Ethylene Polymerization Catalyzed by Neutral Nickel(II) Complex with O^N-Chelating Ligand

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ABSTRACT: We have achieved the synthesis of neutral nickel catalyst with the modified O^N -chelating ligand for the ethylene polymerization. The activity of the catalyst, and the molecular weight and the branching structure of the polymer obtained strongly depend on the ligand structure as well as the presence of Ni(COD)₂ which is used as an activator. The crystal structure of the catalyst was determined and the long nickel–phosphine bond length seems to play an important role for increasing the polymerization activity.

KEY WORDS Neutral Nickel Complex / Ethylene Polymerization / Oligomerization / Polyethylene /

Neutral Ni complexes have been intensively investigated as the catalysts for highly active oligomerization/polymerization of ethylene.¹ While the SHOPtype catalysts based on PO-chelated complexes can produce higher α -olefins as a result of the favorable β -H elimination for those late transition metal alkyl species, several groups recently reported a new class of neutral Ni(II) catalysts with salicylaldiminato ligands which are able to produce high molecular weight polyolefins.² These neutral Ni(II) catalysts are less oxophilic compared to early transition metal or cationic late transition metal catalysts and do not require co-catalysts necessarily to show polymerization activity. They are also attracting strong interests for several unique polymerization systems, for example, single component catalysts^{2,3} or olefin polymerizations in water media.4

EXPERIMENTAL

All manipulations involving organonickel compounds were done under either nitrogen or argon with use of standard Schlenk techniques. All solvents were thoroughly dried over Na/K alloy or passed through Alumina/CuO columns and degassed prior to use.

Nuclear magnetic resonance (NMR) spectra were recorded on a General Electronics GE-300 instrument. The ¹H and ¹³C NMR spectra for ligands and nickel complexes were recorded in chloroform- d_1 or benzene- d_6 , and chemical shifts were determined with the use of the residual proton absorption of chloroform at δ 7.26 (H) and 77.23 (C) and benzene at δ 7.15 (H) and 128.39 (C). The following abbreviations are used for the observed peak multiplicities: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, sep = septet, m = multiplet. Elemental analyses were performed by Atlantic Microlab. Inc. of Norcross, GA.

Synthesis of Ligand for 1

The starting materials, 7-bromoindole⁵ and 7formylindole,⁶ were prepared according to literature procedures. A 0.5 ml of formic acid was added into a solution of 7-formylindole (4.5 g, 31.0 mmol) and 2,6-diisopropylaniline (5.5 g, 31.0 mmol) in ethanol (50 mL). The reaction mixture was stirred overnight at room temperature, and then concentration afforded 1 as a yellow crystalline solid (9.04 g, 96 %). ¹H NMR (300 MHz, CDCl₃, 25 °C): δ 10.76 (br, 1H, NH), 8.41 (s, 1H, -CH=N-), 7.81 (d, J = 8.1 Hz, 1H, Ar-H), 7.37 (d, J = 7.3 Hz, 1H, Ar–H), 7.28 (t, 1H, Ar–H), 7.10-7.25 (m, 4H, Ar-H), 6.63 (t, 1H, Ar-H), 3.06 (sep, 2H, $-CH(CH_3)_2$), 1.17 (d, J = 8.8 Hz, 12H, -CH(CH₃)₂); 13 C NMR (75 MHz, CDCl₃, 25 °C): δ 164.1, 149.4, 138.1, 134.2, 128.8, 126.8, 125.6, 124.8, 123.4, 119.4, 102.6, 28.2, 23.9. Anal. calcd. for C₂₁H₂₄N₂: C, 82.85; H, 7.95; N, 9.20. Found: C, 82.83; H, 8.07; N, 9.19.

Synthesis of 1

A solution of the ligand (0.8 g, 2.63 mmol) in THF (10 ml) was added dropwisely into a suspension of KH (0.2 g. 5.0 mmol) in THF (10 mL) at 0 °C, and then the reaction mixture was stirred for 6 h. The resulting suspension was filtrated and the filtrates were washed with THF (5 mL \times 2). A solid of TlOAc (1.31 g, 5.0 mmol) was added into the combined THF solution at room temperature with stirring vigorously, and the reaction mixture was stirred for 1 d at room temperature. Then the resulting suspension was filtered and

