

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

Mitsufumi NODONO,[†] Bruce M. NOVAK,* and Paul T. BOYLE*

Corporate Research Laboratories, Mitsubishi Rayon Co., Ltd., 20-1 Miyuki-cho, Otake, 739-0693, Japan

*Department of Chemistry, North Carolina State University, Raleigh, NC 27695, U.S.A.

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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 SHOP-type catalysts based on P[−]O-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 = trip-

let, 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 7-formylindole,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(CH₃)₂), 1.17 (d, J = 8.8 Hz, 12H, -CH(CH₃)₂); ¹³C 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 TIOAc (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

[†]To whom correspondence should be addressed (Fax: +81-827-53-8515, Tel: +81-827-53-8507, E-mail: nodono_mi@mrc.co.jp).

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 CH₂Cl₂ (10 mL × 2). The CH₂Cl₂ 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%). ¹H NMR (300 MHz, C₆D₆, 25 °C): δ 8.35 (d, *J* = 8.0 Hz, 1H, –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(CH₃)₂), 1.11 (dd, *J* = 7.3 Hz, 6.6 Hz, 12H, –CH(CH₃)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(Et₂O)(2,4,6-(CHMe₂)₃-C₆H₂)₂}]₂, was synthesized according to a literature procedure.⁷ A solution of [{Li(Et₂O)(2,4,6-(CHMe₂)₃-C₆H₂)₂}] (35.3 mmol) in THF (80 mL) was added into a stirred solution of ZnCl₂ (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 × 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 ~ 90 % pet. ether/10 % ether) to give the target product as yellow crystals in 32 % yield. ¹H NMR (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(CH₃)₂), 1.15 (d, *J* = 7.3 Hz, 6H, –CH(CH₃)₂), 1.10 (d, *J* = 7.3 Hz, 6H, –CH(CH₃)₂); ¹³C NMR (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 C₂₂H₂₉NO: C, 81.69; H, 9.04; N, 4.33. Found: C, 81.81; H, 9.08; N, 4.16.

Synthesis of **2**

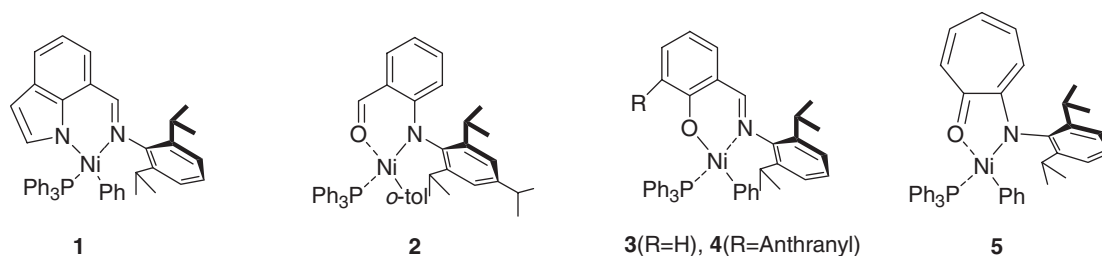
The target organonickel complex **2** was obtained by the similar procedure for **1** except for using *trans*-(PPh₃)₂Ni(*o*-tol)Cl instead of *trans*-(PPh₃)₂Ni(Ph)Cl. *trans*-(PPh₃)₂Ni(*o*-tol)Cl was prepared in similar manner as literature procedure.⁹ Recrystallization from CH₂Cl₂/pentane afforded **2** as red crystals (68%). ¹H NMR (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*-CH₃), 3.14 (sep, 1H, –CH(CH₃)₂), 2.80 (sep, 1H, –CH(CH₃)₂), 1.83 (d, *J* = 6.6 Hz, 3H, –CH(CH₃)₂), 1.31 (d, *J* = 7.4 Hz, 3H, –CH(CH₃)₂), 1.26 (dd, *J* = 1.5 Hz, 6.6 Hz, 6H, –CH(CH₃)₂), 1.10 (d, *J* = 6.6 Hz, 3H, –CH(CH₃)₂), 0.84 (d, *J* = 6.6 Hz, 3H, –CH(CH₃)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 × 150 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 *P*2₁2₁2₁ was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. 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.**Table I.** Selected bond lengths (Å) and angles (°)

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

^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:

$$R_{\text{int}} = \frac{\sum |F_o^2 - \langle F_o^2 \rangle|}{\sum |F_o^2|}$$

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$wR_2 = [\frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]}]^{1/2}$$

where

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

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

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 TI salts of the ligands in toluene/tetrahydrofuran and purified by recrystallizing from methylene chloride/*n*-pentane solution.

