Substituent Effects of Adamantyl Group on Amido Ligand in Syndiospecific Polymerization of Propylene with Ansa-Dimethylsilylene(Fluorenyl)(Amido) Zirconium Complex

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Abstract: A series of new fluorenylamido-ligated zirconium complexes bearing an electron-donating adamantyl group on the amido ligand were synthesized and characterized by elemental analysis, 1H NMR, and single crystal X-ray analysis. The coordination mode of the fluorenyl ligand to the zirconium metal was η3 manner, and all the complexes were Cs-symmetric in solution. The complexes showed moderate activity (1.0 × 10^5 g-polymer mol-Zr⁻¹·h⁻¹), even at a low Al/Zr ratio of 50. The increase of propylene pressure improved the activity by one order of magnitude (up to 1.0 × 10^6 g-polymer mol-Ti⁻¹·h⁻¹). All catalyst systems gave syndiotactic polypropylene, where the complex containing the 3,6-di-β-butyl fluorenyl ligand was more effective for the enhancement of the syndiospecificity. The increase of propylene pressure also improved the syndiospecificity with the syndiotactic pentad of 0.96 and the melting point of 159 °C.

Keywords: constrained geometry catalysts; zirconium complex; adamantyl substituent; propylene polymerization; syndiospecificity

1. Introduction

Developments of single-site catalysts based on group-4 metallocenes demonstrated a well-defined mechanism for the relationship between the symmetry of the complex and the stereospecificity, in which a little change of the ligand dramatically influenced the polymerization performances, such as the activity, stereospecificity, and molecular weight [1-3]. Ewen et al. first reported the preparation of syndiotactic polypropylene (syn-PP) by using Cs-symmetric metallocene in 1988 [4]. Since this report, much effort has been made towards achieving the synthesis of syn-PP with single-site catalysts, including doubly bridged metallocenes [5], constrained geometry catalysts (CGCs) [6], and nonmetallocene catalysts [7-12]. Among these catalysts, group-4 CGCs have attracted much attention for their capabilities of improving copolymerization ability [13-22], stereospecificity [23-27], and living polymerization characteristics [28,29]. Many attempts have been made to improve the catalytic performance of CGC catalysts by changing the electronic and steric properties of the ligand.

Razavi et al. reported that the introduction of t-butyl substituent on the fluorenyl ligand of [Me2Si(t-Bu-N)(di-t-Bu-Flu)ZrCl2] (Zrfa-c), Figure 1) improved both the activity and syn-specificity with syn-pentad (rrrr) of 0.87 [23,24]. Miller et al. demonstrated that sterically expanded zirconium complex (Zr(d), Figure 1) combined with methylaluminoxane (MAO) was strikingly active to give syn-PP with unsurpassed syn-specificity (rrrr > 0.99) and melting temperature (Tm up to 165 °C) [25].
The results indicated that alkyl substituents on the fluorenyl ligand of zirconium complexes play an important role in catalytic activity and syn-specificity. However, the electronic effect of the amido ligand was not investigated.

![Figure 1. Structures of ansa-(fluorenyl)(amido)-ligated complexes.](image)

We previously synthesized the corresponding dimethyltitanium complexes (Ti(a–c), Figure 1) and found that the introduction of t-butyl group on the 3,6-position of the fluorenyl ligand improved both the activity and syn-specificity in the living polymerization of propylene [30]. However, sterically expanded titanium complex (Ti(d), Figure 1) showed low syn-specificity, which differed from that of the corresponding zirconium complex Zr(d) [31]. On the other hand, dimethylzirconium complexes [Me2Si(t-Bu-N)(di-t-Bu-Flu)ZrMe2] (Zr(e–g), Figure 1) showed very low activity for propylene polymerization [32]. Recently, we reported that the introduction of an electron-donating adamantyl substituent on the amido ligand of dimethyltitanium complexes (Ti(e–f), Figure 1) exhibited remarkably high activity with an Al/Ti ratio of 20 without changing syn-specificity or livingness [33,34]. In this paper, we synthesized dimethylzirconium complexes (Zr(1) and Zr(2), Figure 1) by using the same ligand to investigate the substitute effects of the adamantyl group on the amido ligand of fluorenylamido-ligated zirconium complexes in propylene polymerization.