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the THF-soluble part was used for the reaction with trans-(PPh₃)₂Ni(Ph)Cl. To a toluene suspension of trans-(PPh₃)₂Ni(Ph)Cl⁵ (1.83 g, 2.63 mmol), the THF solution obtained was added at room temperature. The color of the reaction mixture turned to deep red immediately. After stirring it overnight, the solvent was removed in vacuo and the residue was extracted with CH_2Cl_2 (10 mL × 2). The CH_2Cl_2 solution was concentrated to *ca*. 10 mL, and then pentane (20 mL) was added slowly. After standing it at room temperature for several days, the organonickel complex 1 was obtained as brown needles (42%). ¹HNMR $(300 \text{ MHz}, C_6 D_6, 25 \degree \text{C}): \delta 8.35 \text{ (d, } J = 8.0 \text{ Hz}, 1 \text{H},$ -CH=N-), 7.94 (d, J = 1.5 Hz, 1H, Ar-H), 7.70 (t, 6H, P(Ar-H)₃), 7.20 (d, 1H, Ar-H), 7.00-7.10 (m, 2H, Ar–H), 6.8–7.0 (m, 9H, P(Ar–H)₃), 6.67 (d, J =7.3 Hz, 2H, Ar–H), 6.50 (d, J = 2.9 Hz, 1H, Ar–H), 6.30 (d, 1H, Ar-H), 6.14 (d, 2H, Ar-H), 4.29 (sep, 2H, $-CH(CH_3)_2$), 1.11 (dd, J = 7.3 Hz, 6.6 Hz, 12H, $-CH(CH_3)_2$; ¹³C NMR (75 MHz, C₆D₆, 25 °C): δ 167.5, 152.0, 147.0, 146.3, 144.6, 144.5, 141.4, 140.37, 138.0, 135.6, 135.5, 133.9, 133.3, 133.0, 130.5, 129.4, 128.3, 127.8, 127.5, 127.0, 126.6, 125.3, 123.5, 121.7, 118.0, 117.5, 103.1, 29.6, 26.2, 23.4. Anal. calcd. for C₄₅H₄₃N₂PNi: C, 77.05; H, 6.18; N, 3.99. Found: C, 76.99; H, 6.26; N, 3.91.

Synthesis of Ligand for 2

The starting material, $[{Li(Et_2O)(2,4,6-(CHMe_2)_3 C_6H_2$, was synthesized according to a literature procedure.⁷ A solution of $[{Li(Et_2O)(2,4,6 (CHMe_2)_3C_6H_2)_2$] (35.3 mmol) in THF (80 mL) was added into a stirred solution of $ZnCl_2$ (6.0 g, 45 mmol) in THF (40 mL) under nitrogen at 0 °C. The resulting organozinc reagent was allowed to warm to room temperature and used immediately for the next reaction. The reaction of the organozinc reagent with anthranil was carried out according to a literature procedure.⁸ The reaction solution was stirred for 3 d at room temperature and then quenched by the addition of 1N HCl (10 mL). The reaction mixture was then poured into water (150 mL) and extracted with ether (100 mL \times 2). The ether extracts were combined, washed, and concentrated to give crude product as yellow oil. The crude product was chromatographed over silica gel (pet. ether $\sim 90\%$ pet. ether/10\% ether) to give the target product as yellow crystals in 32% yield. ¹HNMR (300 MHz, CDCl₃, 25 °C): δ 9.95 (s, 1H, -CH=O, 9.51 (s, 1H, NH), 7.53 (d, J = 7.3 Hz, 1H, Ar-H), 7.22 (t, 1H, Ar-H), 7.08 (s, 2H, Ar-H), 6.70 (t, 1H, Ar–H), 6.25 (d, J = 8.1 Hz, 1H, Ar–H), 3.04 (sep, 2H, -CH(CH₃)₂), 2.94 (sep, 1H, -CH(CH₃)₂), 1.29 (d, J = 7.3 Hz, 6H, $-CH(CH_3)_2$), 1.15 (d, J =7.3 Hz, 6H, $-CH(CH_3)_2$), 1.10 (d, J = 7.3 Hz, 6H, $-CH(CH_3)_2$; ¹³CNMR (75 MHz, CDCl₃, 25 °C): δ

194.5, 151.6, 148.5, 147.1, 136.4, 135.6, 131.2, 122.1, 118.2, 115.8, 113.0, 34.5, 28.7, 24.8, 24.3, 23.4. Anal. calcd. for $C_{22}H_{29}NO$: C, 81.69; H, 9.04; N, 4.33. Found: C, 81.81; H, 9.08; N, 4.16.

