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**Synthesis of Anilinonaphthoquinone-Based Nickel Complexes and Their
Application for Olefin Polymerization**

Mitsuhiro Okada, Yuushou Nakayama and Takeshi Shiono*

Department of Applied Chemistry, Graduate School of Engineering, Hiroshima

University, 1-4-1 Kagamiyama, Higashi-Hiroshima, 739-8527, JAPAN.

*Corresponding author: fax; +81-82-424-5494, E-mail; tshiono@hiroshima-u.ac.jp

Abstract

A series of anilinonaphthoquinone-based nickel complexes, $\text{Ni}(\text{C}_{10}\text{H}_5\text{O}_2\text{NAr})(\text{Ph})(\text{PPh}_3)$ (Ar = $\text{C}_6\text{H}_3\text{-2,6-Me}$ (**1c**); Ar = $\text{C}_6\text{H}_3\text{-2,4,6-Me}$ (**2c**); Ar = $\text{C}_6\text{H}_3\text{-2,6-Et}$ (**3c**)), were synthesized and the structures of **1c-3c** were confirmed by single crystal X-ray analyses. The anilinonaphthoquinone-ligated nickel complexes activated with $\text{B}(\text{C}_6\text{F}_5)_3$ showed high activities for ethylene polymerization at 40 °C under atmospheric pressure of ethylene and gave polyethylene with long chain branches and short chain branches. The activity of these systems was decreased by lowering polymerization temperature accompanied by increase in molecular weight. The number of the chain branches was also decreased with lowering polymerization temperature and increasing the bulkiness of the ligand.

Introduction

Single-site nickel catalysts such as Shell Higher Olefin Process (SHOP) have been known as olefin oligomerization catalysts due to frequent β -hydride elimination¹.

Although high molecular weight polyolefins were obtained by using improved SHOP catalysts, their activities were not so high^{2,3}. Since the discovery of bulky aryl-substituted α -diimine-based cationic nickel catalysts⁴ nearly one decade ago, much effort has been made on the development of nickel complexes for olefin polymerization catalysts.⁵⁻⁹

Neutral nickel catalysts have attracted much attention, because they show good activities for olefin polymerization without any cocatalysts¹⁰⁻¹⁴. These catalysts are tolerant for polar solvents such as water, therefore they are useful for

copolymerization of olefin with polar monomers¹⁵⁻¹⁷ and emulsion polymerizations¹⁸⁻²⁸. In these systems, neutral nickel complexes with five-membered-ring chelating structure such as anilinothoropone²⁹⁻³¹ and anilinoperinaphthenone³² ligands showed higher activity for ethylene polymerization than those with six-membered ones. Although it is not obvious how the chelate size affects the catalytic activities, the decrease in polymerization activity was observed with the expansion of chelate size in the other systems reported by Keim³³, Grubbs¹⁰⁻¹⁴, and Brookhart²⁶⁻²⁹.

The other type of polymerization catalysts containing late transition metals is zwitterionic catalysts. These catalysts have the cationic metal center and the corresponding anion in the same molecule. The absence of the counter ion should

make the metal center more reactive toward monomers. Several zwitterionic catalysts were reported to show superior activity for oligomerization³⁴⁻³⁸ and polymerization³⁹⁻⁴¹. Some of the zwitterionic oligomerization catalysts were used in a tandem reaction^{34, 37} which can synthesize branched polyethylene from only ethylene in feed.

We previously reported that a five-membered ring nickel complex chelated with 2-(2,6-diisopropylanilino)-1,4-naphthoquinone (**4c**) showed excellent activity for ethylene polymerization upon activation with $B(C_6F_5)_3$, in which the active species was speculated to be zwitterionic^{42, 43}. In this study, we synthesized a series of nickel complexes bearing anilidonaphthoquinone derivatives that possessed different substituents, and evaluated their catalytic abilities for ethylene and propylene

polymerization to reveal the effect of the substituents on the catalytic behaviors of the complexes and on the microstructures of the resulting polymers.

Results and Discussions

Synthesis, molecular structures, and properties of anilinonaphthoquinone ligated nickel complexes.

A variety of anilinonaphthoquinone ligands were synthesized by applying the literature procedure⁴³ and the nickel complexes were synthesized by modifying the method for anilintropone-ligated ones reported by Brookhart²⁶. The synthetic route for the complexes is shown in Scheme 1.

