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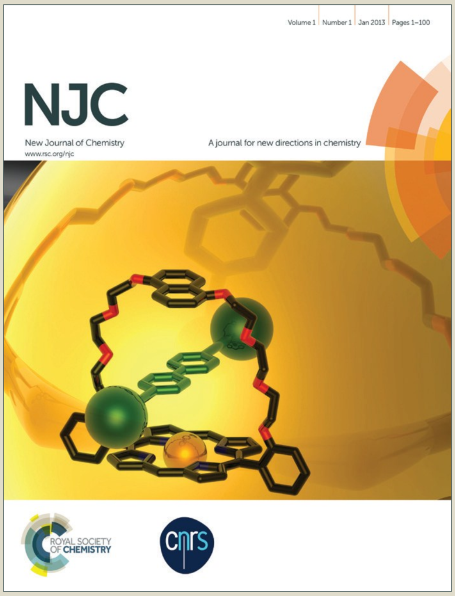

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ARTICLE

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

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ABSTRACT: *N*,*N*′-Bis(2,6-R-phenyl)-2,6-pyridinedicarboxamide (**L:** R = Cl, **L1**; R = F, **L2**; R = H, **L3**; R = Me, **L4**; R = Et, **L5**; R = ^{i}Pr, **L6**) were designed as neutral ligands, and the corresponding nickel complexes **LNiBr$_2$** (**Ni1**-**Ni6**) were synthesized as precatalysts for ethylene oligomerization. All new ligands were fully characterized by NMR, FT-IR spectra, and elemental analysis, while the nickel complexes were examined by FT-IR spectra and elemental analysis. The coordination mode of ligand with nickel in complexes **Ni5** and **Ni6** was tridentate by O^N^O as established by single crystal X-ray diffractions. All the nickel complexes **Ni1**-**Ni6** were tested for ethylene oligomerization with different alkylaluminums as cocatalysts, and diethylaluminum chloride (Et$_2$AlCl) was proved to be the most effective. Upon activation with Et$_2$AlCl, all nickel complexes showed high catalytic activity (up to 7.55 × 10^5 g·mol^{-1}(Ni)·h^{-1}·atm^{-1}) with good selectivity for α-C$_4$.

1. Introduction

Ethylene oligomerization represents a topic of considerable interest in both academia and industry since the productions of linear α-olefins (LAO) are extensively used in the preparation of detergents, lubricants, as well as comonomers for the synthesis of linear low density polyethylene (LLDPE).[1] Late transition metals are promising candidates for the development of oligomerization catalysts due to their favoring chain transfer over propagation during the catalytic cycles.[2] Among them, nickel has been proved the preference for ethylene oligomerization,[3] and many systems based on this metal have provided very intriguing catalytic results.[4] The remarkable catalytic systems include the Shell Higher Olefin Process (SHOP)[5] employing the neutral nickel complex Ni(P,O)(PR$_3$)R′ and Brookhart's cationic Ni(II)-based catalysts of the type [ArN=C(R)C(R)=NAr]MCH$_3^+$.[6] Inspired by the pioneering research, considerable attention has been paid on the development of new nickel complexes bearing bidentate[7] and tridentate ligands[8] for ethylene oligomerization and polymerization. The key part of the development has recently been focused on well-design of suitable ligands in order to improve catalytic performances, and the relationships between catalyst structure and catalytic properties were well summarized in recent review.[9]

The amide bond is one of the most important functional groups in contemporary chemistry and in nature.[10] It is essential to sustain life, forming the peptide bonds in proteins such as enzymes and being found in numerous natural products as well as synthetic pharmaceutical molecules. The amide linkages have the advantage of convenient synthesis and high stability, and could act as chelating sites for transition metals with various coordination modes, which makes it to be a promising ligand and attracts much attention in coordination chemistry.[11] In the earlier work (Chart 1), we studied titanium complexes for ethylene polymerization based on *N*-(2-methylquinolin-8-yl)benzamide (**A**),[12] 6-benzimidazolylpyridine-2-carboxylimidate (**B**)[13] and *N*-(2-benzimidazolylquinolin-8-yl)benzamide (**C**),[14] in which the amide carbonyl groups acted as anionic ligands and exhibit bidentate O^N, monodentate O and N-coordination mode, respectively. We also investigated titanium (**D**) and chromium (**E**) complexes bearing the same ligand, 2-benzimidazolyl-*N*-phenylquinoline-8-carboxamide.[15] The amide group coordinated with the titanium and chromium center by anionic oxygen and neutral oxygen, respectively. Moreover, the amide group exhibits excellent ability to tune the electronic effect of the catalysts due to the resonance and tautomerization (Chart 2),[16] which promises it to be a suitable candidate as the ligand for the synthesis of metal complex catalysts. In this context,

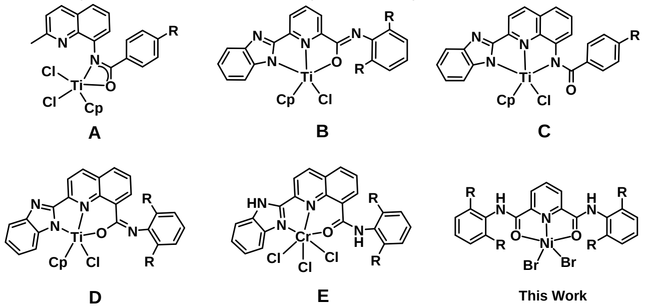

Chart 1. Ethylene Polymerization and Oligomerization Catalysts Supported by Amide Ligands.