Synthesis of 2

The target organonickel complex 2 was obtained by the similar procedure for 1 except for using trans-(PPh₃)₂Ni(o-tol)Cl instead of trans-(PPh₃)₂Ni(Ph)Cl. trans-(PPh₃)₂Ni(o-tol)Cl was prepared in similar manner as literature procedure.9 Recrystallization from CH_2Cl_2 /pentane afforded **2** as red crystals (68%). ¹HNMR (300 MHz, C₆D₆, 25 °C): δ 8.29 (s, 1H, -CH=O), 7.56 (t, 6H, P(Ar-H)₃), 7.21 (br, 1H, Ar-H), 6.85-7.05 (m, 9H, P(Ar-H)₃), 6.77 (d, 1H, Ar-H), 6.70 (s, 1H, Ar-H), 6.4-6.6 (m, 2H, Ar-H), 6.37 (t, 1H, Ar-H), 6.27 (d, 1H, Ar-H), 6.21 (d, 1H, Ar-H), 6.05 (q, 2H, Ar-H), 4.69 (sep, 1H, -CH(CH₃)₂), 3.24 (s, 3H, lut- CH_3), 3.14 (sep, 1H, $-CH(CH_3)_2$), 2.80 (sep, 1H, $-CH(CH_3)_2$), 1.83 (d, J = 6.6 Hz, 3H, $-CH(CH_3)_2$, 1.31 (d, J = 7.4 Hz, 3H, $-CH(CH_3)_2$), 1.26 (dd, J = 1.5 Hz, 6.6 Hz, 6H, $-CH(CH_3)_2$), 1.10 (d, J = 6.6 Hz, 3H, $-CH(CH_3)_2$), 0.84 (d, J =6.6 Hz, 3H, $-CH(CH_3)_2$; ¹³C NMR (75 MHz, C₆D₆, 25 °C): δ 180.3, 157.4, 145.26, 143.1, 142.7, 139.1, 136.1, 135.0, 134.9, 133.6, 132.6, 132.2, 130.1, 128.3, 127.5, 123.6, 123.3, 122.0, 121.7, 121.5, 118.4, 113.5, 35.1, 29.6, 28.4, 26.8, 26.7, 26.6, 25.4, 25.2, 25.0, 23.9. Anal. calcd. for C₄₇H₅₀NOPNi: C, 76.85; H, 6.86; N, 1.91. Found: C, 76.08; H, 6.77; N, 1.90.

General Procedure of Ethylene Polymerization

To a 300 mL of Parr autoclave with a mechanical stirring bar, a 94 mL of toluene was added and degassed with ethylene $(3 \times 150 \text{ psi})$. The catalyst and the prescribed amount of Ni(COD)₂ were dissolved into 4 mL of toluene respectively, and the catalyst solution was transferred into the autoclave by syringe after 5 min. After the prescribed polymerization time under the prescribed ethylene pressure, ethylene pressure was then vented and reaction worked up to afford waxy or solid polyethylene. The branched structure and chain end structure were determined by ¹H and ¹³C NMR by the use of 1,2,4-trichlorobenzene/benzene- d_6 as a solvent at 120 °C.

Structure Solution and Refinement

The structure was solved using SIR92¹⁰ and refined using SHELXL-97.¹¹ The space group $P2_12_12_1$ was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the Emap. Full-matrix least squares/difference Fourier cycles were performed which located the remaining



Figure 1. Neutral nickel complexes with N[^]N- and N[^]O-chelating ligands.

| Ni complexes | Ni–P | Ni–C | Ni–O | Ni–N | X–Ni–Y ^a |
|--------------|------------|----------|-----------------------|-----------------------|---------------------|
| 1 | 2.157(1) | 1.922(3) | 1.946(2) ^b | 1.960(2) ^c | 93.66 |
| 2 | 2.1958(8) | 1.909(2) | 1.9082(19) | 1.942(2) | 92.69 |
| 4 | 2.172(2) | 1.895(5) | 1.910(3) | 1.937(4) | 94.50 |
| 5 | 2.1838(17) | 1.911(6) | 1.906(4) | 1.921(4) | 82.61 |
| | | | | | |

Table I. Selected bond lengths (Å) and angles (°)

^aX/Y: O/N atoms, ^bNi–N (*indole*), ^cNi–N (*imine*)

non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R_1 = 0.0429$ and $wR_2 = 0.1159$ (F^2 , all data). The program PLATON¹² was used for checking the structure.

