

Stereospecific polymerization of propylene with group 4 *ansa*-fluorenylamidodimethyl complexes

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Abstract

Group 4 [η^1 : η^3 -*tert*-butyl(dimethylfluorenylsilyl)amido]dimethyl complexes [*t*-BuNSiMe₂Flu]MMe₂ (M = Ti, **1**; Zr, **2**; Hf, **3**) were synthesized in a one-pot synthesis starting from the ligand, MeLi and MCl₄ (M = Ti, Zr, Hf), respectively. The structures of these complexes were determined by X-ray crystallography and the results obtained revealed that the fluorenyl ligand coordinates to center metal in a η^3 -manner irrespective of center metal employed. Propylene polymerization was conducted at 0 or 20 °C in toluene by **1–3** combined with dried methylaluminoxane (MAO), which was prepared from the toluene solutions of MAO by removing free trialkylaluminiums, and HNMe₂PhB(C₆F₅)₄ in the presence of triisobutylaluminium. The **1**-dried MAO system gave the polymer with syndiotactic triad (rr) of 63% at 0 °C, whereas **2** and **3** did not give any polymer in the same conditions. The **2**-dried MAO system gave the polymer with the highest syndiotacticity (rr = 97%) at 20 °C, although the activity was low. The **3**-dried MAO system did not give any polymer even at 20 °C. When HNMe₂PhB(C₆F₅)₄ was used in place of dried MAO at 20 °C, **1** gave almost atactic polymer, while **2** and **3** gave highly syndiotactic one (rr > 90%). These results indicate that the catalytic performance strongly depended on the center metal of the *ansa*-fluorenylamidodimethyl complexes as well as cocatalysts employed.

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1. Introduction

Since the discovery of metallocene catalysts, a great number of organometallic compounds have been applied for olefin polymerization as so-called single-site catalysts from both the academic and the industrial points of view [1]. During the first half of the 1990's, Bercaw [2], Okuda [3], the researchers of Dow [4] and Exxon [5] reported a new type of half metallocene complexes which contain the N-based ligand attached to the cyclopentadiene derivatives, named *ansa*-monocyclopentadienylamido (CpA) complex [1c,6]. The CpA complexes have been found to

be highly efficient catalysts for synthesis of linear low-density polyethylene and copolymerization of ethylene and styrene [4,5,7]. Several researchers reported the synthesis of a series of group 4 CpA complexes and the influence of the ligand in CpA complexes on the stereospecificity and the regiospecificity of propylene polymerization [8]. Okuda et al. [9] prepared *tert*-butylamidofluorenylzirconium complexes for potentially syndiospecific catalyst. We have found that [*t*-BuNSiMe₂Flu]TiMe₂ (**1**) activated with methylaluminoxane (MAO), B(C₆F₅)₃ or Ph₃CB(C₆F₅)₄ promoted the polymerization of propylene at 40 °C in syndiospecific and highly regiospecific manner [10]. Razavi et al. and Busico et al. reported the introduction of *tert*-butyl group on the fluorenyl ligand ([*t*-BuNSiMe₂(2,7-di-*t*-Bu-Flu)]TiCl₂, [*t*-BuNSiMe₂(3,6-di-*t*-Bu-Flu)]TiCl₂) increased the syndiospecificity and activity [11].

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Shiomura et al. [12] reported that the activation of [*t*-BuNSiMe₂Flu]ZrCl₂ with MAO-ⁱBu₃Al gave syndiotactic polypropylene (PP) ([rrrr] = 77%), whereas the activation with Ph₃CB(C₆F₅)₄-ⁱBu₃Al gave isotactic PP ([mmmm] = 95%). Recently, Fujita et al. [13] reported that the nature of the center metal had a significant effect on catalytic performance and the microstructures of produced PPs using group 4 bis(phenoxy-imine) complex-based catalysts. These results indicate that stereoregularity of PPs obtained should be controlled by the kinds of counter anion and the kinds of center metal.

We have previously reported that **1** activated with B(C₆F₅)₃ produced syndiotactic-enriched PP at -50 °C in a living manner [14a] and the replacement of B(C₆F₅)₃ with trialkylaluminum(Me₃Al, ⁱBu₃Al)-free MAO, named dried MAO and dried modified MAO (MMAO), raised the living polymerization temperature up to 0 °C accompanied by the improvement of syndiospecificity [14b,14c]. These results suggest that stereospecificity and propylene polymerization behavior in the complex **1**-based catalysts strongly depend on the cocatalyst and polymerization conditions employed.

In this paper, we synthesized a series of group 4 *ansa*-fluorenylamidodimethyl complexes by applying the synthetic method reported by Resconi et al. [15] and investigated the effects of center metal and cocatalyst on the catalytic performance of propylene polymerization.

2. Experimental part

2.1. Materials

Dimethylaniliniumtetrakis(pentafluorophenyl)borate (HNMe₂PhB(C₆F₅)₄) and toluene solution of MAO were donated from Tosoh-Finechem Co. Ltd. Dried MAO was prepared from the toluene solution of MAO by vacuum drying followed by washing with hexane as reported previously [14b]. Research grade propylene (Takachiho Chemicals Co.) was purified by passing it through columns of NaOH, P₂O₅, and molecular sieves 3A, followed by bubbling it through a NaAlH₂Et₂/1,2,3,4-tetrahydronaphthalene solution. All solvents were commercially obtained and dried with standard methods.