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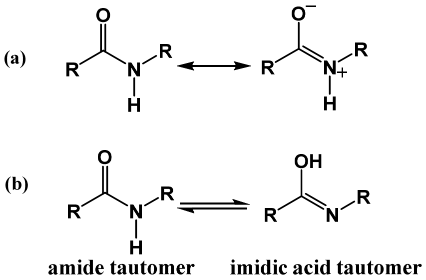


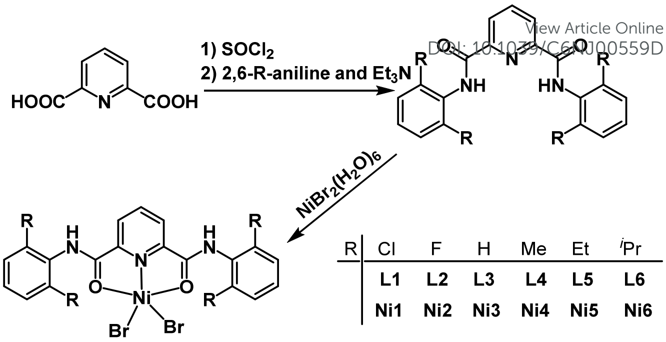
Chart 2. (a) Amide Resonance and (b) Amide Tautomerization.

we report the convenient synthesis and characterization of a series of nickel complexes bearing tridentate neutral *N,N'*-bis(2,6-R-phenyl)-2,6-pyridinedicarboxamide ligands. The two amide groups coordinated with Ni by neutral oxygens confirmed by X-ray diffractions. The catalytic performances for ethylene oligomerization under various reaction conditions were investigated. Upon treatment with aluminum activators, in particular with Et_2AlCl, these nickel (II) complexes showed high catalytic activities up to 7.55×10^5 g·mol^{-1}(Ni)·h^{-1}·atm^{-1} with good selectivity, which is one of the most active nickel catalysts for ethylene dimerization. The effects of reaction parameters and the substituents of ligands on catalytic activity and selectivity were fully studied.

2. Results and discussion

2.1. Synthesis and Characterization of the Ligands and Complexes

With the modification of reported procedure,[11c] the ligands 2,6-pyridinedicarboxamide derivatives were synthesized in high yields (Scheme 1). 2,6-Pyridinedicarboxylic acid was quantitatively transformed to 2,6-pyridine carbonyl dichloride in the presence of excess of thionyl chloride, which directly reacted with 2,6-disubstituted aniline to form the corresponding ligands. All ligands were confirmed by FT-IR and ^{1}H and ^{13}C NMR spectroscopy as well as by elemental analysis. The nickel complexes **Ni1**-**Ni6** were prepared by mixing $NiBr_2·6H_2O$ with 1 equiv. of the corresponding ligands in ethanol at room temperature (Scheme 1). The yellowish nickel complexes were precipitated from the solutions by adding diethyl ether and were collected by filtration, washed with diethyl ether, and dried under vacuum overnight. All nickel complexes were isolated as air-stable yellowish powders in high yields and characterized by FT-IR spectra, elemental analysis and NMR (see experimental section and ESI), which were in agreement with the formula **$LNiBr_2$**. Note that the nickel complexes prepared by this method and also used in the catalytic test (yellowish powder) contained no coordinated solvents as indicated by elemental analysis, although coordinated solvent molecules were found in the crystal structures of **Ni5** and **Ni6** (see Crystal Structures section). The Ni complexes in MeOH or EtOH solutions are probably cationic complexes, similar as ones in solid state as shown by X-ray diffractions, due to solvent molecules coordinated. However, the coordinated solvent molecules were ready to lose under vacuum to give the neutral compounds, of which formula is **$LNiBr_2$** and color is yellowish. This was confirmed by ^{1}H NMR of **Ni5** in CD_3OD (Figure S1 in ESI), in which there were no resonances at 3.60 and 1.19 ppm for coordinated ethanol. This was also confirmed by FT-IR experiments based on yellowish powder sample and green crystal sample (Figure S2 and S3, respectively, in ESI). In the spectrum of green crystal sample, there is a strong signal over 3300 cm^{-1}, which is corresponding to the OH groups (from CH_3OH and H_2O). In contrast, this signal was absent in the spectrum of yellowish powder sample. In terms of FT-IR spectra of Ni complexes and ligands, the C=O stretching frequencies in Ni complexes shifted to lower values between 1635 and 1624 cm^{-1} with somewhat weaker intensity compared with those of the corresponding free ligands (see Experimental section). Such features were consistent with the existence of coordination between the amide oxygen atom and the nickel center.[17]



Scheme 1. Synthesis of Ligands (**L1**-**L6**) and Nickel complexes (**Ni1**-**Ni6**).