(Scheme 1)

The anilinonaphthoquinone ligands, (C₁₀H₅O₂NAr) [Ar = C₆H₃-2,6-Me (**1a**); Ar = C₆H₃-2,4,6-Me (**2a**); Ar = C₆H₃-2,6-Et (**3a**)], were prepared from 2-hydroxy-1,4-naphthoquinone and substituted anilines in good yields. Single crystals

of **1a** and **3a** suitable for X-ray analyses were obtained in acetone (see supporting information). As shown by Brookhart and coworkers in the previous research of anilinetropone ligand²⁹, the aryl plane is nearly perpendicular to the naphthoquinone plane. The two ligands **1a** and **3a** have very similar structure in view of the bond distances and the bond angles.

The anilinonaphthoquinone-ligated complexes, Ni(C₁₀H₅O₂NAr)(Ph)(PPh₃) [Ar = C₆H₃-2,6-Me (**1c**); Ar = C₆H₃-2,4,6-Me (**2c**); Ar = C₆H₃-2,6-Et (**3c**)], were prepared from the reaction of Ni(PPh₃)₂PhCl and the sodium salt of the corresponding ligand, and isolated by recrystallization in THF/pentane solution in moderate yields (**1c**, 45 %; **2c**, 35%; **3c**, 35 %). The crystallographic data and the structure refinement parameters of **1c**, **2c** and **3c** are summarized in Table 1. The ORTEP diagrams of the

complexes are shown in Figures 1-3, which indicate that all the complexes have a square-planar coordination geometry around the nickel center. (Scheme 2)

(Table 1)

(Figure 1)

(Figure 2)

(Figure 3)

In all the complexes, the lengths of Ni-P bond are the longest around the nickel center, and the phosphorus atom is located at *trans* position to nitrogen. The crystal structures of the three complexes **1c-3c** are almost the same with that of the complex **4c** (R = *i*Pr, R' = H) which we reported previously. The ³¹P NMR chemical shifts of PPh₃ in these complexes were strongly dependent on the ligands. The alkyl

substituent of anilines affected the electronic state of the PPh₃ ligand at *trans* position.

Since N⁺O six-membered zwitterionic nickel complexes were isolated by Lee⁴¹, we tried to isolate the N⁺O five-membered zwitterionic nickel complexes by reacting the complexes **1c-3c** with one equivalent of B(C₆F₅)₃. Since the products were not isolated as crystals, the solids obtained were analyzed by ³¹P NMR. In each spectrum, only one peak was observed and the chemical shifts (**1c**; 26.65 ppm, **2c**; 24.69 ppm, **3c**; 24.49 ppm) were shifted to lower field from those of the starting complexes (**1c**; 28.57 ppm, **2c**; 28.13 ppm, **3c**; 27.99 ppm), and completely different from that of PPh₃ (-5.11 ppm) and that of the equimolar mixture of PPh₃ and B(C₆F₅)₃ (45.20 ppm). These chemical shifts suggested that B(C₆F₅)₃ should selectively react with the

oxygen at 4-position of the naphthoquinone ligand without the elimination of PPh_3 .

(Table 2)

Polymerization study

The anilinoanthraquinone-based nickel complexes **1c-3c** did not conduct ethylene polymerization at an atmospheric pressure of ethylene, and exhibited low activity (trace) when the ethylene pressure was increased to 9 atm in the case of **3c**. In contrast, the preactivation of the complexes **1c-3c** with four equivalents of $B(C_6F_5)_3$ at 80 °C for 20 min dramatically enhanced their catalytic activities for ethylene polymerization.

The excess $B(C_6F_5)_3$ should not only coordinate on the carbonyl site of the ligand but also act as a PPh_3 scavenger to give coordinatively unsaturated nickel species.

Ethylene polymerizations were conducted at 40, 20 and 0 °C by the preactivated complexes and the results are summarized in Table 3.

(Table 3)

Ethylene polymerization by the activated complexes proceeded under atmospheric ethylene pressure regardless of the complex used. Complexes **3c** displayed high activity, which is comparable to that of N⁰ five-membered neutral nickel complex under similar polymerization conditions²⁹⁻³². The decreasing the bulkiness of 2,6-substitution on anilines, lowered the polymerization activity as well as the molecular weight of the polymer produced. Moreover, the comparison of complex **1c** (run 1~3) and **2c** (run 4~6) indicates that the methyl substitution at 4-position of aniline increased the polymerization activity and the molecular weight of the products, which indicates that polymerization activity and molecular weight depended on the electronic state of the metal center as well as the bulkiness of 2,6-substitution on anilines.

