

Article

Living Polymerization of Propylene with *ansa*-Dimethylsilylene(fluorenyl)(cumylamido) Titanium Complexes

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Abstract: A series of *ansa*-silylene(fluorenyl)(amido) titanium complexes (**1a–1c**, **2a**, and **2b**) bearing various substituents on the amido and fluorenyl ligands are synthesized and characterized by elemental analysis, ¹H NMR, and single crystal X-ray analysis. The coordination mode of the fluorenyl ligand to the titanium metal is η³ manner in each complex. The propylene polymerization is conducted with these complexes at 0 and 25 °C in a semi batch-type method, respectively. The catalytic activity of **1a–1c** bearing cumyl-amido ligand is much higher than that of **2a** and **2b** bearing naphthyl group in amido ligand. High molecular weight polypropylenes are obtained with narrow molecular weight distribution, suggesting a living nature of these catalytic systems at 0 °C. The polymers produced are statistically atactic, regardless of the structure of the complex and the polymerization temperature.

Keywords: constrained geometry catalysts; propylene; living polymerization; stereospecificity

1. Introduction

Half-sandwich group 4 metal complexes (usually named constrained geometry catalysts, CGC) having an *ansa*-monocyclopentadienylamido ligand (CpA) have captured significant attention due to their various copolymerization abilities and stereospecificity as olefin polymerization catalysts [1–4]. The replacement of the Cp ligand by the fluorenyl ligand was effective for the improvement of polymerization activity, copolymerization ability, syndiospecificity, and living polymerization nature to produce novel random and block copolymers with controlled microstructure [5–10]. The highly syndiospecific polymerization of α-olefin was also achieved with C_s-symmetric Ti or Zr complexes by the introduction of alkyl groups on the fluorenyl ligand [11–15]. Although C₁-symmetric metallocene catalysts normally give highly isospecific polypropylene (PP) [16,17], C₁-symmetric CGC catalysts exert a less positive influence on the isospecific polymerization of propylene. For example, Fink et al. showed that C₁-symmetric CpA complex by the use of naphthylamido ligand produces isospecific PP with isotactic triad (mm) of 0.63 [18]. Therefore, it is important to investigate strategies for understanding the relationship between the complex structure and the stereospecificity.

We have realized syndiospecific living homo- and copolymerization of α -olefins with norbornene using C_s -symmetric *ansa*-(fluorenyl)(amido)dimethyltitanium complexes with high activity [19–22]. We also synthesized C_1 -symmetric complex and the other compounds, and found that the change of the structure of amido ligand did not affect livingness of catalytic system; however, the highest mm value was 0.61 [23,24].

In this paper, we synthesized a series of new (fluorenyl)(amido) titanium complexes (**1** and **2** in Figure 1) and investigated the substitute effects of the bulkiness on the amido and fluorenyl ligands in propylene polymerization.

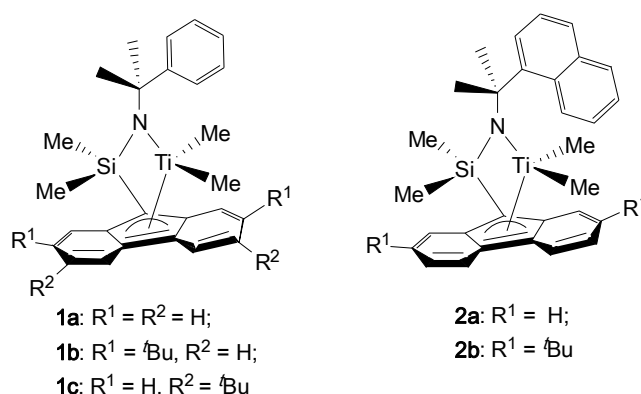


Figure 1. Chemical diagrams of the *ansa*-(fluorenyl)(amido) titanium complexes studied.

2. Experimental Section

2.1. Materials

All operations were performed under nitrogen gas using standard Schlenk techniques, and all solvents were purified by PS-MD-5 (Innovative Technology, Oldham, UK) solvent purification system. Research grade propylene was purified by passing it through a dehydration column of ZHD-20 (Zhonghuida, Dalian, China) and a deoxidation column of ZHD-20A (Zhonghuida, Dalian, China) before used. Modified methylaluminoxane (MMAO) was donated by Tosoh-Finechem Co. (Tokyo, Japan). The ligands and complexes were prepared according to the literature procedure [14,15,24]. We have previously reported the synthesis of complex **1a** [24]. In this work, we report the molecular structure and crystallographic data of complex **1a**.