2. Experimental Section

2.1. Materials

All operations were carried out under N2 by using standard Schlenk techniques, and all solvents were purified by a PS-MD-5 solvent purification system (Innovative Technology (China) Ltd., Hong Kong, China). A research grade propylene was purified by being passed through a dehydration column of ZHD-20 and a deoxidation column of ZHD-20A before use. Modified methylaluminoxane (MMAO) was donated by Tosoh-Finechem Co. (Shunan, Japan). The ligands and zirconium complexes were prepared according to the procedure reported in the literature [32,33].
2.2. Synthesis of Complexes

2.2.1. Synthesis of [(1-Adamantyl)NSiMe₂(2,7-di-t-BuFlu)]ZrMe₂ (Zr(1))

MeLi (1.6 M in ether 10.5 mL, 16.8 mmol) was added dropwise at −20 °C to a solution of ligand (2,7-di-t-BuFlu)SiMe₂(1-Adamantyl) (1.94 g, 4.0 mmol) in 60 mL of diethylether. The resultant orange solution was stirred at room temperature for 4 h. To a solution of ZrCl₄ (0.93 g, 4.0 mmol) in 30 mL pentane, the diethylether solution of the lithium salt was added, which gave a yellow suspension. After stirring for 12 h, the solvent was removed and the residue was extracted with hexane. Then the hexane solution was concentrated and cooled at −30 °C to yield Zr(1) as yellow crystals (0.72 g, 1.24 mmol, 31% yield).

¹H NMR (CDCl₃) (Figure S1): δ = 8.00 (d, 2H, Flu); 7.73 (s, 2H, Flu); 7.45 (dd, 2H, Flu); 2.07 (s, 3H, Ad); 1.80 (d, 6H, Ad); 1.64 (d, 6H, Ad); 1.41 (s, 18H, t-Bu-Flu); 0.84 (s, 6H, SiCH₃); −0.11 (s, 6H, ZrCH₃).

¹³C NMR (CDCl₃) (Figure S2): 150.8 (Flu); 136.0 (Flu); 122.9 (Flu); 122.4 (Flu); 122.1 (Flu); 122.1 (Flu); 120.5 (Flu); 56.1 (Flu); 48.0 (Zr-(CH₃)₂); 39.1 (Ad); 36.5 (Flu-(C(CH₃)₃)₂); 31.8 (Ad); 31.5 (Flu-(C(CH₃)₃)₂); 30.3 (Ad); 7.2 (Si-(CH₃)₂). Elemental analysis for C₃₅H₅₁NSiZr (calc/found, %): C, 69.47/69.26; H, 8.50/8.41; N, 2.31/2.26.

2.2.2. Synthesis of [(1-Adamantyl)NSiMe₂(3,6-di-t-BuFlu)]ZrMe₂ (Zr(2))

Complex Zr(2) was synthesized in a method similar to that for Zr(1), and yellow crystals were obtained in 33% yield.

¹H NMR (CDCl₃) (Figure S3): δ = 8.06 (s, 2H, Flu); 7.70 (d, 2H, Flu); 7.46 (dd, 2H, Flu); 2.06 (s, 3H, Ad); 1.82 (d, 6H, Ad); 1.64 (d, 6H, Ad); 1.46 (s, 18H, t-Bu-Flu); 0.82 (s, 6H, SiCH₃); −1.05 (s, 6H, ZrCH₃). ¹³C NMR (CDCl₃) (Figure S4): 147.1 (Flu); 134.0 (Flu); 127.2 (Flu); 124.4 (Flu); 118.3 (Flu); 56.1 (Flu); 48.1 (Zr-(CH₃)₂); 39.6 (Ad); 36.5 (Ad); 35.1 (Flu-(C(CH₃)₃)₂); 31.9 (Ad); 31.9 (Flu-(C(CH₃)₃)₂); 30.3 (Ad); 7.0 (Si-(CH₃)₂). Elemental analysis for C₃₅H₅₁NSiZr (calc/found, %): C, 69.47/69.38; H, 8.50/8.46; N, 2.31/2.29.