2.2. Crystal Structures

Single crystals of **Ni5** and **Ni6** were grown by diffusing diethyl ether into their methanol solution and ethanol solution, respectively. **Ni5**·$CH_3OH·2H_2O$ and **Ni6**·$3C_2H_5OH$ possessed distorted octahedral coordination geometry around the Ni center, as shown in Figure 1 and 2 with the selected bond lengths and angles. The octahedral geometry around the Ni center was formed by one N atom of pyridine, two O atoms of amide groups, two O atoms of coordinated solvent molecular (methanol and water in **Ni5**·$CH_3OH·2H_2O$ and two ethanol in **Ni6**·$3C_2H_5OH$), and one Br atom. The other Br atom was displaced from its coordinated site and acted as a counterion, which was also found for the previous reported Ni and Cr complexes.[8e, 17] In **Ni5**·$CH_3OH·2H_2O$ the tridentate ligand was situated around the Ni center in a meridional manner (O^N^O) and the two chelating rings (Ni1-O1-C11-C12-N2, Ni1-O2-C17-C16-N2) were coplanar. The nickel atom (Ni1) and the mutually *trans*-disposed bromide (Br1) and oxygen (O3) of coordinated methanol were almost in one line [Br1-Ni1-O3 = 178.34(14)°] with N2, O1, O2, and O4 atoms located in the equatorial plane. The plane of amide groups was almost coplanar with the pyridine ring (2.68°), while the phenyl ring on the nitrogen was perpendicular to this pyridine ring (88.79°) and the coordination plane (89.40°), which was similar to that observed in nickel dibromide complexes ligated by α-dimine and bis(arylimino)pyridyl.[6, 18] The C-O bond (C11-O1 = 1.252(7) Å) was slightly longer than the characteristic C=O bond (1.19-

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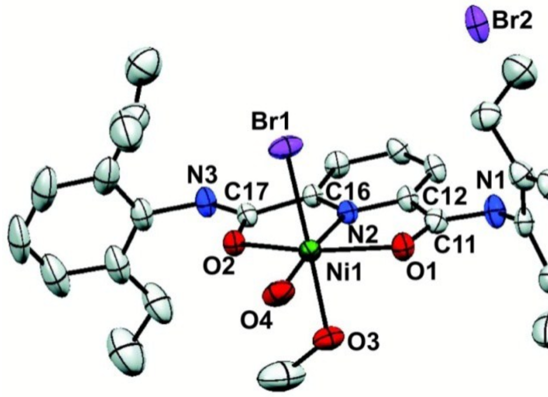

Figure 1. ORTEP of the molecular structure of **Ni5**$\cdot CH_3OH \cdot 2H_2O$. Ellipsoids at 50% probability level. Hydrogen atoms and one H_2O molecular uncoordinated were omitted for clarity. Selected distances (Å) and angles (deg): Ni1-Br1 2.5132(10), Ni1-O1 2.110(4), Ni1-O2 2.138(4), Ni1-O3 2.097(4), Ni1-O4 2.019(4), Ni1-N2 1.992(5), C11-O1 1.252(7), C17-O2 1.253(7), C11-N1 1.322(7), C17-N3 1.323(7); O1-Ni1-N2 78.53(17), O2-Ni1-N2 77.26(16), O1-Ni1-O4 97.17(18), O2-Ni1-O4 106.86(18), O1-Ni1-O2 155.53(15), N3-Ni1-O4 175.11(19), Br1-Ni1-O3 178.34(14).

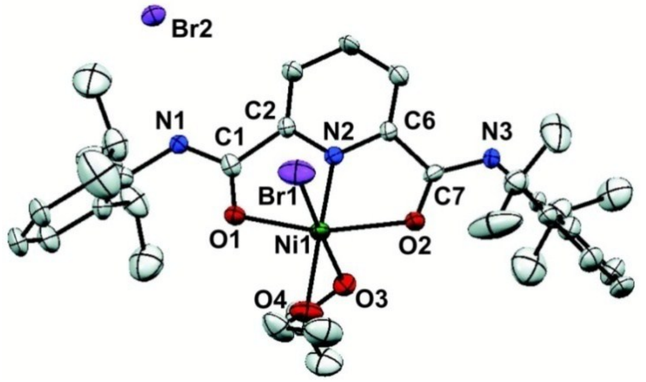

Figure 2. ORTEP of the molecular structure of **Ni6**$\cdot 3C_2H_5OH$. Ellipsoids at 50% probability level. Hydrogen atoms and one free C_2H_5OH molecular uncoordinated were omitted for clarity. Selected distances (Å) and angles (deg): Ni1-Br1 2.5144(10), Ni1-O1 2.093(4), Ni1-O2 2.125(4), Ni1-O3 2.123(4), Ni1-O4 2.018(4), Ni1-N2 1.976(4), C1-O1 1.246(6), C7-O2 1.246(6), C1-N1 1.341(7), C7-N3 1.332(6); O1-Ni1-N2 78.58(16), O2-Ni1-N2 77.75(16), O1-Ni1-O4 100.63(16), O2-Ni1-O4 102.34(16), O1-Ni1-O2 154.91(15), N2-Ni1-O4 175.65(18), Br1-Ni1-O3 175.70(12).

