ISSN 0023-1584, Kinetics and Catalysis, 2007, Vol. 48, No. 5, pp. 664–668. © MAIK "Nauka/Interperiodica" (Russia), 2007.
Published in Russian in Kinetika i Kataliz, 2007, Vol. 48, No. 5, pp. 710–714.

# 2,9-Disubstituted 1,10-Phenanthroline Nickel Complexes: Syntheses, Characterization, and Their Ethylene Oligomerization[1]

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**Abstract**—Nickel complexes **1–4** ligated with 2,9-disubstituted-1,10-phenanthroline were synthesized and characterized by FT-IR spectra and elemental analysis. The molecular structure of complex **2** was confirmed by X-ray crystal diffraction analysis. Activated with methylaluminoxane (MAO), those complexes showed moderate activities for ethylene oligomerization.

**DOI:** 10.1134/S0023158407050114

## INTRODUCTION

Ethylene oligomerization is an important industrial process, in which products α-olefins are major industrial reactants that are extensively used in the preparation of detergents, lubricants, plasticizers, and oil field chemicals, as well as monomers for copolymerization. The nickel complex was evidently proved as a good catalyst for ethylene oligomerization in the SHOP process [1]. Since the report of α-diimino nickel complexes for ethylene polymerization by Brookhart in 1995 [2], late-transition metal catalysts, especially nickel complexes for ethylene oligomerization and polymerization, have drawn great attention [3–5]. During the design of catalysts, various ligands with different coordinative models play important roles. Nickel complexes bearing various organic ligands, such as pyridinylimino analogues [6–8], iminophosphines [9, 10], and *P*,*N*-phosphinopyridine [11], were demonstrated as active catalysts for ethylene oligomerization or ethylene polymerization. During the course of exploring new catalysts for ethylene oligomerization or polymerization in our group, nickel complexes bearing 2,9-bis(imino)-1,10-phenanthroline derivatives showed good catalytic activity for ethylene oligomerization [12]. Furthermore, 1,10-phenanthroline derivates have important meaning in coordination chemistry and catalysis chemistry. The nickel complexes with 2,9-dimethyl-1,10-phenanthroline had been synthesized by Sinn and Hodgson [13–15]; however, there is no report of its application in activating ethylene. In our parallel research works related to the frameworks of 1,10-phenanthroline derivatives as ligands for new nickel catalysts [16], the bidentate nickel model of 2,9-disubstituted 1,10-phenanthrolines would be interesting. Therefore, the nickel complexes bearing 2,9-dimethyl- and 2,9-diphenyl-1,10-phenanthroline were synthesized. It was found that those nickel complexes could be used as active catalysts for ethylene oligomerization in the presence of MAO. The various reaction conditions, such as different cocatalysts, the Al/Ni molar ratio, reaction temperature, and ethylene pressure, were investigated for their effects on the catalytic activity and the distribution of oligomers.

## EXPERIMENTAL

### *General Considerations*

All manipulations for air or moisture-sensitive compounds were carried out under an atmosphere of nitrogen using standard Schlenk and Cannula techniques. IR spectra were recorded on a Perkin-Elmer FT-IR 2000 spectrometer by using a KBr disc in the range of 4000–400 $cm^{-1}$. Elemental analysis was performed on a Flash EA1112 microanalyzer. GC analysis was performed with a Carlo Erba gas chromatograph equipped with a flame ionization detector and a 30 m (0.25 mm i.d., 0.24 μm film thickness) DM-1 silica capillary column.

Toluene and tetrahydrofuran were refluxed over sodium-benzophenone and distilled under argon prior to use. Methylaluminoxane (MAO, 1.46 M in toluene) and modified-methylaluminoxane (MMAO, 1.93 M in heptane) were purchased from Akzo Corp (United States). Triethylaluminum (TEA, 2.0 M in hexane) and ethylaluminum dichloride ($EtAlCl_2$, 1.0 M in hexane) were purchased from Acros Chemicals. 2,9-Dimethyl-1,10-phenanthroline was purchased from Acros Chemicals, and 2,9-diphenyl-1,10-phenanthroline was syn-

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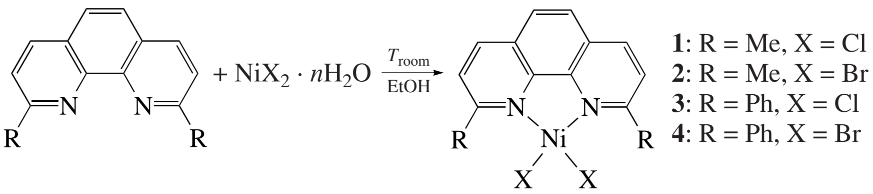
[1] This article was submitted by the authors in English.

thesized by the reaction of 1,10-phenanthroline with phenyllithium in THF. All other chemicals were obtained commercially and used without further purification unless otherwise stated.

