Unprecedentedly High Activity and/or High Regio-/Stereo selectivity of Fluorenyl-Based CGC Allyl-Type \( \eta^3: \eta^1 \)-tert-Butyl(dimethylfluorenylsilyl)amido Ligated Rare Earth Metal Monoalkyl Complexes in Olefin Polymerization

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Abstract: A series of fluorenyl-based constrained-geometry-configuration (CGC) allyl-type rare earth metal monoalkyl complexes bearing the divalent anionic \( \eta^3: \eta^1 \)-FluSiMe\(_2\)N\(_t\)Bu ligand (\( \eta^3: \eta^1 \)-FluSiMe\(_2\)N\(_t\)Bu)Ln(CH\(_2\)SiMe\(_3\))(THF)\(_2\) (1–3) have been synthesized via the alkane elimination reaction between the FluHSiMe\(_2\)NH\(_t\)Bu ligand and rare earth metal tri(trimethylsilylmethyl) complexes Ln(CH\(_2\)SiMe\(_3\))\(_3\)(THF)\(_n\). Their structures are characterized by means of NMR spectrum, elemental analyses, and X-ray diffraction. These complexes 1–3 are isostructural and isomorphous, and each of them adopts a distorted-trigonal-bipyramidal configuration containing one \( \eta^3: \eta^1 \)-FluSiMe\(_2\)N\(_t\)Bu ligand, one CH\(_2\)SiMe\(_3\) ligand, and two THF molecules. Unlike traditional CGC allyl-type rare earth metal complexes showing no or low activity and regio-/stereoselectivity in styrene or MMA polymerization, these complexes 1–3 exhibit high catalytic activities and/or high regio-/stereoselectivities in the cis-1,4-polymerization of isoprene and myrcene or in the syndiotactic polymerization of styrene under the aid of different activators (borate or borane) and AlR\(_3\). The in situ \(^1\)H NMR spectra suggest that the exchanges of chelating ligands such as alkyl groups and divalent anionic \( \eta^3: \eta^1 \)-FluSiMe\(_2\)N\(_t\)Bu ligands between rare earth metal centers and Al centers result in the formation of a heterobimetallic tetraalkylaluminate complex R\(_2\)Al(\( \mu \)-R)\(_2\)Ln(\( \mu \)-R)\(_2\)AlR\(_2\), which is activated by activators to form a divalent cationic species [Ln(\( \mu \)-R)\(_2\)AlR\(_2\)]\(^2+\) as a catalytically active species in the coordination-insertion polymerization of olefins.

Keywords: fluorenyl-based CGC allyl-type rare earth metal catalyst; \( \eta^3: \eta^1 \)-tert-butyl(dimethylfluorenylsilyl) amido ligand; coordination-insertion polymerization; olefins; regio-/stereoselectivity; active species

1. Introduction

The development of highly efficient and highly regio-/stereoselective rare earth metal catalysts has become a hot topic in the coordination-insertion polymerization of olefin over the past two
decades, which brings new opportunities for the synthesis of high-performance (co)polymers unavailable from transition metal catalysts [1–11]. So far, a large number of the metallocene [12–15], constrained-geometry-configuration (CGC) [16–19], half-sandwich [20–23], and non-metallocene rare earth metal catalysts precursors bearing different chelating ligands [24–26] have emerged for the polymerization of olefins. Among them, the metallocene or nonmetallocene rare earth metal catalysts usually show high activities and different regio-/stereoselectivities in the polymerization of conjugated dienes. The half-sandwich or CGC type rare earth metal catalysts exhibit unprecedentedly high activities and high syndiotactic or isotactic selectivities in the polymerization of styrene. Despite these results, the CGC allyl-type rare earth metal catalysts containing an \( \eta^2 \)-allyl bonding mode of cyclopentadiene (Cp), indenyl (Ind), or fluorenyl (Flu) moiety are rare [27–29], and all of them show no or low activities and regio-/stereoselectivities in olefin polymerization (Chart 1). In 2003, Carpentier et al. reported the synthesis of the amido-functionalized Flu-based CGC allyl-type yttrium monoaalkyl complexes \( \langle \eta^3 \cdot \eta^1-(3,6 \text{-} \text{Bu}_2 \text{Flu}) \text{SiR}_2 \text{N} \text{Bu} \rangle \text{Y}(\text{CH}_2 \text{SiMe}_3)(\text{THF})_2 \). However, such complexes showed no activities in the ethylene polymerization in a larger range of temperature or very low activities and tacticities in the polymerization of MMA [27]. In 2012, Cui et al. synthesized the phosphazene-functionalized Cp-based CGC allyl-type rare earth metal dialkyl complexes \( \langle \eta^3 \cdot \eta^1-(C_5 \text{Me}_5) \text{PPh}_2 \text{N}(2,6 \text{-} \text{Pr}_2 \text{C}_6 \text{H}_3) \rangle \text{Y}(\text{CH}_2 \text{SiMe}_3)_2(\text{THF}) \), which were inert even in ethylene polymerization [28]. Subsequently, the pyridyl-functionalized Flu-based CGC allyl-type rare earth metal dialkyl complexes \( \langle \eta^3 \cdot \eta^1-\text{FluC}_5 \text{H}_4 \text{N} \rangle \text{Ln}(\text{CH}_2 \text{SiMe}_3)_2 \text{THF} \) and \( \langle \eta^3 \cdot \eta^1-\text{FluC}_5 \text{H}_4 \text{N} \rangle \text{Y}(\text{CH}_2 \text{C}_6 \text{H}_4 \text{o-NMe}_2)_2 \) also developed by Cui and co-workers could promote the polymerization of styrene (ST) but with low activities and moderate syndiotacticities [29]. Therefore, it is of great interest to develop highly efficient and highly regio-/stereoselective CGC allyl-type rare earth metal catalysts and explore their catalytic performances in the polymerization of olefins.

