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Polymerization of Ethylene Catalyzed by Novel Titanium and Zirconium Sulfonamide Complexes

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Monodentate sulfonamide titanium and zirconium complexes, $(\text{RNSO}_2\text{R}')_2\text{M}(\text{NR}_2)_2$ ($\text{M} = \text{Ti}, \text{Zr}$), which were synthesized *in situ* from $\text{M}(\text{NR}_2)_4$ and 2 equivalents of sulfonamide ligands, $\text{RNHSO}_2\text{R}'$, and which were characterized by ^1H NMR, were used to catalytic polymerization of ethylene with either methylaluminoxane (MAO) or a mixture of $i\text{-Bu}_3\text{Al}$ and $(\text{PhNHMe}_2)^+ \{\text{B}(\text{C}_6\text{F}_5)_4\}^-$ as cocatalyst. Catalytic activities depended on the reaction temperature and steric bulkiness of the sulfonamide ligands. The highest activity (~ 0.505 KgPE / mmol h) was available at 80°C using the complex bearing bulky PhMe_2CNTs ligands. Polyethylenes with higher molecular weight was obtainable when $i\text{-Bu}_3\text{Al}$ and $(\text{PhNHMe}_2)^+ \{\text{B}(\text{C}_6\text{F}_5)_4\}^-$ were used as the cocatalyst. Broad molecular weight distribution ($M_w / M_n = 4.0 - 38$) of the polymer indicates the existence of dual catalytically active species. Effects of the sulfonamide ligand structure and possible active species are discussed.

1. Introduction

Efficient production of polyolefins is one of the important problems in the chemical industry. The discovery of single-site catalysts, in which particular organometallic molecules, e.g. $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$ and other Group IV metallocenes in the presence of methylaluminoxane $[(\text{AlMeO})_n; \text{MAO}]$, act as a catalyst of olefin polymerization, has provided a successful entry to polyolefins with a narrow molecular weight distribution.¹⁾ Lately, much effort has been made in the search for non-metallocene-type polymerization catalysts;²⁻⁴⁾ in particular, Group IV-transition metal amides have received considerable attention from organometallic and polymer chemists.⁴⁾ In our studies on the preparation, structure, and catalysis of organotitanium compounds bearing sulfonamide ligands, we have reported the successful preparation and structure elucidation of four tosylamide complexes of titanium, $(\eta^2\text{-}i\text{-PrNTs})_2\text{Ti}(\text{NMe}_2)_2$, $\{\eta^1;\eta^1\text{-(TsNCH}_2\text{CH}_2)_2\text{O}\}\text{Ti}(\text{NMe}_2)_2$, and $[(\eta\text{-TsNCH}_2\text{CH}_2)_2\text{O}]\text{Ti}(\text{X})(\text{Y})_2$ ($\text{X} = \text{Y} = \text{Cl}$ or $\text{X} = \text{NMe}_2$, $\text{Y} = \text{Cl}$).⁵⁾ Interestingly, these compounds were found to be active as catalysts for ethylene polymerization in the presence of methylaluminoxane. Although a number of titanium or zirconium amides have been reported as catalysts for olefin polymerization, those bearing sulfonamide ligands have not been examined. This prompted us to synthesize a series of compounds, $(\eta^2\text{-RNSO}_2\text{R}')_2\text{M}(\text{NR}_2)_2$ ($\text{M} = \text{Ti}, \text{Zr}$) which were subjected to studies on ethylene polymerization. From the data available we discuss how the metal and structure of sulfonamide ligands affects the polymerization behavior.