Some equations of interest:

$$R_{\text{int}} = \Sigma |F_{o}^{2} - \langle F_{o}^{2} \rangle| / \Sigma |F_{o}^{2}|$$

$$R_{1} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|$$

$$wR_{2} = [\Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}] / \Sigma [w(F_{o}^{2})^{2}]]^{1/2}$$

where

$$w = q/[\sigma^2(F_o^2) + (a^*P)^2 + b^*P + d + e^*\sin(\theta)]$$

GooF = S = [\Sum [\sum (F_o^2 - F_c^2)^2]/(n-p)]^{1/2}

RESULTS AND DISCUSSION

Presumed from the polymerization results of the neutral Ni(II) catalysts previously reported,¹ the reactivity seems to be very sensitive to the electronic nature of the bidentate ligands as well as their bulkiness. To demonstrate those effects, we synthesized two types of N[^]N- and O[^]N-chelating ligands and the corresponding neutral Ni complexes, **1** and **2** (Figure 1),¹³ and examined their ability as the catalysts for the ethylene polymerization as compared to the other catalysts, **3**,^{2a} **4**,^{2a} and **5**,³ reported previously. The complexes were prepared by reacting *trans*-(PPh)₃-NiClAr (Ar: -Ph, -*o*-tolyl) with the Tl salts of the ligands in toluene/tetrahydrofurane and purified by recrystallizing from methylene chloride/*n*-pentane solution.



Figure 2. X-Ray Crystal Structure of 1 (top) and 2 (bottom).

The crystal structures of **1** and **2** are shown in Figure 2, respectively, and the selected bond lengths and the chelating angles are collected in Table I.¹⁴ It should be noted that the most significant difference is seen in the bond lengths between the nickel center and phosphine ligand. The Ni–P bond length in **2** shows the longest one among the Ni complexes listed in Table I. As compared to **1** or **4**, an anionic charge of the ligand of **2** seems to locate on the trans position of the triphenylphosphine ligand that is bound to the nickel center. Our current understanding is that the trans effect of the ligand brings the longest Ni–P bond length in **2**. The catalyst **5** also has long Ni–P bond length, which is one of the most active neutral nickel catalysts without using any cocatalysts.³

The results of our representative ethylene polymer-

| Entry | Cat | Ni(COD) ₂ | ethylene | MW ^c | Branch ^c | C=C (%) ^c | | Activity |
|-----------------|------|----------------------|----------|-----------------|---------------------|----------------------|----------|------------|
| | Cat. | (eq.) | (psi) | (g/mol) | (/1000C) | internal | terminal | (kg/mol h) |
| 1 ^b | 1 | 0 | 150 | | | | _ | 0 |
| 1′ ^b | 1 | 2 | 150 | _ | | | _ | 0 |
| 2 | 2 | 2 | 100 | 11500 | 169 | 100 | 0 | 1.3 |
| 3 | 2 | 0 | 150 | 5000 | 165 | 83 | 17 | 22.6 |
| 4 | 2 | 2 | 150 | 16800 | 116 | 100 | 0 | 24.0 |
| 5 | 2 | 2 | 200 | 24000 | 105 | 100 | 0 | 30.8 |

Table II. Results of ethylene polymerization by neutral nickel complexes^a

^aPolymerizations were carried out by 50 mmol of catalyst in 100 mL of toluene for 24 h without temperature control. ^bPolymerization time is 60 h. ^cDetermined by ¹H and ¹³C NMR analysis

