unique rflns	4935	3646	4053
completeness to θ (%)	99.8 (θ = 25.00)	99.9 (θ = 25.00)	99.8 (θ = 25.00)
abs corr	multiscan	multiscan	multiscan
data/restraints/params	4935/0/338	3646/0/262	4053/1/296
goodness of fit on F^2	1.166	1.139	1.102
final R indices ($I > 2\sigma(I)$)	R1 = 0.0497, wR2 = 0.1003	R1 = 0.0532, wR2 = 0.0900	R1 = 0.0418, wR2 = 0.0654
R indices (all data)	R1 = 0.0619, wR2 = 0.1052	R1 = 0.0760, wR2 = 0.0957	R1 = 0.0630, wR2 = 0.0693
largest diff peak and hole (e Å^{-3})	0.537 and −0.569	0.628 and −0.634	0.584 and −0.518

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.[31] Crystal data and processing parameters for **6a**, **1b**, and **5b** are summarized in Table 5.

4.4. General Procedure for Ethylene Oligomerization. Ethylene oligomerization at 10 atm ethylene pressures was carried out in a 500 mL stainless steel autoclave equipped with a mechanical stirrer and a temperature controller. The catalyst (and PPh_3) was dissolved in toluene in a Schlenk tube with stirring, and 50 mL of toluene and the desired amount of $EtAlCl_2$ were added. Then the mixture and 50 mL of toluene were added into the autoclave under ethylene atmosphere. When the desired reaction temperature was reached, ethylene at the desired pressure was introduced to start the reaction. After the desired time, the reaction was stopped. A small amount of the reaction solution was collected; the reaction was terminated by the addition of 5% aqueous hydrogen chloride and then analyzed by gas chromatography (GC) to determine the distribution of oligomers obtained.

(31) Sheldrick, G. M. *SHELXL-97*, Program for the Refinement of Crystal Structure; Universität of Göttingen, Göttingen: Germany, 1997.

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Supporting Information Available: Crystallographic data for **6a**, **1b**, and **5b** are available free of charge via the Internet at http://pubs.acs.org.

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