2. Results and Discussion

2.1 Preparation of the catalyst. As described earlier, treatment of $\text{Ti}(\text{NMe})_4$ with two equivalents of $i\text{-PrNHTs}$ results in the formation of $(\eta^2\text{-}i\text{-PrNTs})_2\text{Ti}(\text{NMe}_2)_2$ (**1**). Despite a possible formation of $(i\text{-PrNTs})\text{Ti}(\text{NMe}_2)_3$, $(i\text{-PrNTs})_3\text{Ti}(\text{NMe}_2)$, or $(i\text{-PrNTs})_4\text{Ti}$, **1** could be isolated as the single product in quantitative yield. Assignment of the product was unequivocally done by ^1H and ^{13}C NMR spectra, X-ray crystallography, and elemental analysis.⁵⁾ In a previous paper, we reported on results of preliminary ethylene polymerization in a small reaction vessel (100 mL stainless-steel autoclave) by using isolated and crystallized titanium complexes. For the discussion on polymerization behavior in detail, it is desirable to use a larger autoclave (2 L) with efficient stirrer and a gas inlet, which can supply ethylene at a uniform pressure. The uptake of ethylene gas can also

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be measured in this larger equipment. For the experiment, larger amounts of the catalyst must be introduced to the reaction vessel; the method using crystallized titanium complexes is not appropriate because of the highly air- and moisture sensitivity of the titanium compounds. In this context, we devised the following *in situ* preparative method of the catalyst to carry out the polymerization by using **1** and analogous titanium or zirconium compounds: (1) titanium or zirconium amide, $M(NR_2)_4$, was treated with 2 equivalents of $RNHSO_2R'$ in toluene at room temperature for 1 h; (2) formed HNR_2 and the solvent was removed *in vacuo*, and in this step, characterization of the complex was carried out by 1H NMR spectrum (*vide infra*); (3) a toluene solution (10 μ mol of the complex / mL) of the titanium or zirconium-sulfonamide was prepared; (4) a mixture of this catalyst solution and aluminium cocatalysts was used for the polymerization studies described later.

With the *in situ* method, we synthesized five new titanium sulfonamide complexes, $(RNTs)_2Ti(NEt_2)_2$ [$R = i\text{-Pr}$ (**2**), cyclohexyl (**3**), $t\text{-Bu}$ (**4**)], $(PhMe_2CNTs)_2Ti(NMe_2)_2$ (**5**) and $\{t\text{-BuNSO}_2(\text{camphor})\}_2Ti(NMe_2)_2$ (**6**), and a zirconium sulfonamide, $(PhMe_2CNTs)_2Zr(NMe_2)_2$ (**7**), as shown in Fig. 1. The titanium complexes **2**, **3** and **4** were prepared by treatment of $Ti(NEt_2)_4$, which is more stable than $Ti(NMe_2)_4$ and easily handled, with the corresponding sulfonamide, whereas **5** or **7** was done from either $Ti(NMe_2)_4$ or $Zr(NMe_2)_4$ with $PhMe_2CNHTs$. Features of the 1H NMR spectra of these complexes are consistent with those deduced from the spectrum of **1**. As a typical example, the 1H resonance due to the NMe_2 group in **5** and **7** appeared as a sharp singlet at δ 3.08 (**5**) and 2.78 (**7**) ppm in C_6D_6 . This is similar to that of **1** (δ 3.61). 1H signals due to the $PhMe_2C$ moiety were seen at δ 1.47 and 1.76 (Me), 6.97, 7.09, and 7.62 (Ph) in **5**, and at δ 1.52 and 1.63 (Me), 6.97, 7.12, and 7.61 (Ph) in **7**. The assignment of **5** was also supported by X-ray structural determination as shown in Fig. 2. In all of the cases, it was confirmed from the 1H NMR spectra that the desired compounds were formed as the single product, and they are used without further purification.