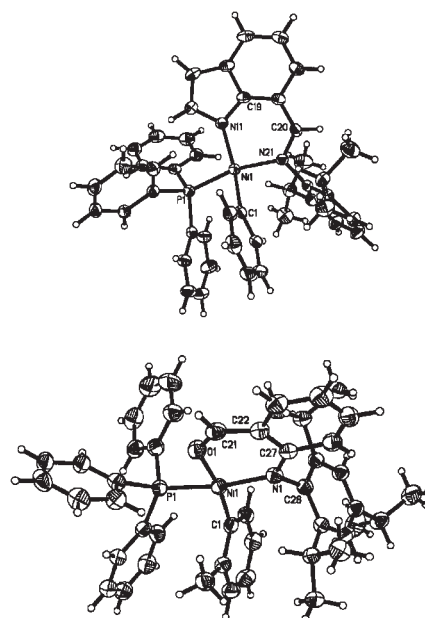


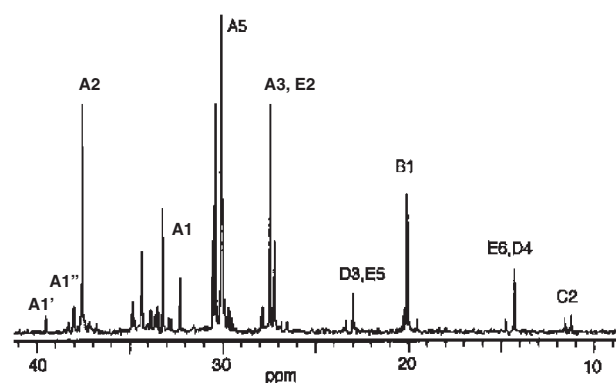
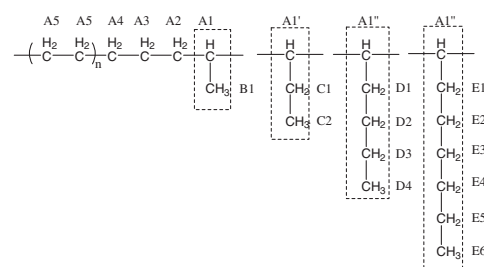
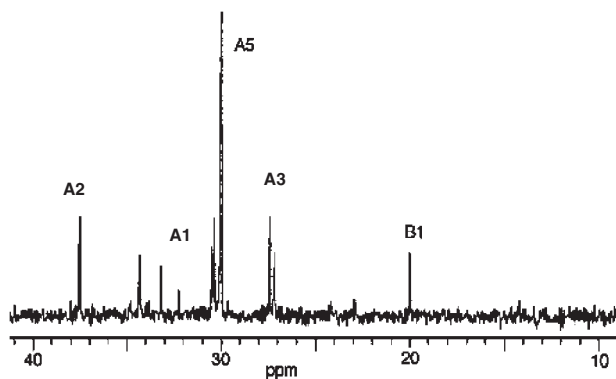
Table II. Results of ethylene polymerization by neutral nickel complexes^a

Entry	Cat.	Ni(COD) ₂ (eq.)	ethylene (psi)	MW ^c (g/mol)	Branch ^c (/1000C)	C=C (%) ^c		Activity (kg/mol h)
						internal	terminal	
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

^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

(a) without Ni(COD)₂(b) with Ni(COD)₂**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

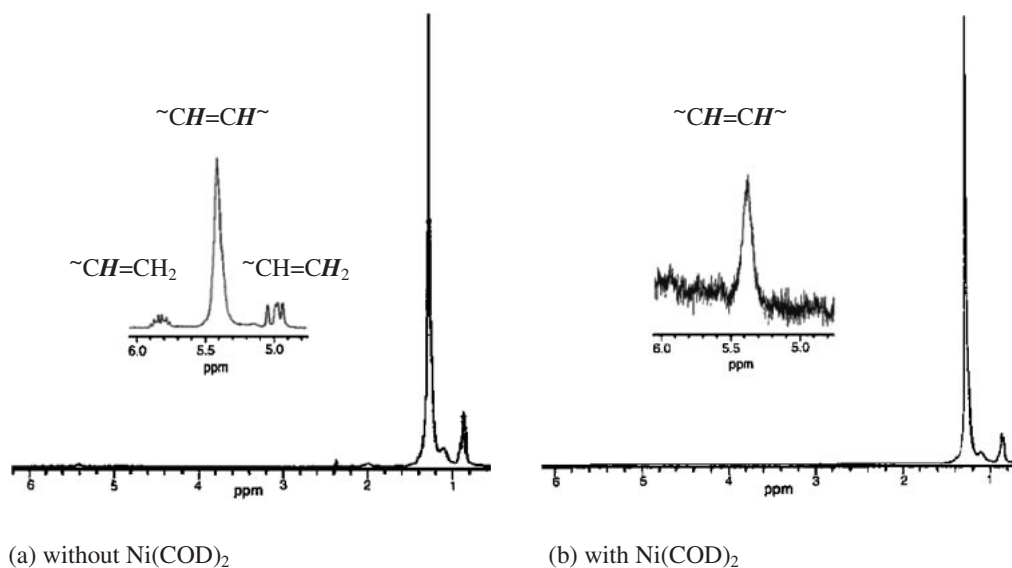


Figure 4. The 300 MHz ^1H NMR spectra of polyethylene obtained in entry 3 (a) and 4 (b) in Table II.

the terminal $\text{C}=\text{C}$ structure was observed, but only internal $\text{C}=\text{C}$ structure was produced in entry 4. This result may indicate that the polymer with terminal $\text{C}=\text{C}$ structure that π -coordinates to Ni after β -H elimination eliminates more easily because the triphenylphosphine ligand is not scavenged by $\text{Ni}(\text{COD})_2$.