2.2. Synthesis of Complexes

2.2.1. Synthesis of (2,7-di-*t*Bu)fluorenyl-cumylamido Titanium Complex (**1b**)

MeLi (1.6 M in ether, 15 mL, 24 mmol) was added dropwise at 0 °C into a solution of (2,7-di-*t*Bu)fluorenyl-cumylamido ligand (2.82 g, 6 mmol) in 60 mL of diethylether. The resultant orange solution was stirred at r.t. for 4 h, then was added to a solution of $TiCl_4$ (0.66 mL, 6 mmol) in 30 mL hexane at room temperature in the stirring condition for 2 h. The solvent was removed, and the residue was extracted with hexane (150 mL). The hexane solution was concentrated to 50 mL and cooled at -30 °C for some days to get **1b** as red crystals (0.92 g, 28%).

1H NMR ($CDCl_3$): 8.04(d, 2H, Flu), 7.63(s, 2H, Flu), 7.58(d, 2H, Flu), 7.41(d, 2H, Cph), 7.30(t, H, Cph), 7.22(d, 1H, Cph), 1.89(s, 6H, CCH₃), 1.39(s, 18H, Flu-*t*-Bu), 0.42(s, 6H, SiCH₃), -0.39 (s, 6H, TiCH₃). Anal. Calc. for $C_{34}H_{47}NSiTi$: C, 74.83; H, 8.68; N, 2.57. Found: C, 74.64; H, 8.85; N, 2.67.

2.2.2. Synthesis of (3,6-di-*t*Bu)fluorenyl-cumylamido Titanium Complex (**1c**)

Complex **1c** was synthesized in a similar way to that for **1b**, and yellow powders were obtained in 28% yield.

^1H NMR (CDCl_3): 8.07(s, 2H, Flu), 7.58(d, 2H, Flu), 7.46(d, 2H, Flu), 7.42(d, 2H, Cph), 7.30(t, 2H, Cph), 7.23(d, 1H, Cph), 1.88(s, 6H, CCH_3), 1.48(s, 18H, Flu-t-Bu), 0.35(s, 6H, SiCH_3), 0.38(s, 6H, TiCH_3). Anal. Calc. for $\text{C}_{34}\text{H}_{47}\text{NSiTi}$: C, 74.83; H, 8.68; N, 2.57. Found: C, 74.60; H, 8.84; N, 2.65.

2.2.3. Synthesis of Fluorenyl-(1-methyl-(1-naphthyl)ethyl)amido Titanium Complex (**2a**)

Complex **2a** was synthesized in a similar way to that for **1b**, and red crystals were obtained in 12% yield.

^1H NMR (CDCl_3): 8.58(d, 1H, Naph), 8.06(d, 2H, Flu), 7.87(d, 1H, Naph), 7.79(d, 1H, Naph), 7.63(d, 2H, Flu), 7.29–7.56(m, 4H, Naph; 4H, Flu), 2.15(s, 6H, CCH_3), 0.03(s, 6H, SiCH_3), -0.19 (s, 6H, TiCH_3). Anal. Calc. for $\text{C}_{30}\text{H}_{33}\text{NSiTi}$: C, 74.52; H, 6.88; N, 2.90. Found: C, 74.77; H, 7.02; N, 2.31.

2.2.4. Synthesis of (2,7-di-tBu)fluorenyl-(1-methyl-(1-naphthyl)ethyl)amido Titanium Complex (**2b**)

Complex **2b** was synthesized in a similar way to that for **1b**, and red crystals were obtained in 11% yield.

^1H NMR (CDCl_3): 8.70(d, 1H, Naph), 8.04(d, 2H, Flu), 7.86(d, 1H, Naph), 7.78(d, 1H, Naph), 7.58(t, 2H, Flu; 3H, Naph), 7.44(m, 2H, Flu), 7.30(t, 1H, Naph), 2.13(s, 6H, CCH_3), 1.39(s, 18H, Flu-t-Bu), 0.09(s, 6H, SiCH_3), -0.23 (s, 6H, TiCH_3). Anal. Calc. for $\text{C}_{38}\text{H}_{49}\text{NSiTi}$: C, 76.61; H, 8.29; N, 2.35. Found: C, 76.39; H, 8.38; N, 2.19.