Although the polymerization activity decreased at low temperature, the molecular weight of the obtained polymer vastly increased in all cases. The number of branches determined by ^1H NMR lowered as the polymerization temperature decreased from 40 °C to 0 °C, and consequently the T_m values of the resulting polymers determined by DSC increased. These phenomena indicate that β -hydride elimination was more suppressed than chain growth at low temperature. The suppression of β -hydride elimination with lowering the temperature was more notable with the less bulky complex of 2,6-position substituent on aniline. Thus, the ligand structure and polymerization temperature strongly influenced both the polymerization activity and the molecular weight of the polymer obtained.

We measured the ^{13}C NMR spectra of the polymers obtained at 40 °C using **1c-3c** to

evaluate the microstructure of the polymers in detail, and the results are summarized in Table 4. The spectra obtained were analyzed according to the literature⁴⁴⁻⁴⁷.

(Table 4)

We have previously reported that the polyethylene produced by **4c**-B(C₆F₅)₃ at 40 °C possessed short chain branches (such as methyl, ethyl and propyl) and long chain branches, the results of which are shown in Table 4 for comparison⁴³. The present complexes **1c-3c** also produced polyethylenes with short and long chains branches at 40 °C. Short chain branches such as methyl, ethyl and propyl as well as long chain branch decreased in the more bulky systems, indicating that chain migration was suppressed by the introduction of bulky substituent at 2,6-position of aniline. Although the polyethylene obtained with **4c** at 0 °C possessed few methyl

branch, a considerable amount of methyl branch existed in the polyethylenes obtained with **2c** and **3c** at 0 °C.

We conducted propylene polymerization with **4c** at 0 °C to evaluate its applicability to α -olefin polymerization. Propylene polymerization proceeded with low activity (16 kg-polymer/mol-Ni·h) and the obtained polymer had low molecular weight ($M_n = 1,000$, MWD = 1.78). The ^{13}C NMR spectrum of the obtained polymer indicated that propylene inserted in 1,2- 2,1- and 3,1- fashions into the polymer chain.

(Figure 4)

Conclusion

Nickel complexes ligated with 2-(anilino)-1,4-naphthoquinone derivatives were synthesized and their crystal structures were determined by single crystal X-ray analysis. The anilinonaphthoquinone-ligated nickel complexes **1c-4c** activated by $B(C_6F_5)_3$ conducted ethylene polymerization with high activity and gave branched and linear polyethylenes depending on the polymerization temperature and the bulkiness of the substituent. Propylene polymerization by **4c** also proceeded at 0 °C with low activity and produced regio-irregular polymer with low molecular weight.

Experimental Section

General considerations All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. All solvents were refluxed and distilled over sodium/benzophenone or calcium hydride.

Analytical Procedure Molecular weights and molecular weight distributions of polyethylenes obtained were determined by gel permeation chromatography (GPC) with a Waters 150CV at 140 °C using *o*-dichlorobenzene as a solvent. The ¹³C NMR spectra of polyethylenes were measured at 120 °C on a JEOL GSX 500 spectrometer operated at 125.65 MHz in the pulse Fourier-transform mode. The pulse angle was 45° and about 4000 - 8000 scans were accumulated in pulse repetition of 5.0 s. Sample solutions were prepared in 1,1,2,2-tetrachloroethane-*d*₂ up to 10 wt-%. The central

peak of 1,1,2,2-tetrachloroethane- d_2 (74.47 ppm) was used as an internal reference.

The ^{31}P NMR spectra of the catalyst components were measured on a JEOL GSX 500 spectrometer operated at 202.35 MHz in the pulse Fourier-transform mode. About 500-1,000 scans were accumulated in pulse repetition of 2.0 s. Sample solutions were prepared in benzene- d_6 . The spectra were referenced to external 85 % H_3PO_4 .

Differential scanning calorimetry (DSC) analyses were performed on a Seiko DSC-220. The samples were encapsulated in aluminum pans and the data were collected from the second heating run from 25-170 °C at a heating rate of 10 °C/min.

Synthesis of Ligand 1a The ligand was synthesized by applying the literature procedure⁴⁹. First, 2,6-dimethylanilines 1.04 g (8.61 mmol) was added dropwisely into a solution of 2-hydroxy-1,4-naphthoquinone 1.50 g (8.61 mmol) in *m*-cresol (30 ml)