**Chart 1.** The known constrained-geometry-configuration (CGC) allyl-type rare earth metal catalysts.

Recently, we have paid much attention to the synthesis of the half-sandwich Flu-ligated rare earth metal dialkyl complexes Flu/Ln(\( \text{CH}_2 \text{SiMe}_3 \))_2(\text{THF})_n and their applications in the coordination–insertion (co)polymerization of olefins such as ST or conjugated dienes. In 2013, these complexes displayed high activities up to \( 3.4 \times 10^7 \) (g of polymer)/(molLn \( \cdot \) h) and syndiotacticities up to >99% in ST polymerization when activated by an activator with or without a small amount of Al\( \text{t} \text{Bu}_3 \) [30]. Moreover, such complexes also showed very high activities up to \( 1.9 \times 10^7 \) (g of polymer)/(mol\( \cdot \) h) and high cis-1,4-selectivities, 93% in the polymerization of isoprene (IP) in the presence of activator and AlR\( \text{t} \text{Bu}_3 \) [31]. In addition, such catalysts were also active in the regioselective polymerization of 1,3-cyclohexadiene and copolymerization with ST and IP [32]. These results demonstrate that the effective adjustment of the skeleton of the Flu ligand of these complexes has an important impact on their catalytical performance in the olefin polymerization, which arouses our interests to explore more Flu-based rare earth metal complexes and detect their catalytic performance in olefin polymerization. Herein, we report the synthesis and structural characterization of three Flu-based CGC allyl-type rare earth metal monoalkyl complexes (\( \eta^3 \cdot \eta^1-\text{FluSiMe}_2 \text{N} \text{Bu} \))\( \text{Ln}(\text{CH}_2 \text{SiMe}_3)(\text{THF})_2 \).
3: Ln = Y) via the alkane elimination reaction between the tert-butyl(dimethylfluorenylsilyl)amido (FluHSiMe₂NH₃Bu) ligand and the rare earth metal trialkyl complexes Ln(CH₂SiMe₃)₃(THF)ₙ. Activated by different cocatalysts, these complexes 1–3 unprecedentedly exhibit high activities and high regio-/stereoselectivities in the polymerization of IP, myrcene (MY), or ST, affording the cis-1,4-poly(conjugated diene)s or syndiotactic polystyrenes with high molecular weights and moderate molecular weight distributions. The possible coordination–insertion polymerization mechanism is investigated by means of the in situ 1H NMR spectrum.

2. Materials and Methods

2.1. Materials

All manipulations that were sensitive to air or moisture were performed in a MBraun glovebox (Munich, Germany). Activator borate and borane were bought from Tosoh Finechem Corporation (Tokyo, Japan). LiCH₂SiMe₃ (1.0 M solution in pentane) and LnCl₃ (Ln = Sc, Y, Lu; 99.9% analytically pure) were bought from Aldrich (St. Louis, MO, USA). AlBu₃ (1.0 M solution in hexane), AlMe₃ (1.0 M solution in toluene), AlEt₃ (1.0 M solution in heptane), fluorine (99% analytically pure), tert-butylamine (98% analytically pure), triethylamine (analytically pure), dichlorodimethylsilane (98% analytically pure), n-BuLi (2.4 M in hexane), Na₂SO₄ (analytically pure), CaH₂ (98% analytically pure), dichloromethane (analytically pure), petroleum ether (analytically pure), and methanol (analytically pure) were obtained from Energy Chemistry (Beijing, China). The FluH(SiMe₂NH₃) ligand was prepared according to the literature (Supplementary Materials) [33]. IP, MY and ST (analytically pure) were purchased from Aldrich and TCI (Tokyo, Japan). Toluene (Tol), THF, and hexane were purified by a solvent purification system (SPS-800, Mbraun, Garching, Germany), and dried over Na in the glovebox. Chlorobenzene (PhCl), ortho-dichlorobenzene (PhCl₂), and 1,1,2,2-tetrachloroethane (C₂H₂Cl₄) were dried over CaH₂ under stirring for 48 h and distilled under reduced pressure before use. The deuterated solvents C₆D₆ (99.6 atom% D), C₇D₈ (99.5 atom% D), and CDCl₃ (99.8 atom% D) were purchased from Cambridge Isotope (Tewksbury, MA, USA).