2.3. Polymerization Procedure

Atmospheric polymerization of propylene was performed in a 100-mL glass reactor equipped with a magnetic stirrer and carried out according to the semi-batch method. At first, the reactor was charged with prescribed amounts of MMAO/2,6-di-tert-butyl-4-methyl phenol (BHT) or dried MMAO (dMMAO) and solvent (heptane). After the solution of the cocatalyst was saturated with gaseous propylene under atmospheric pressure, polymerization was started by the addition of 1 mL solution of the zirconium complex in heptane, and the consumption rate of propylene was monitored by a mass flow meter.

High pressure polymerization of propylene was performed in a 200-mL Quick-Open Micro Autoclaves/Pressure Vessel purchased from Anhui Kemi Machinery Technology Co., Ltd. (Hefei, China) Before polymerization, the reactor was cleaned and evacuated at 110 °C for 1 h. Certain amounts of the MMAO/BHT, heptane were added into the reactor under a nitrogen atmosphere, and the mixture was stirred continuously. When the temperature was established, the catalyst solution of heptane was added into the reactor. The reactor was then pressurized with propylene. The polymerization was conducted for a certain time, and terminated with acidic alcohol. The polymers obtained were washed by alcohol to remove MMAO and ligand residue, and dried under vacuum at 80 °C for 6 h until a constant weight was reached.

2.4. Analytical Procedure

The single crystals were mounted under a nitrogen atmosphere at a low temperature, and data collection was made on a Bruker APEX2 diffractometer (Bruker, Karlsruhe, Germany) using graphite monochromated with Mo Ka radiation (=0.71073 Å). The SMART program package (University of Göttingen, Göttingen, Germany) was used to determine the unit cell parameters. The absorption
correction was applied using the SADABS program (University of Göttingen, Göttingen, Germany) [35]. All structures were solved by direct methods and refined on $F^2$ by full-matrix least-squares techniques with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were placed at calculated positions and were included in the structure calculation. Calculations were carried out using the SHELXS-97, SHELXL-2014, or Olex2 program (Bruker AXS Inc., Madison, WI, USA) [36–41]. Crystallographic data are summarized in Table 1.

| Complex | Zr(1) | Zr(2) |
|---------|-------|-------|
| Formula | $C_{35}H_{51}NSiZr$ | $C_{35}H_{51}NSiZr$ |
| Formula weight | 605.07 | 605.07 |
| Crystal system | Triclinic | Monoclinic |
| Space group | $P1$ | $P1_2_1/c$ |
| $a$ (Å) | 10.530(9) | 12.673(3) |
| $b$ (Å) | 11.668(8) | 19.886(4) |
| $c$ (Å) | 14.661(7) | 14.198(3) |
| $B$ (deg) | 75.818(2) | 111.899(4) |
| $V$ ($Å^3$) | 1584.3(3) | 3320.0(12) |
| Z calculated | 2 | 4 |
| $F$(000) | 644 | 1288 |
| $D_{calcd}$ (g.cm$^{-3}$) | 1.268 | 1.211 |
| $\mu$ (mm$^{-1}$) | 0.408 | 0.390 |

Molecular weights and molecular weight distributions of polymers were measured by a polymer laboratory PL GPC-220 chromatograph (Agilen, Santa Clara, CA, USA) equipped with one PL1110-1120 column and two PL MIXED-B 7.5 × 300 mm columns at 150 °C using 1,2,4-trichlorobenzene as a solvent. The parameters for universal calibration were $K = 7.36 \times 10^{-5}$, $\alpha = 0.75$ for polystyrene standard and $K = 1.03 \times 10^{-4}$, $\alpha = 0.78$ for PP samples. Differential scanning calorimeter (DSC) analyses were performed on a TA Q2000 instrument (Waters, New Castle, DE, USA) and the DSC curves of the samples were recorded under a nitrogen atmosphere at a heating rate of 10 °C/min from 40 to 200 °C. The $^1$H NMR spectra of complexes were recorded and the $^{13}$C NMR spectra of PPs were measured on a Bruker Asend™ 600 spectrometer (Bruker, Karlsruhe, Germany). The chemical shifts of the $^1$H NMR spectra were referenced to the residual proton resonance of chloroform-$d$ ($\delta$: 7.26), and the $^{13}$C NMR spectra of PPs were recorded at 110 °C and referenced to the resonance of 1,1,2,2-tetrachloroethane-$d_2$ ($\delta$: 74.47).