*Synthesis of Complexes **1–4***



**(2,9-Dimethyl-1,10-phenanthroline)NiCl$_2$** (**1**): A solution of $NiCl_2 \cdot 6H_2O$ (109 mg, 0.45 mmol) in EtOH (5 ml) was added dropwise to a solution of 2,9-dimethyl-1,10-phenanthroline (87.4 mg, 0.42 mmol) in EtOH (10 ml). The mixed solution was stirred at room temperature for 9 h. The supernatant solution was removed, and the resultant precipitate was filtrated and washed with 3–5 mL of $Et_2O$ to give a pink powder (105 mg) in 74% yield. FT-IR (KBr disc, cm$^{-1}$): 3300, 1620, 1595, 1571, 1507, 1427, 1368, 1220,1151, 862, 785, 732, 681, 661. Anal. calc. for $C_{14}H_{12}Cl_2N_2Ni$: C, 49.77; H, 3.58; N, 8.29. Found: C, 49.26; H, 3.53; N, 8.04%.

**(2,9-Dimethyl-1,10-phenanthroline)NiBr$_2$** (**2**): In a similar manner as described for complex **1**, complex **2** was obtained as a yellow powder in 84% yield through the reaction of 2,9-dimethyl-1,10-phenanthroline and $NiBr_2 \cdot 4H_2O$. FT-IR (KBr disc, cm$^{-1}$): 3298, 3170, 3056, 2362, 1700, 1595, 1506, 1428, 1369, 1150, 862, 731. Anal. calc. for $C_{14}H_{12}Br_2N_2Ni \cdot H_2O$: C, 37.81; H, 3.17; N, 6.30. Found: C, 37.54; H, 3.25; N, 6.28%.

**(2,9-Diphenyl-1,10-phenanthroline)NiCl$_2$** (**3**): In a similar manner as described for complex **1**, complex **3** was obtained as a pink powder in 50% yield through the reaction of 2,9-diphenyl-1,10-phenanthroline and $NiCl_2 \cdot 6H_2O$. FT-IR (KBr disc, cm$^{-1}$): 3047, 1621, 1586, 1552, 1508, 1487, 1447, 1422, 1361, 1275, 1243, 1156, 867, 774, 740, 703. Anal. calc. for $C_{24}H_{16}Cl_2N_2Ni$: C, 62.39; H, 3.49; N, 6.06. Found: C, 62.90; H, 3.58; N, 5.85%.

**(2,9-Diphenyl-1,10-phenanthroline)NiBr$_2$** (**4**): In a similar manner as described for complex **1**, complex **4** was obtained as a purple powder in 86% yield through the reaction of 2,9-diphenyl-1,10-phenanthroline and $NiBr_2 \cdot 4H_2O$. FT-IR (KBr disc, cm$^{-1}$): 3060, 2361, 1700, 1651, 1621, 1588, 1554, 1511, 1487, 1446, 1421, 1360, 1152, 1120, 862, 762, 743. Anal. calc. for $C_{24}H_{16}Br_2N_2Ni$: C, 52.32; H, 2.93; N, 5.09. Found: C, 52.14; H, 2.93; N, 5.09%.

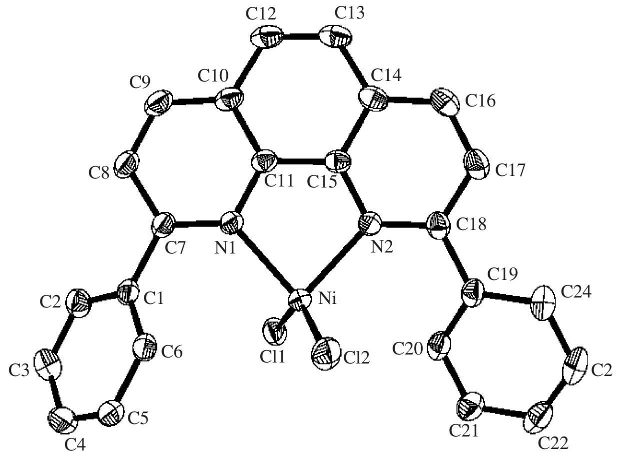
### *Ethylene Oligomerization*

Ethylene oligomerization at 1 atm of ethylene pressure was carried out as follows: The catalyst precursor was dissolved with toluene in a Schlenk tube stirred with a magnetic stirrer under 1 atm of ethylene atmosphere, and the reaction temperature was controlled by a water bath. The reaction was initiated by adding the desired amount of cocatalyst. After the desired period of time, a small amount of the reaction solution was collected with a syringe and terminated by the addition of 5% aqueous hydrogen chloride; the analysis by gas chromatography (GC) was carried out for determining the composition and distribution of oligomers.