2.3. Polymerization Procedure

Polymerization was performed in a 100 mL glass reactor equipped with a magnetic stirrer and carried out using semi-batch method. The reactor was charged with prescribed amounts of MMAO/2,6-di-*tert*-butyl-4-methyl phenol (BHT) and solvent (30 mL). After the solution of cocatalyst was saturated with gaseous propylene under atmospheric pressure, polymerization was started by the addition of 1 mL solution of the Ti complex (20 μmol) in reactor, and the consumption rate of propylene was monitored by a mass flow meter. Polymerization was conducted for a certain time and terminated with acidic methanol. The polymers obtained were adequately washed with methanol and dried under vacuum condition at 80 °C for 6 h to be a constant weight.

2.4. Analytical Procedure

Single crystal of complex was obtained from a solution of hexane at -30 °C. The single crystals were mounted under nitrogen atmosphere at low temperature, and data collection was made on a Bruker APEX2 diffractometer using graphite monochromated with Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). The SMART program package was used to determine the unit cell parameters. The absorption correction was applied using SADABS program [25]. 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 [26–32]. Crystallographic data are summarized in Table 1, and CIF files and check are provided in the Supporting Information.

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 mm \times 300 mm columns at 150 °C using 1,2,4-trichlorobenzene as solvent and calibrated by polystyrene standards. The ^1H NMR spectra of complexes and ^{13}C NMR spectra of PPs were measured on a Bruker AsendTM 600 spectrometer (Bruker, Karlsruhe, Germany). Differential scanning calorimeter (DSC) analyses were performed on 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.

Table 1. Crystallographic data and parameters for **1a**, **1b**, **2a**, and **2b**.

Complex	1a	1b	2a	2b
deposition numbers	CCDC 1539490	CCDC 1539499	CCDC 1540563	CCDC 1539502
formula	C ₂₆ H ₃₁ NSiTi	C ₃₄ H ₄₇ NSiTi	C ₃₀ H ₃₃ NSiTi	C ₃₈ H ₄₉ NSiTi
formula weight	433.51	545.71	483.56	595.77
crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
space group	<i>P</i> 1 2 ₁ / <i>c</i> 1	<i>P</i> $\bar{1}$	<i>P</i> 1 2 ₁ / <i>c</i> 1	<i>P</i> $\bar{1}$
<i>a</i> (Å)	8.8160(15)	10.0609(13)	12.742(3)	10.3445(13)
<i>b</i> (Å)	27.430(5)	11.5953(15)	17.562(4)	11.8424(16)
<i>c</i> (Å)	9.9361(18)	15.4910(3)	11.404(2)	15.4920(3)
β (deg)	108.372(4)	100.124(3)	95.269(4)	99.822(4)
<i>V</i> (Å ³)	2280.3(7)	1561.1(4)	2541.1(9)	1636.8(4)
<i>Z</i>	4	2	4	2
<i>F</i> (000)	920	588	1024	640
<i>D</i> _{calcd.} (g·cm ⁻³)	1263	1161	1264	1209
μ (mm ⁻¹)	0.440	0.334	0.402	0.325
theta range for data collection	2.284° to 30.611°	2.002° to 30.542°	1.980° to 30.772°	1.965° to 25.499°
reflections collected	23,087	15,856	25,451	11,599
independent reflections	7002	9413	7920	6105
final R indices [<i>I</i> > 2 δ (<i>I</i>)]	[R(int) = 0.1147] R1 = 0.0512, wR2 = 0.0963	[R(int) = 0.0235] R1 = 0.0398, wR2 = 0.0940	[R(int) = 0.0610] R1 = 0.0455, wR2 = 0.1040	[R(int) = 0.0569] R1 = 0.0508, wR2 = 0.1051

3. Results and Discussion

3.1. Molecular Structure of Complexes

The complexes were synthesized in good yield using one-pot reaction of the corresponding ligand with a two-fold excess of MeLi and TiCl₄ in hexane. The molecular structure of complexes determined by single crystal X-ray analysis are shown in Figure 2, and the selected bond lengths and angles of complexes are shown in Table 2. The bond lengths between the titanium and the fluorenyl carbons (C(1), C(2), C(3), C(4), and C(5)) are almost the same as that of previously reported C_s-symmetric (fluorenyl)(amido) titanium complexes [24], which suggests that the fluorenyl ligand is coordinating to the titanium metal with η^3 -form, irrespective of the substituent structure.