3. Results and Discussion

3.1. Molecular Structure of Complexes

The zirconium complexes were synthesized by a one-pot reaction of the corresponding ligand with 4 equivalent of methyl lithium and 1 equiv of ZrCl$_4$. $^1$H NMR spectrum of the methyl groups bonded to Zr and Si atoms in both zirconium complexes indicated that the complexes exhibited a $C_s$-symmetric nature in solution, respectively. The molecular structures of Zr(1) and Zr(2) were characterized by single crystal X-ray analysis. The structures are shown in Figure 2, and the selected bond lengths and angles of complexes are shown in Table 2. The lengths between the zirconium metal and five-member carbons of fluorenyl ligand in Zr(1) and Zr(2) are very close to those previously
reported for t-butyl amido complex (Zr(f)), in which the fluorenyl ligand was coordinated to the zirconium in a \( \eta^3 \) manner. We applied Tolman cone angles of the amino ligand (\( \theta \) value in Table 1) to evaluate the steric effect of the amido ligand [42]. The \( \theta \) values of Zr(1) and Zr(2) were 71.06 and 68.80°, respectively, which were close to that of the previously reported Zr(f) (70.12°). These results indicated that t-butyl and 1-admantyl groups possess a similar steric environment around the cationic zirconium metal, thus maintaining the hapticity of the fluorenyl ligand. We therefore can investigate the true electronic effect of the adamantyl substituent on the amido ligand with these fluorenylamido-ligated zirconium complexes for propylene polymerization.

![Structure of fluorenylamidotitanium complexes Zr(1) and Zr(2). Hydrogen atoms are omitted for clarity. Atoms are drawn at the 40% probability level.](image)

**Figure 2.** Structure of fluorenylamidotitanium complexes Zr(1) and Zr(2). Hydrogen atoms are omitted for clarity. Atoms are drawn at the 40% probability level.

| Parameters | Zr(1)     | Zr(2)     | Zr(f)     |
|------------|-----------|-----------|-----------|
| Zr(1)-C(1) | 2.3960(17)| 2.402(5)  | 2.385(3)  |
| Zr(1)-C(2) | 2.5443(17)| 2.535(5)  | 2.563(3)  |
| Zr(1)-C(3) | 2.4948(17)| 2.524(5)  | 2.486(3)  |
| Zr(1)-C(4) | 2.6871(17)| 2.664(4)  | 2.702(3)  |
| Zr(1)-C(5) | 2.6706(17)| 2.655(4)  | 2.667(3)  |
| Zr(1)-N(1) | 2.0536(15)| 2.061(4)  | 2.058(3)  |
| Zr(1)-Si(1)| 2.9867(6) | 3.005(16) | 2.981(3)  |

\( \theta = \frac{2}{3} (\theta_1 + \theta_2 + \theta_3) \) = 71.06°, 68.80° and 70.12°. These results indicated that t-butyl and 1-admantyl groups possess a similar steric environment around the cationic zirconium metal.

Table 2. Selected bond lengths (Å) and bond angles (degrees) for related complexes.

3.2. Propylene Polymerization

Propylene polymerizations were performed by Zr(1) and Zr(2) activated with trialkylaluminium-free dried MMAO (dMMAO) under atmospheric pressure of propylene in heptane at 0 and 20 °C, and the results are summarized in Table 3. For comparison, the same polymerization conditions as those previously reported for propylene polymerization using Zr(f) and Zr(g) were employed [32]. The complexes Zr(f) and Zr(g) conducted propylene polymerization at 20 °C, although they did not show any activity at 0 °C. On the other hand, Zr(1) and Zr(2) carried out propylene polymerization with moderate activity of \( \sim 1.2 \times 10^5 \) g-polymer mol\( ^{-1} \) h\(^{-1} \) to produce low molecular weight PP, even at 0 °C. The activities of Zr(1) and Zr(2) were higher than those of Zr(f) and Zr(g) at 20 °C. The results testified that the electronic effect of the adamantyl group on the amido ligand plays an important role in this catalyst system rather than having a steric effect, since Zr(1), Zr(2), and Zr(g) possess a similar steric environment around the amido ligand. The high
performance of Zr(1) and Zr(2) can be ascribed to the decreased electrophilicity of the zirconium cation caused by the electron-donating adamantyl group [43], which enhances the separation of the counter anion.