Ethylene oligomerization at 10 atm of ethylene pressure was carried out in a 250 ml autoclave stainless steel reactor equipped with a mechanical stirrer and a temperature controller. The solution of the catalyst precursor in 30 ml toluene, the desired amount of MAO, and 120 ml of toluene were in turn added to the reactor under ethylene atmosphere. At the desired reaction temperature, ethylene with the desired pressure (10 atm) was introduced to start the reaction. The pressure in the autoclave was kept during the reaction by the connection with an ethylene cylinder. After 0.5 h, the pressure was released and a small amount of the reaction solution was collected and terminated by the addition of 5% aqueous hydrogen chloride, which was then analyzed by GC for the composition and distribution of oligomers.

### *Date Collection, Structural Determination, and Refinement*

A purple single crystal with dimensions of 0.55 mm × 0.20 mm × 0.10 mm was selected and mounted on a Brucker Smart Apex II CCD diffractometer at 50 kV and 20 mA by using a graphite-monochromatized Mo$K_\alpha$ ($\lambda$ = 0.71073 Å) radiation using the $\omega$–$2\theta$ scan mode, at 293(2) K. Unit cell dimensions were obtained with least squares refinements. A total of 13154 reflections were collected, and 4659 reflections with $I > 2\sigma(I)$ were used in the structure determination and refinement. The structures were solved by direct methods and refined by full-matrix least squares on $F^2$. Each hydrogen atom was placed in a calculated position and refined using a riding model. All non-hydrogen atoms were refined anisotropically. Structure solution and



Molecular structure of complex **3** with all the hydrogen atoms omitted for clarity.

refinement were performed using SHELXL-97 package [17]. Its crystallographic data were deposited with the Cambridge Crystallographic Data Centre, CCDC 285876.

## RESULTS AND DISCUSSION

### *Synthesis and Characterization*

2,9-Dimethyl-1,10-phenanthroline was commercially available and 2,9-diphenyl-1,10-phenanthroline was prepared through the reaction of 1,10-phenanthroline and phenyl lithium according to the literature method [18]. The 2,9-disubstituted-1,10-phenanthrolines reacted with $NiCl_2 \cdot 6H_2O$ or $NiBr_2 \cdot 4H_2O$ to form the title complexes **1**–**4**. The complexes were characterized by FT-IR spectra and elemental analysis as well as X-ray single crystal diffraction analysis. The molecular structures of complex **1** and **2** were confirmed as centro symmetric dimmers with a chloro- or bromo-bridge, which are the same as the results observed by Sinn [13], while complex **3** exists as a monomer.

Single crystals of complex **3** suitable for X-ray diffraction analysis were obtained through the slow diffusion of diethyl ether into its $CH_3OH$–$CH_3CN$ solution.

**Table 1.** Selected bond lengths (Å) and bond angles (deg) for complex **3**

| Bond | Bond length, Å | Bond | Bond angle, deg |
|---|---|---|---|
| Ni–N1 | 2.0060(14) | N1–Ni–N2 | 84.28(6) |
| Ni–N2 | 2.0252(14) | N1–Ni–Cl2 | 114.92(5) |
| Ni–Cl1 | 2.2294(6) | N2–Ni–Cl2 | 100.01(5) |
| Ni–Cl2 | 2.2219(6) | N1–Ni–Cl1 | 96.66(5) |
| | | N2–Ni–Cl1 | 112.31(5) |
| | | Cl2–Ni–Cl1 | 136.81(2) |

The molecular structure of complex **3** is shown in the figure. The selected bond lengths and bond angles are listed in Table 1. Complex **3** consists of discrete monomelic molecules, and the coordination geometry around the nickel atom can be described as a distorted tetrahedron with two nitrogen atoms of the phenanthroline and two terminal chlorine atoms. The two Ni–N bonds differ in length (Ni–N1, 2.0060(14) Å and Ni–N2, 2.0252(14) Å). However, they are a little shorter than those in dimeric complex **1** and **2** [13], which are ascribed to the reduction of the coordination number from 5 to 4. There is no large difference in the bond length of the Ni–Cl linkage (Ni–Cl1, 2.2294(6) Å and Ni–Cl2, 2.2219(6) Å). There is a little larger distortion in bond angles of N1–Ni–N2 (84.28(6)°) and Cl1–Ni–Cl2 (136.81(2)°). The two phenyl rings and the phenanthroline plane are almost coplanar with the dihedral angles of 4.5° (C1, C2 C3, C4, C5, C6) and 1.8° (C19, C20, C21, C22, C23, C24), respectively.