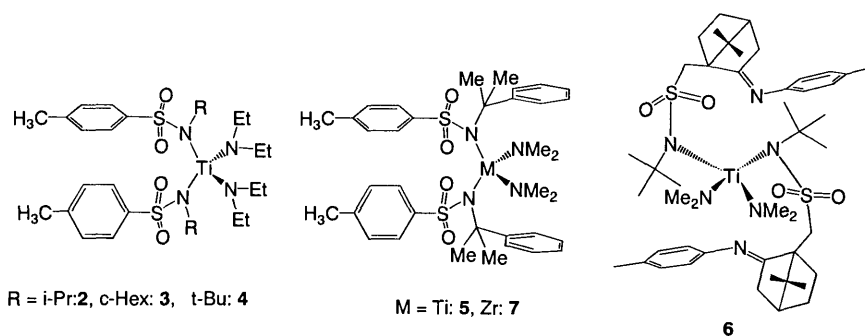


Fig.1 sulfonamide complexes

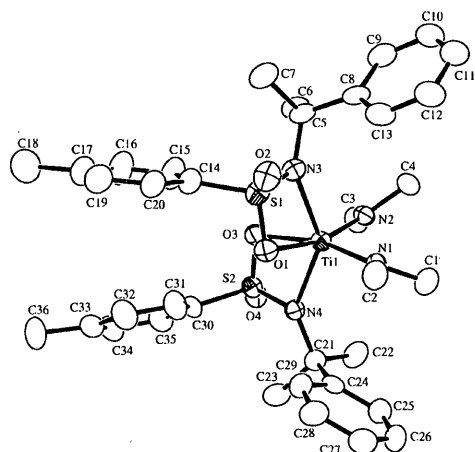


Fig.2 ORTEP Drawing of **5**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 50 % probability. Selected bond length (\AA) and angles ($^\circ$): Ti-N(1) 1.909(3), Ti-N(2) 1.909(3), Ti-N(3) 2.145(3), Ti-N(4) 2.127(3), Ti-O(1) 2.181(3), Ti-O(3) 2.221(3), S(1)-O(1) 1.492(3), S(1)-O(2) 1.439(3), S(2)-O(3) 1.474(3), S(2)-O(4) 1.437(3), S(1)-N(3) 1.567(3), S(2)-N(4) 1.578(3), N(1)-Ti-N(2) 94.88(15), N(3)-Ti-N(4) 141.38(13), N(3)-S(1)-O(1) 65.03(12), N(4)-S(2)-O(3) 64.54(11).

Crystal Data: Formula $C_{36}H_{48}N_4O_4S_2Ti$, $FW = 712.82$, monoclinic, $P2_1/a$, $a = 13.068(4) \text{ \AA}$, $b = 16.608(3) \text{ \AA}$, $c = 17.790(3) \text{ \AA}$, $\beta = 108.90(1)^\circ$, $V = 3653(1) \text{ \AA}^3$, $Z = 4$, $D_{calc} = 1.296 \text{ g/cm}^3$, $T = 223 \text{ K}$, 8687 unique reflections ($R_{int} = 0.061$) were collected, $R = 0.0515$, $R_w = 0.1710$.

Table 1 Ethylene Polymerization Results¹⁾

Run	Complex ²⁾	Temp / °C	Time / min	Yield / g	Activity / KgPE / mmol·h	T _m ³⁾ / °C	HLMI / g/10min	M _w / ×10 ⁴	M _w /M _n
1	4	40	60	3.94	0.197	140	< 0.01	74	30
2	4	60	60	7.59	0.380	142	0.074	50	12
3	4	80	60	8.18	0.409	139	14	7.2	4.0
4	2	80	60	3.67	0.184	141	2.7	9.2	4.1
5	3	80	60	6.63	0.332	140	1.5	7.7	4.8
6	5	80	60	10.09	0.505	138	31	6.6	3.4
7	7	80	30	6.85	0.685	136	14	14	38
8	6	80	30	4.29	0.429	140	0.56	14	7.2
9	Ti(NEt ₂) ₄	80	60	6.93	0.347	139	5.7	14	5.5

1) Polymerization was carried out in toluene (500 mL) under ethylene pressure (0.8 MPa) using a 2L autoclave. 2) [complex] = 20 μmol, [MAO] = 20 mmol. 3) Measured by differential scanning calorimetry.

Table 2 Ethylene Polymerization Results¹⁾ (Comparison of the Behavior of Cocatalyst)

Run	Complex ²⁾	Cocatalyst ³⁾	Yield / g	Activity / KgPE / mmol·h	T _m ⁴⁾ / °C	HLMI / g/10min
1	4	i-Bu ₃ Al / PhNHMe ₂ B(C ₆ F ₅) ₄	13.47	0.674	138	< 0.01
2	4	MAO	8.18	0.409	139	14
3	5	i-Bu ₃ Al / PhNHMe ₂ B(C ₆ F ₅) ₄	5.48	0.548	142	0.15
4	5	MAO	10.09	0.505	138	31
5	7	i-Bu ₃ Al / PhNHMe ₂ B(C ₆ F ₅) ₄	11.30	1.13	138	1.8
6	7	MAO	6.85	0.685	136	14
7	6	i-Bu ₃ Al / PhNHMe ₂ B(C ₆ F ₅) ₄	12.0	1.20	137	0.58
8	6	MAO	4.29	0.429	140	0.56