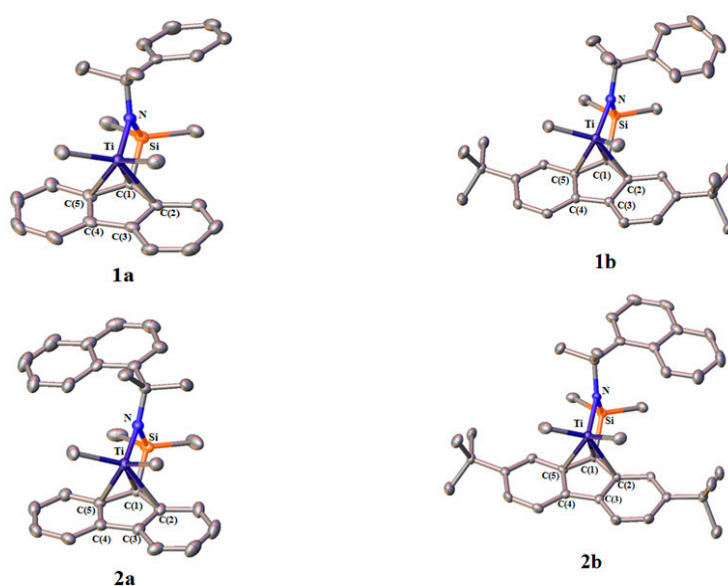


Figure 2. Structure of fluorenylamidotitanium complexes **1a**, **1b**, **2a**, and **2b**. Hydrogen atoms are omitted for clarity. Atoms are drawn at the 40% probability level.

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

Parameter	1a	1b	2a	2b
Ti(1)–C(1)	2.241(2)	2.250(14)	2.260(19)	2.267(3)
Ti(1)–C(2)	2.409(3)	2.384(14)	2.414(19)	2.413(3)
Ti(1)–C(3)	2.586(3)	2.599(14)	2.556	2.576(3)
Ti(1)–C(4)	2.594(3)	2.615(15)	2.538	2.569(3)
Ti(1)–C(5)	2.398(2)	2.430(15)	2.396(19)	2.394(3)
Ti(1)–N(1)	1.919(2)	1.922(12)	1.922(17)	1.920(2)
Ti(1)–Si(1)	2.836(9)	2.828(6)	2.850	2.848(11)
N(1)–Ti(1)–C(1)	78.35(9)	78.56(5)	78.01(7)	77.74(11)
Ti(1)–N(1)–Si(1)	100.88(10)	100.40(6)	101.30(8)	101.76(12)
N(1)–Si(1)–C(1)	93.66(10)	94.20(6)	93.75(8)	93.88(13)

In each complex, no symmetry plane or axis was observed, indicating the C_1 -symmetric nature in solid state. On the other hand, the ^1H NMR spectra of all the complexes showed that the methyl groups bonded to the Si and Ti atoms are equivalent, which can be explained by the fast rotation of the amido ligand on the NMR time-scale at room temperature.

3.2. Propylene Polymerization

Propylene polymerizations were conducted with **1a–1c**, **2a**, and **2b** activated by MMAO in a semi batch-type operation under an atmospheric pressure of propylene in toluene at 0 and 25 °C (Table 3). Cumyl-amido complexes **1a–1c** showed much higher activity (1900–2500 kg PP/(mol Ti·h)) than naphthyl-amido complexes **2a** and **2b** (20–120 kg PP/(mol Ti·h)), of which value increased according to the increase of polymerization temperature and was independent of the introduction of *t*-butyl group on the fluorenyl ligand. Significantly lower activity in **2a** and **2b** can be attributed to the steric hindrance of the amido group, where the steric hindrance of naphthyl group ($102^\circ/103^\circ$) is bigger than the cumyl group ($86^\circ/90^\circ$) as estimated by Tolman cone angle (Table 4) [33].