### *Ethylene Oligomerization*

On treatment with methylaluminoxane (MAO), complexes **1**–**4** were active for ethylene oligomerization and the results at 1 atm and 10 atm of ethylene pressure were summarized in Table 2. At 1 atm of ethlylene pressure, complexes **1**–**4** showed moderate activity for ethylene oligomerization and butenes among the oligomers obtained was the main product. The substituents on the phenanthroline and the nature of halide had no large influence on the catalytic activity, and complex **2** displayed relatively higher activity under the same conditions. However, complexes **3** and **4** with phenyls on the phenanthroline could produce a little larger amount of hexene (compare entry 3, 4 and 1, 2). When ethylene pressure was enhanced to 10 atm, the catalytic activity also increased. except for complex **2**, and complex **3** gave the highest catalytic activity ($1.71 \times 10^6$ g mol(Ni)$^{-1}$ h$^{-1}$). For the diphenyl-substituted complexes **3** and **4**, the mass content of hexene among the oligomers exceeded 20 wt % (entries 7 and 8).

In order to find the optimum condition, complex **2**, which showed the highest activity at 1 atm ethylene pressure, was investigated in detail by varying the reaction conditions such as different cocatalysts, reaction temperature, and the Al/Ni molar ratio at 1 atm of ethylene pressure (Table 3). When 10 equiv. of ethylaluminum dichloride was used as a cocatalyst, complex **2** showed no activity for ethylene. When triethylaluminum and MMAO were employed, the catalytic activity largely increased, while MAO was still the most effective cocatalyst, which is possibly due to the bulky MAO molecular linking to the metal center after activation. When the reaction temperature was enhanced from 0 to 80°C, the catalytic activity of complex **2**/MAO increased gradually, but the distribution of the produced oligomers had no large difference. The dependence of catalytic activity on the Al/Ni molar ratio was also studied in the range of 250 to 2000. As the Al/Ni molar ratio

**Table 2.** Ethylene oligomerization by complexes **1–4**/MAO[a]

| Entry | Complex | $P$[b], atm | Toluene, ml | Activity[c] | Distribution of oligomers[d] | |
|---|---|---|---|---|---|---|
| | | | | | $C_4$ | $C_6$ |
| 1 | 1 | 1 | 30 | 1.98 | 100 | 0 |
| 2 | **2** | 1 | 30 | 2.16 | 98.2 | 1.8 |
| 3 | **3** | 1 | 30 | 1.88 | 87.3 | 12.7 |
| 4 | **4** | 1 | 30 | 1.59 | 86.7 | 13.3 |
| 5 | **1** | 10 | 150 | 6.27 | 98.7 | 1.3 |
| 6 | **2** | 10 | 150 | 1.19 | 98.6 | 1.4 |
| 7 | **3** | 10 | 150 | 17.10 | 75.5 | 23.7 |
| 8 | **4** | 10 | 150 | 7.24 | 76.1 | 23.9 |

Note: [a] General conditions: complex: 5 μmol; Al/Ni = 500; reaction temperature: 20°C; reaction time: 30 min. [b] Ethylene pressure; [c] The unit of activity: $10^5$ g mol(Ni)$^{-1}$ h$^{-1}$. [d] Determined by GC.

**Table 3.** Ethylene oligomerization by complex **2**[a]

| Entry | Cocat | Al/Ni | $T$[b], °C | Activity[c] | Distribution of oligomers[d] (%) | |
|---|---|---|---|---|---|---|
| | | | | | $C_4$ | $C_6$ |
| 1 | $AlEtCl_2$ | 10 | 20 | – | – | – |
| 2 | TEA | 500 | 20 | 0.29 | 100 | 0 |
| 3 | MMAO | 500 | 20 | 1.63 | 98.7 | 1.3 |
| 4 | MAO | 500 | 20 | 2.16 | 98.2 | 1.8 |
| 5 | MAO | 500 | 0 | 0.17 | 95.2 | 4.8 |
| 6 | MAO | 500 | 40 | 3.44 | 97.8 | 2.2 |
| 7 | MAO | 500 | 60 | 3.58 | 95.1 | 4.9 |
| 8 | MAO | 500 | 80 | 4.11 | 95.9 | 4.1 |
| 9 | MAO | 250 | 20 | 0.30 | 93.7 | 6.3 |
| 10 | MAO | 1000 | 20 | 2.28 | 98.0 | 2.0 |
| 11 | MAO | 1500 | 20 | 1.56 | 98.0 | 2.0 |
| 12 | MAO | 2000 | 20 | 0.94 | 96.5 | 3.5 |

Note: [a] General conditions: complex: 5 μmol; solvent: toluene (30 ml); reaction time: 30 min; ethylene pressure: 1 atm. [b] Reaction temperature. [c] The unit of activity: $10^5$ g mol(Ni)$^{-1}$ h$^{-1}$. [d] Determined by GC.

increased, the catalytic activity first increased and then decreased and the highest value was obtained at the ratio of 1000. However, the Al/Ni molar ratio had little influence on the distribution of oligomers.

## ACKNOWLEDGMENTS

This work was supported by NSFC (no. 20473099).

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