1) Polymerization was carried out in toluene (500 mL) under ethylene pressure (0.8 MPa) at 80 °C for 30 min using a 2L autoclave. In the cases of run 1, 2, 4, the reaction time was 60 min. 2) complex 20 μmol. 3) [i-Bu₃Al] / [(PhNHMe₂)⁺B(C₆F₅)₄⁻] = 5.0 mmol / 100 μmol, [MAO] = 20 mmol. 4) Measured by differential scanning calorimetry.

2.2 Ethylene Polymerization. Polymerization of ethylene was carried out in the presence of two types of cocatalysts. In the case of the first cocatalyst, methylaluminoxane [(AlMeO)_n; MAO] (1000 eq.) is added to the titanium or zirconium catalyst, whereas in the other case the catalyst is treated with i-Bu₃Al followed by addition of (PhNHMe₂)⁺{B(C₆F₅)₄}⁻. Detailed experimental procedures are summarized in the experimental section. The results of the polymerization using MAO as the cocatalyst under 0.8 MPa of ethylene are shown in Table 1. Polymerizations using the catalyst **4** at 40, 60, and 80 °C for 1 h gave 4 ~ 8 g of polyethylene with the activity of 0.197, 0.380, and 0.409 kgPE / mmol·h (entries 1 ~ 3); the highest activity was available at 80 °C. In general, the activity is dependent on the reaction temperature in homogeneous olefin polymerization catalyzed by organometallic complexes; each catalyst has a specific temperature for attaining the highest activity. For example, the activity of Kaminsky's catalyst (Cp₂ZrCl₂ / MAO) reaches its maximum at 60 ~ 70 °C.⁶⁾ In the case of **4**, efficient polymerization occurred at 60 ~ 80 °C.

Experiments changing the sulfonamide ligands of the catalyst in titanium complex-catalyzed ethylene polymerization at 80 °C (entries 3 ~ 6) revealed that the activity was increased in the order of **2** < **3** < **4** < **5**. This order roughly corresponds with the order of steric bulkiness of the sulfonamide ligands. Activity of the titanium complex bearing the most bulky PhMe₂CNTs ligand reached 0.505 kgPE / mmol·h, which is 2.5 times that catalyzed by **2** having the smallest sulfonamide ligand, i-PrNTs. It is known that activity exhibited by non-metallocene type catalysts is sensitive to the steric parameters around the metal center, and the introduction of bulky substituents in the ligand often increases the catalytic activity.^{3a)} The results shown in entries 3 ~ 7 are consistent with this trend. The

result shown in entry 7 shows that the zirconium complex exhibits somewhat higher activity than the titanium homologue **5**. The catalyst **6** exhibits an activity similar to **4**; this can be attributed to steric bulkiness of the camphor moiety in **6** comparable to that of the t-butyl group in **4**. It is worthwhile to point out that possible coordination of the C=N group to the titanium center of the catalytic species may contribute to an increase of the activity, though unequivocal evidence for this is so far unavailable.

In Table 2 are summarized the results of the polymerization using $i\text{-Bu}_3\text{Al}$ / $(\text{PhNHMe}_2)^+\{\text{B}(\text{C}_6\text{F}_5)_4\}^-$ as the cocatalyst in comparison with those in the presence of MAO. As shown in entries 5 ~ 8, the activity obtained with $i\text{-Bu}_3\text{Al}$ / $(\text{PhNHMe}_2)^+\{\text{B}(\text{C}_6\text{F}_5)_4\}^-$ as the cocatalyst is twice as high as that using MAO in the polymerization catalyzed by **6** or **7**. The fact that the activity is dependent on the cocatalyst has already been pointed out in ethylene polymerization catalyzed by several non-metallocene complexes; for example, Jordan and coworkers have reported a similarly high activity of certain zirconium catalyst when $i\text{-Bu}_3\text{Al}$ / $(\text{PhNHMe}_2)^+\{\text{B}(\text{C}_6\text{F}_5)_4\}^-$ was used as the cocatalyst.^{3c)}