### Table 3. Results of propylene polymerization with zirconium complexes.

| Entry | cat. | Cocatalyst | Al/Zr | P (atm) | Temp (°C) | Time (min) | Yield (g) | Activity [g of PP/(mol of Ti h)] | $M_n$ [g/mol] | MWD | $T_m$ (°C) |
|-------|------|------------|-------|---------|-----------|------------|-----------|------------------|-------------|------|------------|
| 1     | Zr(1)| dMMAO     | 400   | 1       | 0         | 30         | 1.29      | 129             | 4.4         | 1.51 | 139        |
| 2     | Zr(2)| dMMAO     | 400   | 1       | 0         | 30         | 1.17      | 117             | 3.8         | 1.42 | 155        |
| 3     | Zr(1)| dMMAO     | 400   | 1       | 20        | 30         | 3.23      | 323             | 2.5         | 1.67 | 132        |
| 4     | Zr(2)| dMMAO     | 400   | 1       | 20        | 30         | 3.56      | 356             | 3.1         | 1.53 | 148        |
| 5     | Zr(1)| dMMAO     | 400   | 1       | 0         | 30         | 0         | 0                | -           | -    | -          |
| 6     | Zr(2)| dMMAO     | 400   | 1       | 0         | 30         | 0         | 0                | -           | -    | -          |
| 7     | Zr(1)| dMMAO     | 400   | 1       | 20        | 30         | 1.77      | 177             | 1.17        | 1.43 | 125        |
| 8     | Zr(2)| dMMAO     | 400   | 1       | 20        | 30         | 1.39      | 139             | 1.39        | 1.67 | 145        |
| 9     | Zr(1)| MMAO/BHT  | 400   | 1       | 0         | 30         | 2.12      | 212             | 5.2         | 1.55 | 139        |
| 10    | Zr(2)| MMAO/BHT  | 400   | 1       | 0         | 30         | 1.52      | 152             | 4.8         | 1.43 | 138        |
| 11    | Zr(1)| MMAO/BHT  | 400   | 1       | 0         | 30         | 0.99      | 99              | 4.1         | 1.5  | 138        |
| 12    | Zr(2)| MMAO/BHT  | 50    | 1       | 0         | 30         | 0.95      | 95              | 3.8         | 1.47 | 138        |
| 13    | Zr(1)| MMAO/BHT  | 400   | 8       | 0         | 8          | 1.2       | 900             | 7.4         | 1.81 | 142        |
| 14    | Zr(2)| MMAO/BHT  | 400   | 8       | 0         | 8          | 1.35      | 1012            | 2.8         | 2.32 | 159        |

* a Polymerization conditions: Heptane = 30 mL, Zr = 20 µmol, propylene = 1 atm; b Data taken from Reference [32]; c Zr = 10 µmol; d Activity in g of PP/(mol of Ti h); e Number-average molecular weight and molecular weight distribution determined by gel-permeation chromatography GPC using universal calibration; f Melting points determined by DSC.

The use of the modification of trialkylaluminum in MMAO with 2,6-di-tert-butyl-4-methyl phenol (BHT) as the cocatalyst [44,45] resulted in levels of activity approximately twice as high (up to $2.1 \times 10^5$ g-polymer mol-Zr$^{-1}$h$^{-1}$). The same phenomenon was also observed in propylene polymerization with fluorenylamido-ligated dimethyl titanium catalysts (Ti(e–f)), where the presence of iBu$_2$Al(OCH$_3$)$_2$/Bu$_2$Me derived from the reaction of iBu$_3$Al and BHT promoted the efficient separation of the active ion pair to improve the activity [33].