The N^-N -chelated complex **1** does not show any activity for the ethylene polymerization. From the ^1H NMR 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**, $\text{Ni}(\text{COD})_2$ 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 $\text{B}(\text{C}_6\text{F}_5)_3$ and MAO as other activators, however, these Lewis acids completely inhibited the polymerization activity both of **1** and **2**.¹⁵

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REFERENCES AND NOTES

1. a) S. D. Ittel, L. K. Johnson, and M. Brookhart, *Chem. Rev.*, **100**, 1169 (2000).
b) R. Soula, J. P. Broyer, M. F. Llauro, A. Tomov, R. Spitz, J. Claverie, X. Drujon, J. Malinge, and T. Saudemont, *Macromolecules*, **34**, 2438 (2001).
c) V. C. Gibson and S. K. Spitzmesser, *Chem. Rev.*, **103**, 283 (2003).
2. a) C. Wang, S. Friedrich, T. R. Younkin, R. T. Li, R. H. Grubbs, D. A. Bansleben, and M. W. Day, *Organometallics*, **17**, 3149 (1998).
b) L. K. Johnson, A. M. A. Bennett, S. D. Ittel, L. Wang, A. Parthasarathy, E. Hauptman, R. D. Simpson, J. Feldman, and E. B. Coughlin, WO Patent Application 9830609 to DuPont.
c) T. R. Younkin, E. F. Conner, J. I. Henderson, S. K. Friedrich, R. H. Grubbs, and D. A. Bnasleben, *Science*, **287**, 460 (2000).
3. F. A. Hicks and M. Brookhart, *Organometallics*, **20**, 3217 (2001).
4. a) F. M. Bauers and S. Mecking, *Macromolecules*, **34**, 1165 (2001).
b) R. Soula, C. Novat, A. Tomov, R. Spitz, J. Claverie, X. Drujon, J. Malinge, and T. Saudemont, *Macromolecules*, **34**, 2022 (2001).
c) R. Soula, B. Saillard, R. Spitz, J. Claverie, M. F. Llauro, and C. Monnet, *Macromolecules*, **35**, 1513 (2002).
d) S. Mecking, *Angew. Chem. Int. Ed.*, **40**, 534 (2001).
e) S. Mecking, A. Held, and F. M. Bauers, *Angew. Chem., Int. Ed.*, **41**, 544 (2002).
5. G. Bartoli, G. Palmieri, M. Bosco, and R. Dalpozzo, *Tetrahedron Lett.*, **30**, 2129 (1989).
6. D. R. Dobson, J. Gilmore, and D. A. Long, *SYNLETT*, 79 (1992).
7. R. A. Betlett, H. V. R. Dias, and P. P. Power, *J. Organomet. Chem.*, **341**, 1 (1988).
8. J. S. Baum, M. Condon, and D. A. Shook, *J. Org. Chem.*, **52**, 2983 (1987).
9. M. Hidai, T. Kashiwagi, T. Ikeuchi, and Y. Uchida, *J. Organomet. Chem.*, **30**, 279 (1971).
10. A. Altomare, G. Cascarno, C. Giacovazzo, and A. Gualardi, *J. Appl. Crystallogr.*, **26**, 343 (1993).
11. Bruker Analytical X-Ray Systems, Madison, WI (1998).
12. A. L. Spek, *Acta Crystallogr., Sect. A*, **46**, C34 (1990). PLATON, A Multipurpose Crystallographic Tool, Utrecht Uni-

- versity, Utrecht, The Netherlands, A. L. Spek (2000).
13. B. M. Novak, G. Tian, M. Nodono, and P. Boyle, *PMSE-Prepr.*, 223rd ACS Natl. Meet., Orland, FL, April 7–11, 2002; Am. Chem. Soc., Washington D.C., 2002, Vol. 86, p. 326.
 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 *P*2₁/*c*, *Z* = 4, $\mu(\text{Mo-K}\alpha) = 0.606 \text{ mm}^{-1}$, 26281 reflections collected, independent reflections = 6511 ($R_{\text{int}} = 0.065$), final $wR_2 = 0.0812$.
 15. The polymerization by **2** with B(C₆F₅)₃ (2eq.) or MAO (2eq.) was conducted under the same condition of entry 4 in Table II. Crystal data for **2**: C₄₇H₅₀NNiOP, M = 734.56, orthorhombic, temperature = 173(2) K, crystal size 0.38 × 0.23 × 0.10 mm³, *a* = 11.3284(12), *b* = 18.380(2), *c* = 18.663(2) Å, *V* = 3885.9(7) Å³, *T* = 173(2) K, space group *P*2₁2₁2₁, *Z* = 4, $\mu(\text{Mo-K}\alpha) = 0.577 \text{ mm}^{-1}$, 34364 reflections collected, independent reflections = 8866 ($R_{\text{int}} = 0.0311$), final $wR_2 = 0.1093$.