using trifluoroacetic acid (0.20 ml, 2.69 mmol) as a catalyst. The mixture was heated at 100 °C for 4 h with stirring and then was poured into 900 ml of 5 wt% aqueous sodium hydroxide. The precipitate formed was then filtered, washed with water, and dried under vacuum at 80 °C for 6 h. The crude powder was then recrystallized from acetic acid to give ligand **1a** as orange crystals. Yield: 1.63 g (5.88 mmol), 68 %. ¹H NMR (300 MHz, C₆D₆): δ 8.19 (dd, *J* = 1.5, 7.5 Hz, 1H), 7.99 (dd, *J* = 1.5, 7.5 Hz, 1H), 7.07 (dt, *J* = 1.5, 7.5 Hz, 1H), 6.97 (dt, *J* = 1.5, 7.5 Hz, 1H), 6.89 (d, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 2H), 6.07 (d, *J* = 8.1 Hz, 1H), 6.57 (br, 1H), 5.54 (s, 1H), 1.80 (s, 6H). ¹³C NMR (75 MHz, C₆D₆): δ 182.5, 182.0, 146.4, 135.8, 134.6, 134.1, 134.1, 131.8, 131.1, 128.8, 127.9, 126.4, 126.1, 103.1, 17.7. Anal. calcd.: C, 77.95; H, 5.46; N, 5.05. found: C, 77.24; H, 5.45; N, 5.05.

Synthesis of Ligand 2a Following the synthetic procedure for ligand **1a**, 1.16 g (8.61 mmol) of 2,4,6-trimethylaniline and 1.50 g (8.61 mmol) of 2-hydroxy-1,4-naphthoquinone were converted to ligand **2a**. Yield: 1.85 g (6.35 mmol), 74 %. ¹H NMR (300 MHz, C₆D₆): δ 8.10 (dd, *J*=1.2, 7.5 Hz, 1H), 8.00 (dd, *J*=1.2, 7.5 Hz, 1H), 7.07 (dt, *J* = 1.2, 7.5 Hz, 1H), 6.97 (dt, *J* = 1.2, 7.5 Hz, 1H), 6.61 (s, 1H), 6.58 (br, 1H), 5.59 (s, 1H), 2.07 (s, 3H), 1.81 (s, 6H). ¹³C NMR (75 MHz, C₆D₆): δ 182.5, 182.1, 146.8, 137.4, 135.4, 134.5, 134.2, 131.8, 131.5, 131.1, 129.6, 126.4, 126.1, 103.0, 20.9, 17.6. Anal. calcd.: C, 78.32; H, 5.89, N, 4.80. found: C, 78.18; H, 6.05, N, 4.92.

Synthesis of Ligand 3a Following the synthetic procedure for ligand **1a**, 1.28 g (8.61 mmol) of 2,6-diethylaniline and 1.50 g (8.61 mmol) of

2-hydroxy-1,4-naphthoquinone were converted to ligand **3a**. Yield: 2.03 g (6.97 mmol), 77 %. ¹H NMR (300 MHz, C₆D₆): δ 8.18 (dd, *J* = 1.2, 7.5 Hz, 1H), 7.99 (dd, *J* = 1.2, 7.5 Hz, 1H), 7.06 (dt, *J* = 1.2, 7.5 Hz, 1H), 7.01 (t, *J* = 7.8 Hz 1H), 7.00 (dt, *J* = 1.2, 7.5 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 2H), 6.79 (br, 1H), 5.63 (s, 1H), 2.25 (m, 4H), 0.92 (t, *J*=7.2 Hz, 6H). ¹³C NMR (75 MHz, C₆D₆): δ 182.5, 182.1, 147.4, 141.8, 134.6, 134.1, 133.0, 131.9, 131.0, 128.6, 127.0, 126.4, 126.1, 103.3, 24.6, 14.6. Anal. calcd.: C, 78.65; H, 6.28, N, 4.59. found: C, 77.56, H, 6.21, N, 5.06.

Sodium Salt of Ligand 1b A solution of the ligand **1a** 1.63 g (5.88 mmol) in THF (20 ml) was slowly added through a dropping funnel into a reactor containing the slurry of sodium hydride (0.14 g, 5.88 mmol) in THF (10 ml) cooled in ice-water bath at 0 °C. After stirring the mixture in the ice-water bath for 2 h, the mixture was

warmed to room temperature. The slurry obtained was filtered under an argon atmosphere. The residue was washed with THF, and dried in vacuo to produce the desired salt with one THF addition product. The solid residue was immediately used in the next step without further purification. Yield: 1.79 g (4.82 mmol), 82.1 %.

Sodium Salt of Ligand 2b Following the synthetic procedure for the sodium salt of ligand **1b**, 1.85 g (6.35 mmol) of 2-(2,4,6-trimethylanilino)-1,4-naphthoquinone and 0.15 g (6.35 mmol) of sodium hydride were converted to sodium salt of ligand **2b**. Yield: 1.88 g (4.88 mmol), 77 %.