The high cost of single-site catalysts, owing to the requirement of a very high Al/metal ratio to achieve high activity, is a serious limitation for industrial applications. The effect of the Al/Zr ratio in these catalysts was thus investigated (entries 9–12). Although the activity decreased according to the decrease of the Al/Zr ratio from 400 to 100, complex Zr(1) still showed moderate activity of $1.0 \times 10^5$ g-polymer mol-Zr$^{-1}$h$^{-1}$ even with an Al/Zr ratio of 50 (entry 12), the value of which was comparable to those of Zr(1) and Zr(2) activated by dMMAO with Al/Ti = 400.

The increase of propylene pressure from 1.0 to 8.0 atm resulted in the increase of the activity by one order of magnitude (up to $\sim 1.0 \times 10^6$ g-polymer mol-Ti$^{-1}$h$^{-1}$, entries 13 and 14). We previously reported that the propagation rate of propylene polymerization with Ti(a–c)–dMMAO at 0 °C was increased linearly against the propylene pressure [46].

The melting temperatures of the PPs obtained are also shown in Table 2. All of the catalyst systems gave crystalline polymers with high $T_m$ values. The PP obtained with Zr(2) showed a higher $T_m$ value than that obtained with Zr(1) in the same polymerization conditions, and the $T_m$ value slightly increased with the increase of the propylene pressure in each catalyst system. A higher $T_m$ value should be ascribed to the higher syn-tacticity of PP.

The steric pentad distributions calculated by the $^{13}$C NMR spectra (Figures S5 and S6) of the methyl region of PPs are shown in Table 4. The results indicated that the PPs obtained were syndiotactic with high rrrr value, and the PP obtained by Zr(2) showed a higher rrrr value of 0.96. The syn-specific polymerization was conducted via an enantiomorphic site-controlled mechanism with a Cs$_3$-symmetric catalyst. In this system, two types of stereodefects are present: one is rmrr arising from the chain migration without monomer insertion, and the other is rmmr arising from the monomer mis-insertion [4]. Both rmrr and rmmr values were decreased in the following order: Zr(1) (0.026) > Zr(2) (0.003) and Zr(1) (0.021) > Zr(2) (0.007). These results indicated that the tert-butyl groups at the 3,6-position of the fluorenyl ligand effectively improve the chain migration and enantioselectivity of the propylene monomer. This result is in agreement with that of propylene polymerization with
Ti(b–c–dMMAO), where the 3,6-position was more effective than the 2,7-position in improving syn-specificity [30].

Table 4. Steric pentad distributions for samples in Table 3 (entries 13 and 14) a.

| Catalyst | Stereosequence Distribution a |
|----------|-------------------------------|
|          | mmmm | mmrr | rmmm + rmrr | rrmm | rrrr |
| Zr(1)    | 0.00  | 0.021| 0.026       | 0.021| 0.820|
| Zr(2)    | 0.00  | 0.007| 0.014       | 0.003| 0.958|

a Determined by 13C NMR spectroscopy.

4. Conclusions

The substituent effects of an electron-donating adamantyl group on the amido ligand of fluorenlylamido-ligated zirconium catalysts were investigated. Complexes Zr(1) and Zr(2) showed moderate activity of ~1.0 × 10^5 g-polymer mol-Zr^-1·h^-1 with a low Al/Ti ratio of 50. Complex Zr(2) containing 3,6-di-t-butyl fluorenly ligand and the increase of propylene pressure were effective for the improvement of polymerization activity (up to 1.0 × 10^6 g-polymer mol-Zr^-1·h^-1) and syn-specificity to produce a highly syn-tactic PP with an rrrr value of 0.96 and a melting point of 159 °C. These results are in good agreement with the substituent effects of the adamantyl group on the amido ligand of the fluorenlyamido-ligated titanium complex.

Supplementary Materials: The following are available online at www.mdpi.com/2073-4360/9/11/632/s1, Figure S1: 1H NMR spectrum of complex Zr(1), Figure S2: 13C NMR spectrum of complex Zr(1), Figure S3: 1H NMR spectrum of complex Zr(2), Figure S4: 13C NMR spectrum of complex Zr(2), Figure S5: 13C HMR spectrum of the methyl region of polypropylene obtained with Zr(1) (entry 13, Table 3), Figure S6: 13C HMR spectrum of the methyl region of polypropylene obtained with Zr(2) (entry 14, Table 3).

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Conflicts of Interest: The authors declare no conflict of interest.

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