Table 3. Propylene polymerization with Ti complexes **1a–2b** activated by MMAO ^a.

Entry	Cat.	Temp. (°C)	Time (min)	Yield (g)	Activity ^b	M_n ^c ($\times 10^4$)	M_w/M_n ^c	N ^d (μmol)
1	1a	0	5	3.21	1930	25.2	1.49	13
2	1b	0	5	3.46	2080	23.9	1.37	14
3	1c	0	5	3.59	2150	26.1	1.58	14
4	1a	25	5	4.05	2430	16.8	2.05	24
5	1b	25	5	4.06	2430	19.4	1.70	21
6	1c	25	5	4.21	2530	16.6	1.93	25
7	2a	0	12	0.271	69	5.18	1.18	5.2
8	2b	0	12	0.084	21	1.73	1.16	4.9
9	2a	25	12	0.474	119	4.81	1.43	9.9
10	2b	25	12	0.362	91	4.38	1.27	8.3

^a Polymerization conditions: toluene = 30 mL, Ti = 20 μmol , Al/Ti = 600, propylene = 1 atm; ^b Activity in kg of PP/(mol of Ti·h); ^c Number-average molecular weight and molecular weight distribution determined by gel-permeation chromatography (GPC) using universal calibration; ^d Calculated from yield and M_n .

Table 4. Tolman's cone angle of amido groups of complexes **1a**, **1b**, **2a**, and **2b**.

Catalyst	Fluorenyl	N-alkyl	θ (°)
1a	Flu	Ph	86
1b	2,7-di- <i>t</i> Bu-Flu	Ph	90
2a	Flu	Naphthyl	103
2b	2,7-di- <i>t</i> Bu-Flu	Naphthyl	102

1a–1c gave high molecular weight PP ($M_n > 230,000$) for 5 min at 0 °C with narrow molecular weight distribution, and the number of polymer chains (N) were about 65–70% of the titanium

complex used. These results suggest that the propylene polymerization proceeded in a living manner. The molecular weights of PPs were decreased by raising the polymerization temperature, with broader molecular weight distribution accompanied by the increase of *N* value, indicating that the chain transfer reaction frequently occurred by the improvement of polymerization temperature. The molecular weights of PPs obtained by **2a** and **2b** were lower, but the molecular weight distributions were extremely narrow. The *N* values were about 25% of the titanium used, which indicates poor catalytic efficiency by the introduction of the bulky naphthyl group.

All the PPs obtained were amorphous measured by the DSC analysis. To investigate the substituent effect of the amido group on the stereospecificity, we conducted ¹³C NMR analysis of PPs obtained. The steric pentad distributions are summarized in Table 5. All the polymers obtained in each catalyst system were statistically atactic. The result indicates that the introduction of sterically demanded *N*-alkyl and *t*-butyl groups on the amido and the fluorenyl ligand, respectively, had little influence on the stereospecificity.

Table 5. Steric pentad distributions for samples in Table 3 (entries 4–6 and 10).

Entry	Stereosequence distribution ^a								
	mmmm	mmmr	rmmr	mmrr	mmrm + rmrr	rmm	rrrr	mrrr	mrrm
4	0.04	0.05	0.06	0.22	0.22	0.13	0.09	0.14	0.05
5	0.02	0.03	0.04	0.18	0.22	0.11	0.15	0.19	0.06
6	0.03	0.05	0.03	0.13	0.20	0.14	0.16	0.21	0.05
10	0.12	0.10	0.08	0.29	0.16	0.05	0.03	0.08	0.09

^a Determined by ¹³C NMR spectroscopy.

4. Conclusions

(Fluorenyl)(amido) titanium complexes **1a–1c**, **2a**, and **2b** were synthesized and characterized by ¹H NMR, elemental analysis, and single crystal X-ray analysis. All synthetic catalysts are C_s-symmetric in solution, irrespective of the bulkiness of the amido ligand. The cumyl-amido complexes **1a–1c** showed much higher activity than the naphthyl-amido complexes **2a** and **2b** because of the steric hindrance of the amido group. The modification of the structure did not change the livingness of the catalytic system, whereas the change of ligand structure was not efficient for the isospecificity of CGC catalyst.

Supplementary Materials: The following are available online at www.mdpi.com/2073-4360/9/4/131/s1.

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

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