Sodium Salt of Ligand 3b Following the synthetic procedure for the sodium salt of ligand **1b**, 5.32 g (17.4 mmol) of 2-(2,6-diethylanilino)-1,4-naphthoquinone and 0.50 g (20.9 mmol) of sodium hydride were converted to sodium salt of ligand **3b**. Yield:

4.94 g (12.4 mmol), 71 %.

Synthesis of Complex 1c The nickel complex **1c** was synthesized according to the

literature procedure for the synthesis of **4c**. The sodium salts of ligand **1b** (0.63 g,

1.70 mmol) and *trans*-[Ni(PPh₃)₂PhCl]⁵⁰ (1.18 g, 1.70 mmol) were mixed in THF (10

ml) at room temperature in a Schlenk tube and stirred for one day. After the reaction

mixture was filtered under a nitrogen atmosphere, THF was removed from the filtrate

under vacuum. The crude product was recrystallized using a mixture of THF/pentane

= 1/5 to give complex **1c** as blue crystals. Yield: 0.57 g (0.76 mmol), 45 %. ¹H NMR

(300 MHz, C₆D₆): δ 8.27 (d, *J* = 7.5 Hz, 1H), 7.46 (m, 6H), 7.0 (m, 14H), 6.80 (s, 1H),

6.73 (t, *J* = 7.5 Hz, 1H), 6.40 (q, *J* = 7.5 Hz, 1H), 6.36 (t, *J* = 7.5 Hz, 2H), 5.64 (s, 1H),

2.42 (s, 6H). ³¹P NMR (202 MHz, C₆D₆): δ 28.57. Anal. calcd.: C, 74.79; H, 5.09; N,

2.08. found: C, 74.53; H, 5.33; N, 2.22.

Synthesis of Complex 2c Following the synthetic procedure for complex **1c**, 0.92 g

(2.38 mmol) of the sodium salt of **2b** and 1.65 g (2.38 mmol) of

trans-[Ni(PPh₃)₂PhCl] were converted to complex **2c**. ¹H NMR and elemental analysis

revealed that **2c** contained one THF as a crystalline solvent. ¹H NMR (300 MHz,

C₆D₆): δ 8.23 (d, *J* = 7.5 Hz, 1H), 7.44 (m, 15H), 6.70 (t, *J* = 7.5 Hz, 1H), 6.57 (s, 2H),

6.40 (q, *J* = 7.5 Hz, 1H), 6.34 (t, *J* = 7.5 Hz, 2H), 5.62 (s, 1H), 3.63 (THF), 2.38 (s,

6H), 2.02 (s, 3H), 1.38 (THF). ³¹P NMR (202 MHz, C₆D₆): δ 28.13. Anal.

calcd.(included one THF): C, 74.22; H, 5.84; N, 1.84. found: C, 74.61; H, 5.82; N,

1.99.

Synthesis of Complex 3c Following the synthetic procedure for complex **1c**, 0.60 g

(1.51 mmol) of the sodium salt of **3b** and 1.03 g (1.51 mmol) of *trans*-[Ni(PPh₃)₂PhCl] were converted to complex **3c**. ¹H NMR (300 MHz, C₆D₆): δ 8.24 (d, *J* = 7.5 Hz, 1H), 7.43 (m, 15H), 6.9 (m, 16H), 6.69 (t, *J* = 7.5 Hz, 1H), 6.36 (q, *J* = 7.5 Hz, 1H), 6.31 (t, *J* = 7.5 Hz, 2H), 5.63 (s, 1H), 2.97 (q, *J* = 7.2 Hz, 4H), 1.23 (t, *J* = 7.2 Hz, 6H). ³¹P NMR (202 MHz, C₆D₆): δ 27.99. Anal. calcd.: C, 75.22; H, 5.46; N, 1.99. found: C, 75.28; H, 5.68; N, 2.12.

Polymerization Polymerization was performed in a 100 ml glass reactor equipped with a magnetic stirrer and carried out as the following method. After a certain amount of gaseous ethylene or propylene was dissolved in toluene, polymerization was started by the addition of a prescribed amount of the complex pre-reacted with 4 eq. of B(C₆F₅)₃. Polymerization was conducted for a certain time and terminated with

acidic methanol. The polymers obtained were adequately washed with methanol and dried under vacuum at 60 °C for 6 h.

Supplementary material

CCDC 649724 - 649726 contain the supplementary crystallographic data for 1c – 3c.

These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/>

[conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html), or from the Cambridge Crystallographic Data Centre, 12 Union

Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail:

deposit@ccdc.cam.ac.uk.

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Supporting Information Available

ORTEP diagrams and X-ray Crystallographic data of **1a** and **4a**.