Table 1. Effect of cocatalysts on ethylene reactivity with **Ni5**[a].

entry	cocat.	Al/Ni	activity[b]	TON[c]	oligomers distribution (%)[d]		
					$C_4/\Sigma C$	α-C_4	$C_6/\Sigma C$
1	MAO	1500	4.42	7900	98.9	90.1	1.1
2	MMAO	1500	4.15	7400	98.2	92.0	1.8
3	Et_2AlCl	200	70.3	125000	98.9	72.0	1.1
4	$EtAlCl_2$	200	14.7	26200	97.1	75.0	2.9

[a]Conditions: 5 μmol **Ni5**; 10 atm of ethylene; 20 °C, 30 min, toluene (total volume 100 mL). [b]10^4 $g\cdot mol^{-1}(Ni)\cdot h^{-1}\cdot atm^{-1}$. [c]Turnover number = mol of ethylene consumed/mol of Ni catalyst. [d]Determined by GC.

1.23 Å), indicating partial electron donation by oxygen to the central metal, but this was shorter than the C-O single bond (1.42-1.46 Å). Similar phenomena were also observed in our other reported chromium systems containing the amide group as a neutral ligand.[17] Moreover, The C11-N1 bond length (1.322(7) Å) was shorter than a typical C-N single bond (1.33-1.36 Å) in free amide linkages but longer than a C=N double bond (1.26-1.29 Å), indicating the resonance and tautomerization features of the amide group due to coordination with metal center.[16] These features endue the amide group with the advantage of tuning electronic effect and make it to be a suitable candidate as the ligand for metal complex catalysts. The coordination geometry around Ni in **Ni6**$\cdot 3C_2H_5OH$ was similar as that in **Ni5**$\cdot CH_3OH \cdot 2H_2O$ and the only difference was that the coordinated solvent molecular were two ethanol.

2.3. Ethylene Oligomerization

Activated by methylaluminoxane (MAO) or MMAO, **Ni5** showed moderate activities for ethylene oligomerization (entrie 1 and 2, Table 1). However, when diethylaluminum chloride (Et_2AlCl) or ethylaluminum dichloride ($EtAlCl_2$) were used as the activators, the catalytic activities were an order of magnitude higher (Table 1) with relatively lower selectivity for α-olefins, which was also observed for other tridentate nickel systems.[19] In particular, **Ni5**/Et_2AlCl system showed the highest activity (7.03×10^5 $g\cdot mol^{-1}(Ni)\cdot h^{-1}\cdot atm^{-1}$), which was 16× higher as compared to that of **Ni5**/MAO system (entry 1 vs entry 3, Table 1). Based on the results observed for complex **Ni5**, Et_2AlCl was selected as the cocatalyst for further investigation.

2.3.1. Effects of the Ratio of Et_2AlCl, Reaction Temperature and Time on Catalytic Behavior

The effects of the reaction parameters (Al/Ni, reaction temperature and time) on the catalytic activities were investigated with complex **Ni5** and the results were summarized in Table 2. Both Al/Ni and temperature significantly affected the catalytic performance (activity and distribution of oligomers). Initial experiments tested the Al/Ni molar ratio (100 to 300) at 20 °C for 30 min. The catalytic activities reached the optimum value of 7.03×10^5 $g\cdot mol^{-1}(Ni)\cdot h^{-1}\cdot atm^{-1}$ with the Al/Ni ratio of 200 (entry 3 in Table 2), which is much higher than well known bidentate α-diimine Ni catalysts (1.36×10^5 $g\cdot mol^{-1}(Ni)\cdot h^{-1}\cdot atm^{-1}$; 35 °C, 28 atm and 60 min),[20] trihydroquinolin-amino Ni catalysts (4.54×10^5 $g\cdot mol^{-1}(Ni)\cdot h^{-1}\cdot atm^{-1}$; 20 °C, 10 atm and 30 min)[21] and tridentate pyridyl-quinolin-amine Ni catalysts (0.66×10^5 $g\cdot mol^{-1}(Ni)\cdot h^{-1}\cdot atm^{-1}$; 20 °C, 10 atm and 20 min).[8e] This catalyst exhibited high activity and represented a unique characteristic for ethylene oligomerization, in particular, considering its convenient synthesis. Upon further increasing the Al/Ni ratio, a slight decrease of the catalytic activity and the selectivity for α-C_4 was observed. Besides the Al/Ni ratio, the reaction temperature also affected the catalytic activity and selectivity. Generally, increasing the reaction temperature could lead to a significant decrease in activity for nickel catalysts,[8e, 22] owing to the decomposition of the active species and lower ethylene solubility at higher temperature. In the case of current

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Table 2. Ethylene Oligomerization of the **Ni5**/Et_2AlCl System[a].