Characterization of the formed polymers is another important aspect for understanding features of the catalyst. The melting point of the polymer (T_m) is an indication of microstructure, in particular of the existence of polymer branching; T_m decreases with the increase of polymer branching. HLMI (High Load Melt Index, JIS K 7210) is an indication of molecular weight; smaller HLMI values correspond to higher molecular weight. Molecular weight was alternatively measured by GPC. The molecular weight distribution of the polymer as determined by GPC shows whether a single catalytically active species operates in the polymerization; in the ideal case where chain transfer occurs smoothly, M_w / M_n reaches 2.0. The polymers obtained in the experiments shown in Tables 1 and 2 showed the following: (1) the T_m values indicate the formation of typical HDPE in all cases; (2) molecular weights of the polymers formed by the catalyst, **2**, **3**, **4**, or **5** in the presence of MAO were $6 \sim 9 \times 10^4$, which correspond to the HLMI values of 1.5 ~ 31, whereas those available by **6** or **7** activated by MAO or by **4**, **5**, **6**, and **7** in the presence of $i\text{-Bu}_3\text{Al}$ / $(\text{PhNHMe}_2)^+\{\text{B}(\text{C}_6\text{F}_5)_4\}^-$ were over 10^5 (HLMI = 0.01 ~ 14); (3) comparison of the molecular weight among **2**, **3**, **4**, and **5** revealed that increasing steric bulkiness of the ligand tended to decrease the molecular weight; (4) dispersity of the polymers were in the range of 4.0 ~ 38, indicating the existence of dual catalytically active species during the polymerization.

It is known that the metallocene catalyst, for example, Cp_2ZrCl_2 / MAO, catalyzed the ethylene polymerization under similar conditions with an activity of over 10 kgPE / mmol. The activity of the catalysts described in this paper is a tenth of that of Kaminsky's catalyst. However, it is worthwhile to point out that the activity of the catalyst and molecular weight of the formed polymer are dependent on the steric bulkiness of the sulfonamide ligands in the catalyst, suggesting the involvement of the tosylamide ligands in the catalytically active species. It is considered that the alkylation ability and Lewis acidic nature of the cocatalyst could afford three possible catalytic species, **A** or **B**, which are formed by activation of either NR_2 or RNTs groups. The species **C** available by activation of two RNTs moieties is not likely to be involved due to the characteristics of the sulfonamide ligands described above. Furthermore, **C** can also be formed by $\text{M}(\text{NR}_2)_4$; however, the catalytic activity and molecular weight of the formed polymer catalyzed by $\text{Ti}(\text{NR}_2)_4$ were different from those available by titanium-sulfonamide catalysts **2**, **3**, **4**, **5**, and **6**, as shown in Table 1,

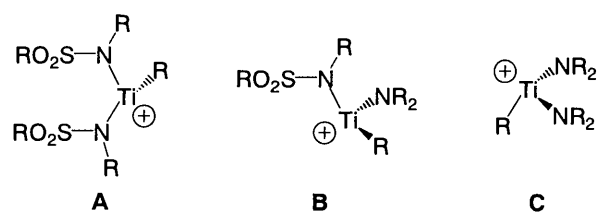


Fig 3 Possible catalytic species

entry 9.

3. Conclusion

In this paper, we have described that sulfonamide titanium and zirconium complexes *in situ* prepared are useful as novel ethylene polymerization catalysts. Polymerization behavior is dependent on the polymerization conditions and structure of the complex; especially, introduction of sterically bulky sulfonamide ligands to the metal and performing the reaction at 60 ~ 80 °C are important to attain high polymerization activity. This suggests that polymerization is promoted by metal species bearing sulfonamide ligands; in other words, an appropriate choice of the sulfonamide ligand causes increase of catalytic activity. Of interest from the point of catalyst design is that the possible catalytic species have neighboring sulfonamide oxygen atoms, which are known to be a factor to inhibit the polymerization. Although polymerization activity is moderate compared with typical metallocene catalysts, (1/10 of Cp₂ZrCl₂ / MAO), the sulfonamide complexes show several interesting features in polymerization behavior. In particular, the boron cocatalyst provides higher activities and production of polyethylene with relatively high molecular weight. These results indicate that further research on complexes bearing sulfonamides could be an intriguing entry to new polymerization catalysts.