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Figure captions

Figure 1. ORTEP drawing of the molecular structure of **1c**. Hydrogen atoms are omitted. Selected interatomic distances (Å) and torsion angle (deg): Ni(1)-P(1) = 2.1818(4), Ni(1)-O(1) = 1.971(1), Ni(1)-N(1) = 1.920(1), Ni(1)-C(19) = 1.886(2), C(2)-N(1)-C(11)-C(12) = 93.4(2).

Figure 2. ORTEP drawing of the molecular structure of **2c**. Crystalline solvent (THF) and hydrogen atoms are omitted. Selected interatomic distances (Å) and torsion angle (deg): Ni(1)-P(1) = 2.1733(8), Ni(1)-O(1) = 1.960(2), Ni(1)-N(1) = 1.918(2), Ni(1)-C(1) = 1.878(4), C(8)-N(1)-C(17)-C(18) = 83.3(4).

Figure 3. ORTEP drawing of the molecular structure of **3c**. Hydrogen atoms are omitted. Selected interatomic distances (Å) and torsion angle (deg): Ni(1)-P(1) =

2.1802(7), Ni(1)-O(1) = 1.953(2), Ni(1)-N(1) = 1.930(2), Ni(1)-C(1) = 1.877(2),

C(17)-N(1)-C(7)-C(8) = 88.2(6).

Figure 4. ^{13}C NMR spectrum of polypropylene at 0 °C

Scheme 1. Synthetic scheme of nickel complexes **1c-3c**

Table 1. Crystallographic Data for Complexes **1c**, **2c** and **3c**

	1c	2c	3c
Empirical Formula	C ₄₂ H ₃₄ PO ₂ NNi	C ₄₇ H ₄₄ PO ₃ NNi	C ₄₄ H ₃₈ PO ₂ NNi
Formula Weight	674.41	760.54	702.46
Crystal System	triclinic	triclinic	triclinic
<i>a</i> / Å	9.3917(6)	16.464(5)	9.904(5)
<i>b</i> / Å	10.9664(6)	17.419(6)	12.670(6)
<i>c</i> / Å	17.1180(8)	18.047(6)	14.365(7)
<i>V</i> / Å ³	1656.0(2)	3846.5(21)	1734.2(15)
<i>α</i> / deg	75.137(2)	118.279(2)	96.673(7)
<i>β</i> / deg	87.891(3)	90.0177(13)	102.457(10)
<i>γ</i> / deg	76.438(3)	118.183(3)	95.602(4)
Space Group	P-1	P-1	P-1
<i>Z</i>	2	4	2
<i>D</i> _{calcd} / g·cm ⁻³	1.352	1.313	1.345
<i>μ</i> / cm ⁻¹	6.73	5.89	6.45
<i>F</i> ₀₀₀	704.00	1600.00	736.00
<i>R</i>	0.034	0.055	0.033
<i>R</i> _w	0.125	0.158	0.045
Goodness of Fit	1.084	1.060	0.948
Indicator			
Max Shift / Error in Final Cycle	0.002	0.001	0.003

Table 2. ^{31}P NMR Chemical Shifts of the Complexes with and without $\text{B}(\text{C}_6\text{F}_5)_3$ ^a

	Chemical Shift δ / ppm	Chemical shift $\delta_{+\text{B}}$ / ppm	$(\delta_{+\text{B}})-(\delta)$
1c	28.57	24.65	-3.92
2c	28.13	24.69	-3.44
3c	28.99	24.49	-4.50
4c	27.52	23.78	-3.74
PPh_3	-5.11	45.20	50.31

^aThe ^{31}P NMR (202 MHz, C_6D_6) spectra were referenced to external 85 % H_3PO_4 .

Table 3. Substituent Effects of the Complexes **1c-3c** on Ethylene Polymerization^a

run	complex	Temp. / °C	Activity ^b	M_n^c	MWD ^c	Branches / 1000 C ^d	T_m / °C ^e
1		40	363	5,100	2.24	41	109
2	1c	20	39	47,000	2.24	5	n/a
3		0	trace	-	-	-	-
4		40	421	5,900	2.44	32	102
5	2c	20	176	114,000	2.24	9	124
6		0	60	236,000	1.69	6	135
7		40	881	5,800	2.57	34	105
8	3c	20	394	91,000	2.04	12	124
9		0	102	228,000	2.08	3	134
10		40	1,320	18,000	3.95	21	113
11	4c ⁴²	20	957	324,000	2.88	7	127
12		0	249	1,160,000	4.11	<1	144

^aPolymerization conditions: toluene = 30 ml, Ni = 5 μ mol, B(C₆F₅)₃ = 20 μ mol,

ethylene = 1 atm. ^bActivity in kg-polyethylene / (mol-Ni·h). ^c M_n and MWD

determined by GPC using polystyrene standards. ^dCalculated by the following

equation; $(CH_3/3)/[(CH+CH_2+CH_3)/2] \times 1,000 =$ branches per 1000 carbons. CH₃, CH₂,

CH refer to the intensities of the methyl, methylene and methine resonances in ¹H

NMR spectra. ^eDetermined by DSC.