entry	Al/Ni	T (°C)	t (min)	activity[b]	oligomers distribution (%)[c]		
					$C_4/\Sigma C$	α-C_4	$C_6/\Sigma C$
1	100	20	30	4.73	100	84.9	-
2	150	20	30	5.93	98.5	79.2	1.5
3	200	20	30	7.03	98.9	72.0	1.1
4	250	20	30	6.38	98.7	60.7	1.3
5	300	20	30	5.84	98.7	61.0	1.3
6	200	50	30	4.24	99.3	68.9	0.7
7	200	80	30	1.65	96.8	68.4	3.2
8	200	20	15	7.70	99.0	72.4	1.0
9	200	20	60	5.93	98.5	67.2	1.5

[a]Conditions: 5 μmol **Ni5**; 10 atm of ethylene; toluene (total volume 100 mL). [b]In units of 10^5 g·mol^{-1}(Ni)·h^{-1}·atm^{-1}. [c]Determined by GC.

catalytic system, although the similar tendency was observed for complex **Ni5**, the activities at high temperature still remained excellent. Note that even at 80 °C the activity was as high as 1.65 × 10^5 g·mol^{-1}(Ni)·h^{-1}·atm^{-1} (entry 7 in Table 2), indicating the title nickel complexes had relatively good thermal stability. Moreover, the selectivity for α-C_4 decreased slightly at elevated temperature, indicating that isomerization was favorable at higher temperature. The stability of catalytic system with time was investigated at 15 min, 30 min and 60 min. Note that from 15 min to 30 min the catalytic system exhibited excellent stability in the terms of activity and selectivity for α-C_4 (entry 8 vs entry 3 in Table 2). With the reaction time extending to 60 min, the activities decreased from 7.70 × 10^5 g·mol^{-1}(Ni)·h^{-1}·atm^{-1} (entry 8 in Table 2) to 5.93 × 10^5 g·mol^{-1}(Ni)·h^{-1}·atm^{-1} (entry 9 in Table 2), meantime the selectivity also decreased slightly.

2.3.2. Effect of the Nature of the Complexes on Their Catalytic Activities

Employing the optimum reaction conditions selected by using complex **Ni5** (molar ratio of Et_2AlCl/Ni = 200, temperature = 20 °C, 30 min and 10 atm ethylene), **Ni1**-**Ni6** displayed high catalytic activities and the results were summarized in Table 3. The substituents had remarkable influence on both of the activity and selectivity for α-C_4, which was also observed for other tridentate catalytic nickel systems.[19, 22-23] In Table 3 and Figure 3, the complexes **Ni1** and **Ni2** bearing R as halides (Cl and F) showed much lower activity (blue) but higher selectivity for α-C_4 (red) of the product as compared to **Ni5**, suggesting that electron withdrawing substituent R was not favorable for better catalytic activities but could depress the isomerization. The highest activity was obtained for complex **Ni6** (R = ^{i}Pr) with 7.55 × 10^5 g·mol^{-1}(Ni)·h^{-1}·atm^{-1} (entry 6 in Table 3 and Figure 3), then followed by complex **Ni5** (R = Et), **Ni4** (R = Me) and **Ni3** (R = H), suggesting the bulkier substituents would lead to increase in the catalytic activity of the nickel complexes. This is also consistent with the phenomenon observed for **Ni1** (R = Cl) and **Ni2** (R = F). It was believed that the active species with less bulky substituents were exposed to not only ethylene but also other reactants (impurities), and this resulted in the deactivation. In addition, the bulkier substituents enhanced the solubility of the complexes. As far as the selectivity for α-C_4 of the product, both of electon-withdrawing effect and bulky steric effect leaded to higher selectivity due to the depression of isomerization (Figure 3, red).

Table 3. Ethylene Oligomerization of the **Ni1**-**Ni6**/Et_2AlCl System[a].

entry	Cat.	R	activity[b]	Oligomers distribution (%)[c]		
				$C_4/\Sigma C$	α-C4	$C_6/\Sigma C$
1	**Ni1**	Cl	1.27	98.3	82.4	1.7
2	**Ni2**	F	1.08	96.8	76.0	3.2
3	**Ni3**	H	2.18	98.8	67.2	1.2
4	**Ni4**	Me	5.76	98.9	67.4	1.1
5	**Ni5**	Et	7.03	98.9	72.0	1.1
6	**Ni6**	^{i}Pr	7.55	99.0	77.2	1.0

[a]Conditions: 5 μmol metal complex; 10 atm of ethylene; 20 °C, 30 min, toluene (total volume 100 mL). [b]In units of 10^5 g·mol^{-1}(Ni)·h^{-1}·atm^{-1}. [c]Determined by GC.

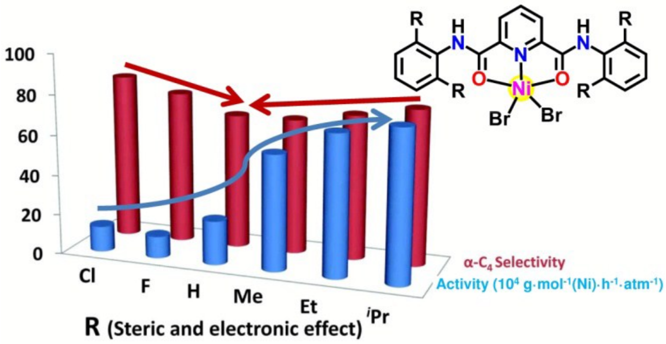

Figure 3. Effect of the nature of the complexes on ethylene reactivity (Table 3).