2.2. Synthesis of *t*-BuNHSiMe₂Flu (Flu = C₁₃H₉) ligand

All the syntheses were carried out under N₂ by standard Schlenk techniques. The *t*-BuNHSiMe₂Flu ligand was prepared according to the literature (Scheme 1) [9,16]. To a solution of fluorene (24 g, 144 mmol) in Et₂O (300 mL) was added *n*-butyl lithium (96 mL, 1.50 M solution in hexane, 144 mmol) at 0 °C within 1 h. After stirring for 3 h at room temperature, the solvent was removed in vacuo to give Li[Flu]. To a solution of excess dichlorodimethylsilane (40 mL) was added the suspension of Li[Flu] in hexane (250 mL) at -78 °C. The resultant suspension was stirred

for 8 h at room temperature, and the solvent and the remained dichlorodimethylsilane were removed in vacuo. After the addition of hexane (150 mL), lithium chloride was precipitated and the solution was decanted, followed by removal of the solvent, 34.2 g (132 mmol) of 9-(chlorodimethylsilyl)fluorene was obtained as off-white solid.

To a solution of 9-(chlorodimethylsilyl)fluorene 34.2 g (132 mmol) in THF (200 mL) was added *t*-butylamine (20 mL, 264 mmol) at 0 °C. Stirring overnight at room temperature gave a yellow-orange suspension. Lithium chloride was precipitated and the solution was decanted. Removal of the solvent gave *t*-BuNHSiMe₂Flu as yellow oil (28.5 g, 96.5 mmol, 67% yield). ¹H NMR (C₆D₆, ref. C₆H₆; 7.15 ppm): δ = 7.79 (d, 2H, C₁₃H₉), 7.61 (d, 2H, C₁₃H₉), 7.29 (dd, 4H, C₁₃H₉), 3.76 (s, 1H, C₁₃H₉), 1.02 (s, 9H, C(CH₃)₃), 0.42 (s, 1H, NH), -0.09 (s, 6H, Si(CH₃)₂).

2.3. Synthesis of [*t*-BuNSiMe₂Flu]TiMe₂ (**1**)

To a solution of *t*-BuNHSiMe₂Flu (1.56 g, 5.28 mmol) in Et₂O (50 mL) was slowly added excess MeLi (24.0 mL of a 1.20 M solution in Et₂O, 28.2 mmol) at room temperature and the mixture was stirred for 5 h. To TiCl₄ (0.58 mL, 5.29 mmol) diluted with 50 mL of pentane was added a solution of the dilithium salt in Et₂O at room temperature. The resulting dark brown suspension was stirred overnight at room temperature. After the solvent was removed, the residue was extracted with hexane (120 mL) and the hexane solution was decanted. To the hexane solution was added MeMgBr (3.0 mL of a 3.0 M solution in Et₂O), and the resulting mixture was stirred for 5 h at room temperature. After the solvent was removed, the residue was extracted with hexane (80 mL). The hexane solution was concentrated and cooled overnight at -30 °C to give **1** (route I in Scheme 1) as yellow-orange microcrystals (0.840 g, 2.26 mmol, 42.8%). ¹H NMR (C₆D₆): δ = 7.82 (dd, 2H, C₁₃H₈), 7.67 (dd, 2H, C₁₃H₈), 7.22 (ddd, 2H, C₁₃H₈), 7.09 (ddd, 2H, C₁₃H₈), 1.37 (s, 9H, C(CH₃)₃), 0.67 (s, 6H, SiCH₃), -0.02 (s, 6H, TiCH₃). ¹³C NMR (C₆D₆): δ = 135.0, 129.2, 127.8, 127.7, 124.8, 123.7 (C₁₃H₈), 58.6 (C(CH₃)₃), 56.7 (Ti(CH₃)₂), 34.3 (C(CH₃)₃), 5.7 (Si(CH₃)₂). Anal. Calc. for C₂₁H₂₉NSiTi: C, 67.91; H, 7.87; N, 3.77. Found: C, 68.03; H, 7.87; N, 3.89.

2.4. Synthesis of [*t*-BuNSiMe₂Flu]ZrMe₂ (**2**)

The same procedure for the preparation of **1** was applied except ZrCl₄ was used in the final step. The hexane solution was concentrated and cooled overnight at -30 °C to give **2** as yellow microcrystals (yield, 42.4%). ¹H NMR (C₆D₆): δ = 7.77–7.80 (m, 4H, C₁₃H₈), 7.13–7.16 (m, 4H, C₁₃H₈), 1.29 (s, 9H, C(CH₃)₃), 0.74 (s, 6H, SiCH₃), -0.58 (s, 6H, ZrCH₃). ¹³C NMR (C₆D₆): δ = 136.2, 128.7, 125.7, 124.2, 123.8 (C₁₃H₈), 55.6 (C(CH₃)₃), 41.4 (Zr(CH₃)₂), 34.9 (C(CH₃)₃), 7.0 (Si(CH₃)₂). EI-MS: *m/z* = 413 (M⁺).

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