Table 4. Number of Alkyl Branches of Polyethylene Produced by **1c-3c**

run	complex	Temp / °C	Branches / 1000 C			
			Me	Et	Pr	Long
1	1c	40	18	5	2	16
2		20				
4	2c	40	12	5	3	15
5		20	9	0	0	0
6		0	6	0	0	0
7	3c	40	13	4	2	13
8		20	12	0	0	0
9		0	3	0	0	0
10	4c	40	7	3	1	10
11		20	7	0	0	0
12		0	<1	0	0	0

Fig.1

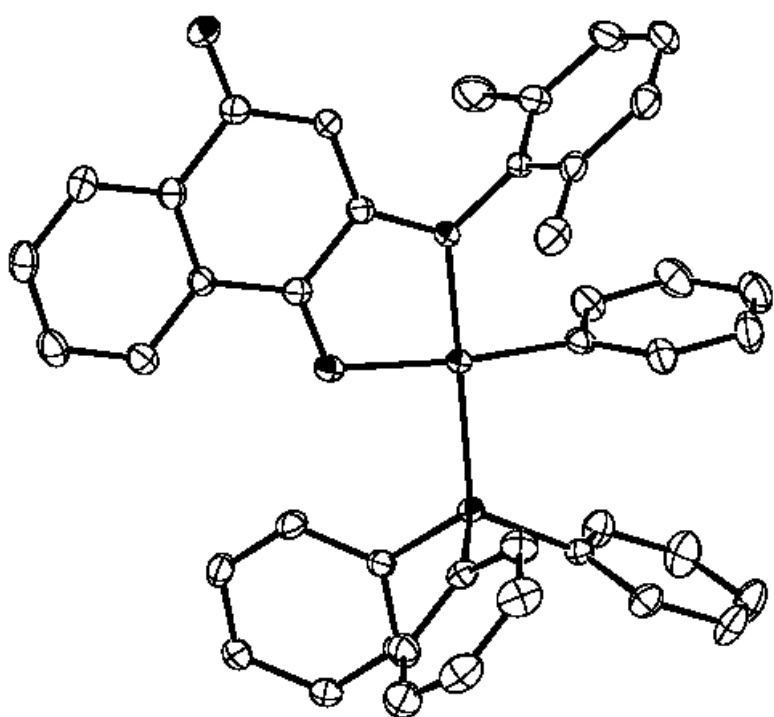


Fig.2

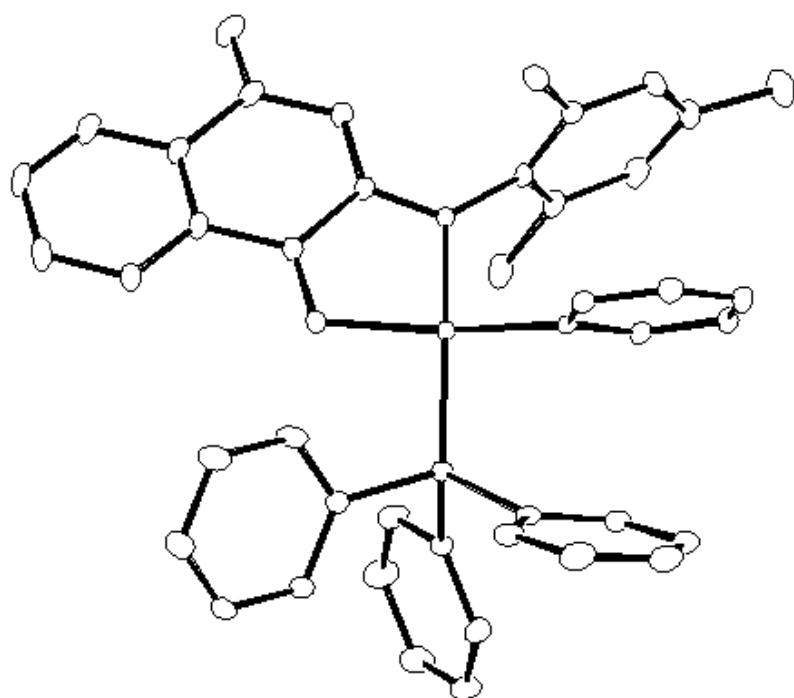


Fig.3

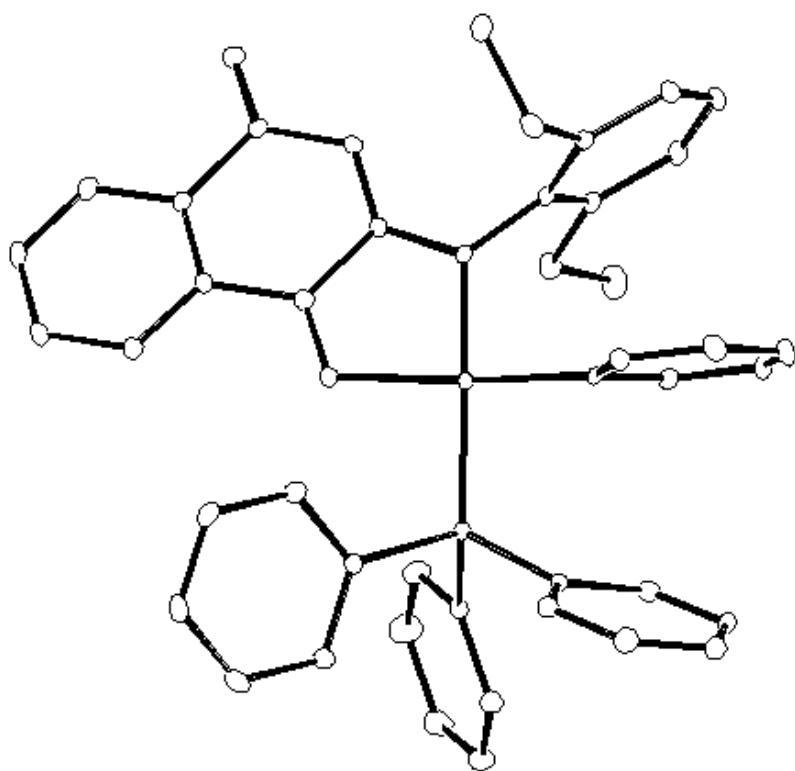
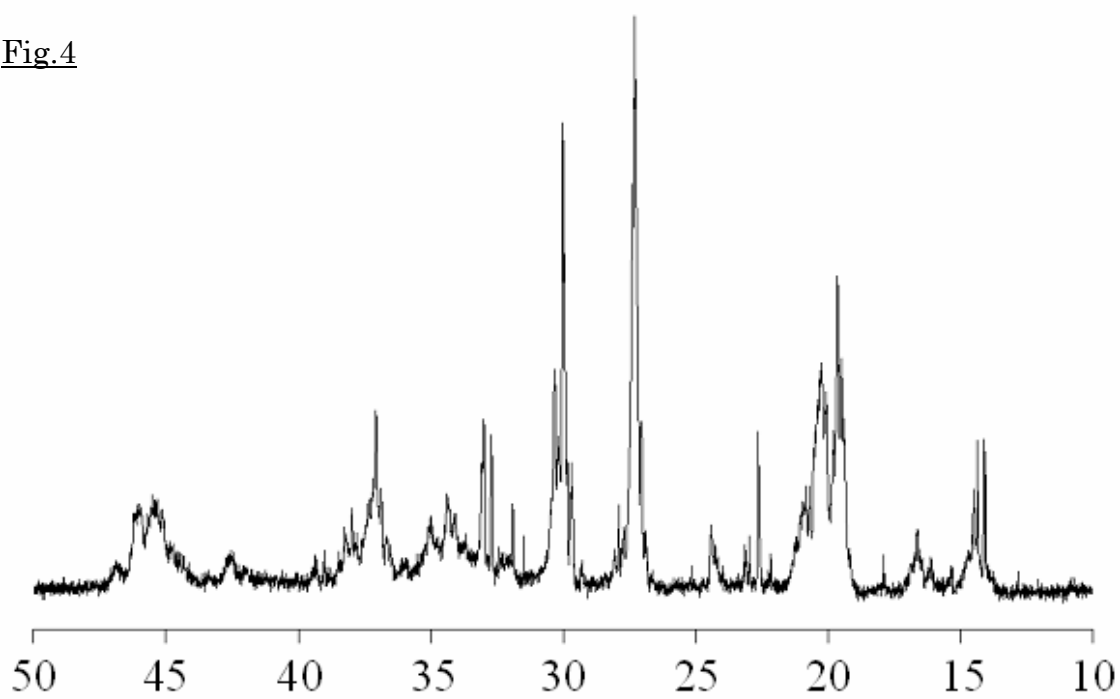


Fig.4



Scheme 1