3. Conclusions

A series of stable and conveniently synthetic (O^N^O) ligands, *N*,*N*′-bis(2,6-R-phenyl)-2,6-pyridinedicarboxamide derivatives (**L1**-**L6**), were prepared, and used as neutral ligands to form the nickel complexes (**Ni1**-**Ni6**). All Ni(II) complexes were characterized by elemental and spectroscopic analysis along with X-ray crystallographic analysis for the representative complex **Ni5** and **Ni6**. Upon treatment with Et_2AlCl, these nickel (II) complexes showed high catalytic activities of up to 7.55 × 10^5 g·mol^{-1}(Ni)·h^{-1}·atm^{-1}. Both of the electron-donating and bulky R-substituents on the *N*-aryl ring significantly exerted positive effects on the catalytic activities. Thus, their catalytic activities varied in the order of **Ni1** (with ^{i}Pr substituents) ＞ **Ni2** (with Et) ＞**Ni3** (with Me) ＞**Ni4** (with H) ＞**Ni6** (with Cl) ＞**Ni5** (with F).

4. Experimental

4.1. General Considerations

All manipulations of air and/or moisture sensitive compounds were performed under N_2 using standard Schlenk techniques. Toluene was dried over sodium-benzophenone under N_2. Methylaluminoxane (MAO, a 1.46 M solution in toluene),

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modified methylaluminoxane (MMAO, 1.93 M in heptane), diethylaluminum chloride (Et_2AlCl, 1.7 M in toluene) and other reagents were purchased from Akzo Nobel Corp., Acros Chemicals, Aladdin or Aldrich. FT-IR spectra were performed on a Perkin-Elmer System 2000 spectrometer or Bruker Tensor 27 instrument. ^1H NMR and ^{13}C NMR spectra were performed on a Bruker DMX 500 instrument. Elemental analysis was tested with a Flash EA 1112 microanalyzer. GC analysis was recorded on Varian CP-3800 equipped with a flame ionization detector and a 30 m CP-Sil 5 CB column.

4.2. Syntheses and Characterization of the Ligands L1-L6

4.2.1. N,N′-Bis(2,6-dichlorophenyl)-2,6-pyridinedicarboxamide (L1)

The ligand was synthesized through a modification of publication procedure.[11c] 2,6-Pyridinedicarboxylic acid (1.67 g, 10 mmol) and thionyl chloride (20 mL) were added to a 100 mL flask under nitrogen. The reaction mixture was refluxed with stirring for 24 h. The excess of thionyl chloride was removed in vacuum, and a white residue of 2,6-pyridine carbonyl dichloride was obtained. The residue was dissolved in 20 mL CH_2Cl_2, followed by an addition of a solution of 2,6-dichloroaniline (20 mmol, 3.24 g) and triethylamine (3.03 g, 30 mmol) in dichloromethane (20 mL) at 0 °C. The resulted reaction mixture was refluxed overnight. All the volatiles were removed in vacuum and the residue was washed successively with water and CH_2Cl_2 to give a white solid (3.60 g, 7.92 mmol, 79.2% yield). ^1H NMR (500 MHz, $CDCl_3$) δ: 9.41 (br, 2 H, N-H), 8.56 (d, J = 7.8 Hz, 2 H, py), 8.20 (t, J = 7.8 Hz, 1 H, py), 7.45 (d, J = 8.1 Hz, 4 H, Ph), 7.26 (t, J = 8.1 Hz, 2 H, Ph). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 161.15 (s), 148.09 (s), 139.53 (s), 133.38 (s), 131.60 (s), 128.67 (s), 128.54 (s), 126.20 (s). Anal. Calcd for $C_{19}H_{11}Cl_4N_3O_2$: C, 50.14; H, 2.44; N, 9.23. Found: C, 50.18; H, 2.27; N, 9.16. FT-IR (KBr, cm^{-1}): 3302 (s), 3084 (w), 1680 (s), 1569 (m), 1506 (s), 1455 (s), 1306 (m), 1274 (w), 1224 (w), 1197 (m), 1130 (m), 1101 (m), 1000 (m), 951 (m), 909 (s), 832 (w), 784 (s), 749 (m), 709 (m), 659 (m).

4.2.2. N,N′-Bis(2,6-fluorophenyl)-2,6-pyridinedicarboxamide (L2)

Using the above procedure, *N*,*N*′-bis(2,6-fluorophenyl)-2,6-pyridinedicarboxamide was prepared in 78.5% yield (3.05 g, 7.85 mmol). ^1H NMR (500 MHz, $CDCl_3$) δ: 9.29 (br, 2 H, N-H), 8.53 (d, J = 7.8 Hz, 2 H, py), 8.16 (t, J = 7.8 Hz, 1 H, py), 7.32-7.20 (m, 2 H, Ph), 7.01 (t, J = 8.2 Hz, 4 H, Ph). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 161.25 (s), 158.54 (s), 156.80 (s), 148.06 (s), 139.18 (s), 127.86 (s), 126.09 (s), 111.75 (d). Anal. Calcd for $C_{19}H_{11}F_4N_3O_2$: C, 58.62; H, 2.85; N, 10.79. Found: C, 58.56; H, 3.07; N, 10.30. FT-IR (KBr, cm^{-1}): 3262 (s), 3102 (w), 1678 (s), 1623 (w), 1599 (m), 1525 (s), 1470 (s), 1439 (w), 1290 (m), 1243 (s), 1138 (m), 1072 (m), 1016 (s), 898 (m), 843 (m), 783 (s), 760 (m), 706 (m), 677 (w), 646 (w).