izations are collected in Table II. The polymerizations were conducted in toluene without any temperature control. The O^N-chelated catalyst 2 shows moderate activity for the ethylene polymerization. Increasing the ethylene pressure from 100 psi to 150 psi during the polymerization resulted not only in the significant increase of productivity but also in the increase of molecular weight. Under lower pressure (50 psi, 24 h), the polymerization activity was not observed. On the other hand, increasing the ethylene pressure to 200 psi (entry 5 in Table II), the molecular weight of polyethylene slightly increased, but the activity did not change drastically as seen in entry 2 and 3. Moreover, 2 can show comparable polymerization activity even in the absence of $Ni(COD)_2$ which is usually used as an activator. The activity does not seem to depend on the presence of Ni(COD)₂, particularly under higher pressure, but the addition of Ni(COD)₂ affects the molecular weight and the polymer microstructures. As mentioned in the details of the X-Ray crystal structures, the Ni-P bond should play an important role in the ethylene polymerization. Comparing 2 to 3, 3 is not active for the ethylene polymerization in the absence of $Ni(COD)_2$,² but 2 shows activity as high as the case in the presence of $Ni(COD)_2$. The solid PE with higher molecular weight was obtained in entry 2 and 4 than in entry 3 ($M_W < 5000$). It means that the presence of $Ni(COD)_2$ has a crucial influence not on the propagation rate but on the mechanism of the chain transfer reaction such as the β -hydride elimination.

The ¹H and ¹³C NMR measurements of the polyethylene obtained have revealed that the structure of the chain end as well as the branches (Table II). Interestingly, the polymerization by **2** in the absence of Ni(COD)₂ (entry 3) gave highly branched polyethylene (165 branches per 1000C), whereas the polyethylene in entry 4 produced less branched structure (116/ 1000C). These results indicate that the chain transfer reaction which produces branching structures is more preferred in the absence of Ni(COD)₂ as compared to the polymerization with Ni(COD)₂. Interestingly, while the polyethylene obtained in entry 4 has C1–6



Figure 3. ¹³C NMR spectra of polyethylene obtained in entry 3 (a) and 4 (b) in Table II.

branches, one component polymerization gave predominantly methyl branches (Figure 3). The chain end structure also depends on the use of $Ni(COD)_2$ as seen in Table II and Figure 4. As a result of the chain transfer reaction, the polyethylene has an unsaturated C=C bond on the chain end. In entry 3, 17 % of



Figure 4. The 300 MHz ¹H NMR spectra of polyethylene obtained in entry 3 (a) and 4 (b) in Table II.

the terminal C=C structure was observed, but only internal C=C structure was produced in entry 4. This result may indicate that the polymer with terminal C=C structure that π -coordinates to Ni after β -H elimination eliminates more easily because the triphenylphosphine ligand is not scavenged by Ni(COD)₂.

The N^N-chelated complex 1 does not show any activity for the ethylene polymerization. From the ¹HNMR analysis of the reaction of **1** with ethylene, no insertion of ethylene into Ni-Ph bond was observed at 23 °C under 100 psi of ethylene in benzene- d_6 . It is supposed that the Ni-Ph bond could be too stabilized to initiate the polymerization due to the lower electro negativity of nitrogen atom than that of oxygen. To activate 1, $Ni(COD)_2$ was added to the polymerization solution of 1 but it resulted in affording precipitates of metal mirror probably due to the immediate reductive elimination. In the same reaction of 2, no Ni(0) precipitates appeared. Additionally, we examined $B(C_6F_5)_3$ and MAO as other activators, however, these Lewis acids completely inhibited the polymerization activity both of 1 and 2.¹⁵

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- 14. Crystal data for 1: C₄₅H₄₃N₂NiP, M = 701.49, monoclinic, temperature = 173(2) K, crystal size 0.40 × 0.40 × 0.22 mm³, a = 16.832(3), b = 11.7136(18), c = 19.943(3) Å, V = 3672.8(10) Å³, T = 173(2) K, space group P2₁/c, Z = 4, μ(Mo-Kα) = 0.606 mm⁻¹, 26281 reflections collected, indipendent reflections = 6511 (*R*_{int} = 0.065), final

 $wR_2 = 0.0812$. Crystal data for **2**: C₄₇H₅₀NNiOP, M = 734.56, orthorhombic, temperature = 173(2) K, crystal size $0.38 \times 0.23 \times 0.10 \text{ mm}^3$, a = 11.3284(12), b = 18.380(2), c = 18.663(2) Å, V = 3885.9(7) Å³, T = 173(2) K, space group $P2_12_12_1$, Z = 4, μ (Mo-K α) = 0.577 mm⁻¹, 34364 reflections collected, indipendent reflections = 8866 ($R_{\text{int}} = 0.0311$), final $wR_2 = 0.1093$.

15. The polymerization by **2** with $B(C_6F_5)_3$ (2eq.) or MAO (2eq.) was conducted under the same condition of entry 4 in Table II.