4. Experimental Section

General. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. All of the solvents were distilled over drying reagents just before use. Ti(NMe₂)₄^{7a}, Ti(NEt₂)₄^{7a} and Zr(NMe₂)₄^{7b} were prepared according the literature procedure. The ¹H NMR spectra were taken with a JEOL GX-400 spectrometer at room temperature unless otherwise noted. Chemical shifts were recorded in ppm from the solvent signal. Measurement of HLMI was performed according to the procedure of JIS K 7210 (190 °C / 21.6 Kg). DSC analysis was performed on a SEIKO DSC-200 instrument (heating rate, 10 °C / min). GPC measurement was performed at TOSOH analysis and research center.

Preparation of the catalyst. The preparative method for the catalyst solution was described in the text. In a typical example, Ti(NMe₂)₄ (0.442 g, 1.97 mmol) was treated with PhMe₂CNHTs (1.03 g, 3.55 mmol) in toluene (10 mL) at room temperature. After 1 h, the solvent and HNMe₂ were removed *in vacuo*, and formation of the desired complex was confirmed by ¹H NMR in C₆D₆. The formed complex (44.2 mg, 61.6 μmol) was dissolved in toluene (6.16 mL) to produce 10 mM the catalyst solution used for the polymerization. ¹H NMR in C₆D₆:

2; δ = 1.17 (t, *J* = 7.0 Hz, 12H, CH₂CH₃), 1.29 (br, 12H, *i*-Pr-CH₃), 1.77 (s, 6H, Ts-CH₃), 3.86 (6H, br, 6H, one of CH₂CH₃), 3.93 (sept, 2H, *i*-Pr-CH), 4.67 (br, 4H, the other of CH₂CH₃), 6.70 (d, *J* = 8.1 Hz, 4H, C₆H₄), 8.37 (d, *J* = 8.1 Hz, 4H, C₆H₄). **3;** δ = 0.96 - 2.00 (m, 11H, cyclohexyl ring), 1.22 (t, *J* = 7.0 Hz, 12H, CH₂CH₃), 1.76 (s, 6H, Ts-CH₃), 3.57 (m, 2H, N-CH), 4.01 (br, 4H, one of CH₂CH₃), 4.67 (br, 4H, the other of CH₂CH₃), 6.72 (d, *J* = 8.4 Hz, 4H, C₆H₄), 8.41 (d, *J* = 8.4 Hz, 4H, C₆H₄). **4;** δ = 1.21 (t, *J* = 7.0 Hz, 12H, CH₂CH₃), 1.40 (s, 18H, *t*-Bu), 1.75 (s, 6H, Ts-CH₃), 4.37 (br, 8H, CH₂CH₃), 6.61 (d, *J* = 8.6 Hz, 4H, C₆H₄), 8.26 (d, *J* = 8.6 Hz, 4H, C₆H₄). **5;** δ = 1.47 (s, 6H, Ph(CH₃)₂C), 1.76 (s, 12H, Ph(CH₃)₂C and Ts-CH₃), 3.08 (s, 12H, N(CH₃)₂), 6.58 (d, *J* = 8.3 Hz, 4H, C₆H₄), 6.97 (t, *J* = 7.3 Hz, 2H, Ph-H_p), 7.09 (t, *J* = 7.3, 8.4 Hz, 4H, Ph-H_m), 7.62 (d, *J* = 8.4 Hz, 4H, Ph-H_o), 8.23 (d, 4H, *J* = 8.3Hz, C₆H₄). **6;** δ (-50 °C) 0.77 (s, 3H, C(CH₃)₂), 1.04 (2H, 3-H), 1.21 (s, 3H, C(CH₃)₂), 1.37 (s, 3H, C(CH₃)₂), 1.47 (1H, 5-H), 1.48 (1H, 3-H_a), 1.48 (1H, 5-H_c), 1.50 (2H, 4-H), 1.51 (s, 18H, *t*-Bu), 1.60 (s, 3H, C(CH₃)₂), 1.68 (d, *J* = 17.6 Hz, 1H, 3-H_a), 1.85 (m, 2H, 6-H_c), 2.04 (d, *J* = 17.6 Hz, 2H, 3-H_c), 2.18 (s, 3H, Ar-CH₃), 2.19 (s, 3H, Ar-CH₃), 3.13 (1H, 6-H_a), 3.20 (d, *J* = 15.2, 1H, SO₂CH₂), 3.35 (1H, 6-H_c), 3.40 (br, 6H, N(CH₃)₂), 3.50 (s, 6H, N(CH₃)₂), 3.86 (d, *J* = 15.2, 1H, SO₂CH₂), 4.16 (d, *J* = 15.2, 1H, SO₂CH₂), 4.45 (d, *J* = 15.2, 1H, SO₂CH₂), 6.65 (d, *J* = 8.1 Hz, 1H, Ph-H_o), 6.74 (d, *J* = 8.1 Hz, 1H,