N,N′-phenyl-2,6-pyridinedicarboxamide (**L3**),[24] N,N′-bis(2,6-dimethylphenyl)-2,6-pyridinedicarboxamide (**L4**),[25] N,N′-bis(2,6-diethylphenyl)-2,6-pyridinedicarboxamide (**L5**)[26] and N,N′-bis(2,6-diisopropylphenyl)-2,6-pyridinedicarboxamide (**L6**)[27] were prepared using the above procedure and confirmed by NMR in according with the literature reports.

4.3. Synthesis of Nickel Complexes

General Procedure: A solution of $NiBr_2{\cdot}6H_2O$ in ethanol was added to a solution of the corresponding ligand in ethanol. The reaction mixture was stirred at room temperature for 12 h and diethyl ether was added to form a precipitate. The resulted precipitate was collected, washed with diethyl ether, and dried under vacuum overnight.

Ni1: yellowish powder in 84%. ^1H NMR (500 MHz, CD_3OD) δ: 8.41 (br, 2 H, py), 8.26 (br, 1 H, py), 7.48 (br, 4 H, Ph), 7.32 (br, 2 H, Ph). ^{13}C NMR (125 MHz, CD_3OD) δ: 164.32, 158.25, 147.95, 141.03, 129.56, 126.77, 114.30, 112.46. FT-IR (KBr disk, cm^{-1}): 3270 (s), 1630 (s), 1590 (m), 1548 (s), 1496 (m), 1447 (s), 1334 (m), 1242 (m), 1157 (w), 1144 (w), 1079 (m), 999 (m), 782 (s), 755 (s), 737 (m), 722 (s), 749 (m), 688 (w), 507 (m). Anal. Calcd for $C_{19}H_{11}Br_2Cl_4N_3NiO_2$: C, 33.88; H, 1.65; N, 6.24. Found: C, 33.75; H, 1.78; N, 6.20.

Ni2: yellowish powder in 81%. ^1H NMR (500 MHz, CD_3OD) δ: 8.05 (br, 2 H, py), 7.90 (br, 1 H, py), 7.00 (br, 2 H, Ph), 6.71 (br, 4 H, Ph). ^{13}C NMR (125 MHz, CD_3OD) δ: 164.01, 158.33, 148.84, 140.62, 129.42, 126.31, 114.32, 112.25. FT-IR (KBr, cm^{-1}): 3387 (s), 3084 (w), 1635 (s), 1598 (m), 1527 (s), 1473 (s), 1292 (w), 1244 (m), 1155 (w), 1076 (w), 1014 (s), 949 (m), 904 (w), 837 (w), 784 (s), 760 (w), 705 (w), 646 (w). Anal. Calcd for $C_{19}H_{11}Br_2F_4N_3NiO_2$: C, 37.55; H, 1.82; N, 6.91. Found: C, 37.83; H, 1.95; N, 7.02.

Ni3: yellowish powder in 88%. ^1H NMR (500 MHz, CD_3OD) δ: 8.43 (d, J = 7.1 Hz, 2 H, py), 8.22 (t, J = 7.1 Hz, 1 H, py), 7.77 (d, J = 7.5 Hz, 4 H, Ph), 7.39 (t, J = 7.5 Hz, 4 H, Ph), 7.17 (t, J = 7.5 Hz, 2 H, Ph). ^{13}C NMR (125 MHz, CD_3OD) δ: 164.05, 148.99, 140.71, 135.60, 134.75, 128.80, 128.11, 126.12. FT-IR (KBr disk, cm^{-1}): 3270 (s), 1629 (s), 1590 (m), 1545 (s), 1499 (m), 1448 (s), 1335 (m), 1246 (m), 1134 (m), 1079 (m), 1002 (m), 905 (m), 848 (m), 758 (s), 737 (m), 687 (s), 505 (m). Anal. Calcd for $C_{19}H_{15}Br_2N_3NiO_2$: C, 42.59; H, 2.82; N, 7.84. Found: C, 42.88; H, 2.97; N, 7.56.

Ni4: yellowish powder in 90%. ^1H NMR (500 MHz, CD_3OD) δ: 8.37 (br, 2 H, py), 8.21 (br, 1 H, py), 7.09 (br, 6 H, Ph), 2.22 (s, 12 H, Me). ^{13}C NMR (125 MHz, CD_3OD) δ: 164.16, 149.86, 140.78, 136.67, 134.89, 128.86, 128.30, 126.15, 18.20. FT-IR (KBr disk, cm^{-1}): 3180 (s), 3054 (m), 1630 (s), 1583 (m), 1536 (s), 1475 (m), 1327 (m), 1284 (w), 1218 (w), 1155 (w), 1034 (m), 952 (m), 874 (w), 836 (w), 780 (m), 756 (w), 709 (w), 622 (w). Anal. Calcd for $C_{23}H_{23}Br_4N_3NiO_2$: C, 46.67; H, 3.92; N, 7.10. Found: C, 46.55; H, 3.71; N, 7.03.

Ni5: yellowish powder in 88%. ^1H NMR (500 MHz, CD_3OD) δ: 8.41 (d, J = 7.6 Hz, 2 H, py), 8.26 (t, J = 7.5 Hz, 1 H, py), 7.24 (t, J = 7.4 Hz, 2 H, Ph), 7.17 (d, J = 7.4 Hz, 4 H, Ph), 2.63 (q, J = 7.3 Hz, 8 H, CH_2), 1.17 (t, J = 7.4 Hz, 12 H, CH_3). ^{13}C NMR (125 MHz, CD_3OD) δ: 164.82, 149.73, 142.49, 140.34, 133.47, 129.45, 127.04, 125.78, 25.40, 14.77. FT-IR (KBr disk, cm^{-1}): 3168 (s), 3045 (m), 1624 (s), 1580 (m), 1538 (s), 1463 (m), 1376 (w), 1321 (m), 1283 (w), 1153 (w), 1037 (m), 953 (m), 841 (w), 809 (w), 762 (m), 722 (w), 622 (m). Anal. Calcd for $C_{27}H_{31}Br_2N_3NiO_2$: C, 50.04; H, 4.82; N, 6.48. Found: C, 50.41; H, 4.62; N, 6.19.

Ni6: yellowish powder in 86%. ^1H NMR (500 MHz, CD_3OD) δ: 8.36 (d, J = 6.8 Hz, 2 H, py), 8.21 (t, J = 6.8 Hz, 1 H, py), 7.26 (t, J = 7.1 Hz, 2 H, Ph), 7.19 (d, J = 7.2 Hz, 4 H, Ph), 3.17-3.05 (m, 4 H, CH), 1.14 (d, J = 6.1 Hz, 24 H, CH_3). ^{13}C NMR (125 MHz, CD_3OD)

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δ: 161.24, 149.96, 147.24, 140.67, 132.09, 129.10, 126.20, 124.10, 29.59, 23.71. FT-IR (KBr disk, cm^{-1}): 3191 (s), 3047 (w), 2964 (m), 1626 (s), 1581 (m), 1538 (s), 1463 (m), 1324 (m), 1285 (w), 1218 (w), 1153 (w), 1037 (m), 955 (m), 838 (w), 799 (m), 759 (w), 726 (m), 622 (w). Anal. Calcd for $C_{31}H_{39}Br_2N_3NiO_2$: C, 52.88; H, 5.58; N, 5.97. Found: C, 53.05; H, 5.29; N, 5.77.

4.4. X-ray Crystallographic Studies

Single crystals of **Ni5** and **Ni6** were obtained by diffusing diethyl ether into their methanol and ethanol solutions, respectively. Single crystal X-ray diffraction studies for **Ni5** and **Ni6** were carried out on a Rigaku RAXIS Rapid IP diffractometer with graphite monochromated Mo KR radiation (λ = 0.71073 Å). Using Olex2,[28] the structure was solved with the XS[29] and refined with the ShelXL[30]. The hydrogen atoms were introduced into the geometrically calculated positions and refined riding on the corresponding parent atoms. Crystal data and processing parameters for **Ni5** and **Ni6** were summarized in Table S1 of Electronic Supplementary Information (ESI). CCDC reference numbers 1445082 and 1445083 are for complexes **Ni5** and **Ni6**, respectively.

4.5. General Procedure for Ethylene Oligomerization

Ethylene oligomerizations were carried out in a 500 mL stainless steel autoclave. The nickel complex was loaded in a Schlenk tube, and 50 mL of toluene and the desired amount of Et_2AlCl were added. This mixture and another 50 mL toluene were added into the autoclave under ethylene atmosphere. When the desired temperature was reached, 10 atm of ethylene was introduced to start the reaction. After the reaction, a small amount of the reaction solution was collected, ceased with 5% aqueous hydrogen chloride and analyzed by GC. The yields of oligomers were calculated by referencing with the mass of toluene and the mass of each fraction was approximately proportional to its integrated areas in GC.

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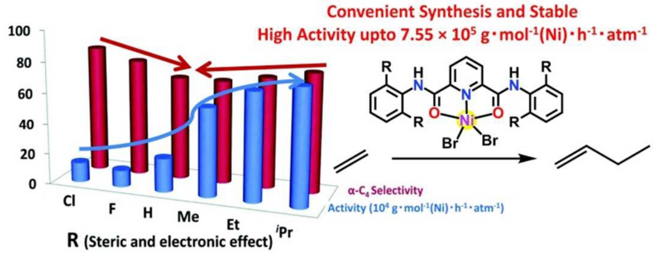

Ni(II) complexes chelated by a neutral tridentate amide ligand are conveniently prepared and highly active for ethylene oligomerization.