Ph-H_o), 6.99 (d, $J = 8.1$ Hz, 2H, Ph-H_m). 7; $\delta = 1.52$ (s, 6H, Ph(CH₃)₂C), 1.63 (s, 6H, Ph(CH₃)₂C), 1.72 (s, 6H, Ts-CH₃), 2.78 (s, 12H, N(CH₃)₂), 6.53 (d, $J = 8.3$ Hz, 4H, C₆H₄), 6.97 (t, $J = 8.4$ Hz, 2H, Ph-H_p), 7.12 (t, 4H, Ph-H_m), 7.61 (d, $J = 8.4$ Hz, 4H, Ph-H_o), 8.19 (d, $J = 8.3$ Hz, 4H, C₆H₄).

X ray structure determination of 5. Single crystals of **5** were grown from a mixture of toluene and hexane solution at -30 °C. X-ray crystallography measurement was performed on a Rigaku RAXIS RAPID imaging plate diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71070\text{\AA}$). The data of all were collected at 223(2) K to a maximum 2θ value of 55.0 deg. The structure was solved by Patterson method (DIRDIF94 PATTY) and were refined using full-matrix least squares (SHELXL97) based on F^2 of all independent reflections measured. All H atoms were located at ideal positions and were included in the refinement, but they were restricted to riding on the atom to which they were bonded. Isotropic thermal factors of H atoms were held to 1.2 to 1.5 times (for methyl groups) U_{eq} of the riding atoms.

Polymerization studies. In a typical example, toluene (500 mL) and MAO (20 mmol, 7.14 mL in 2.8 M toluene solution) was measured into a 1.0 L Schlenk tube, and the mixture was stirred for 10 min. The catalyst solution (20 μmol , 2.0 mL in 10 mM) prepared by the method described above was added, and the solution was stirred for 10 min. Alternatively, toluene (500 mL) and *i*-Bu₃Al (5.0 mmol, 5.90 mL in 0.848 M toluene solution) was measured into a 1.0 L Schlenk tube, and the mixture was stirred for 10 min. The catalyst solution (20 μmol , 2.0 mL in 10 mM) prepared by the method described above was added, and the solution was stirred for 10 min. Then, (PhNHMe₂)⁺{B(C₆F₅)₄}⁻ (100 μmol , 10 mL in 10 mM toluene solution) was added, and the mixture was stirred for 10 min.. The resulting catalyst / cocatalyst solution was loaded to a 2L stainless steel autoclave. After the internal temperature of the autoclave reached at the desired temperature (40 ~ 80 °C), ethylene was introduced (0.8 MPa). Continuous supply of ethylene kept the gas pressure at 0.8 MPa during the polymerization. The polymerization was terminated by addition of ethanol (10 mL), and by terminating ethylene supply. The product was added to ethanol (500 mL) / HCl (5 mL) for the removal of aluminium compounds. Polyethylene was isolated as a colorless precipitate by filtration. It was washed with ethanol, and then dried *in vacuo* (100 °C, 8 h).

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