2.2. Method

By using J. Young valve NMR tubes, the samples of rare earth metal catalysts were prepared for NMR spectroscopic measurements in the glove box. 1H, 13C NMR spectra of ligand and catalysts were tested on a Bruker AVANCE 400 spectrometer in C₆D₆ or C₇D₈ at room temperature. 1H, 13C NMR spectra of polyisoprene (PIP), polymyrcene (PMY) and polystyrene (PST) samples were recorded on a Bruker AVANCE 400 spectrometer in CDCl₃ at room temperature or at 60 °C. The molecular weights and the molecular weight distributions (PDI) of the poly(conjugated dienes) were performed at 25 °C by gel permeation chromatography (GPC) on a WATERS 1515 apparatus. THF was selected as the eluent at a flow rate of 1 mL/min. For SPSTs, GPC data were performed in 1,2,4-trichlorobenzene at 150 °C using IR detection and calibration against polystyrene. Differential scanning calorimetry (DSC) measurements were carried out on a TA 60 (TA Co.) at a rate of 10 °C/min. Any thermal history difference in the poly(conjugated diene)s was eliminated by first heating the specimen to 100 °C, cooling at 10 °C/min to −100 °C, and then recording the second DSC scan. For SPSTs, DSC parameter was set to 10 °C/min to speed up to 300 °C, then cooled at 10 °C/min to room temperature, before recording the second DSC scan. Elemental analyses were performed on an Elementary Vario MICRO CUBE (Germany).

2.3. X-ray Crystallographic Analysis

The crystals of complexes 1–3 were oil sealed under a microscope in the glove box. For data collection at −100 °C, a CCD area detector using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) was chosen on a Bruker Smart-Apex CCD diffractometer. The SMART program package was used to determine the crystal class and unit cell parameters. SAINT and SADABS were...
adopted to process the original frame data and generated the reflection data file. Shelxtl-97 program was applied to solve the structure. F2 anisotropic non-hydrogen atoms were refined by using the full matrix least square method. All the non-hydrogen atoms were anisotropy refined, and all hydrogen atoms were introduced in the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-1904924 (1), CCDC-1904923 (2), and CCDC-1904925 (3) containing the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif from The Cambridge Crystallographic Data Centre.

2.4. Synthesis of (η^3;η^1-FluSiMe_{2}N^6Bu)Ln(CH_{2}SiMe_{3})(THF)_2 1–3

To a colorless hexane solution (15.0 mL) of Ln(CH_{2}SiMe_{3})_{2}(THF)_2 1–3 (1: Ln = Sc; 2: Ln = Lu; 3: Ln = Y, 84%). yield was added a solution of the FluHSiMe_{2}N^6Bu ligand (1.0 mmol) in hexane (15.0 mL) at room temperature. The mixture was stirred at room temperature for 2–3 h. After removal of all volatiles in vacuo, the residue was recrystallized from toluene/hexane at −30 °C to give Flu-based CGC allyl type rare earth metal monoalkyl complexes [η^3;η^1-FluSiMe_{2}N^6Bu]Ln(CH_{2}SiMe_{3})(THF)_2 1–3 (1: Ln = Sc, 63%; 2: Ln = Lu, 67%; 3: Ln = Y, 84%).

1H NMR of complex 1 (400 MHz, Tol-d8): δ 8.10 (d, J = 7.8 Hz, 2H, Flu), 8.02 (d, J = 8.0 Hz, 2H, Flu), 7.41 (t, J = 7.3 Hz, 2H, Flu), 7.12 (d, J = 7.4 Hz, 2H, Flu), 3.00 (br, 8H, THF-). 13C NMR of complex 1 (100 MHz, C6D6): δ 142.83, 131.10, 125.80, 120.91, 117.65, 116.96, 84.13 (C1), 69.92 (α-THF), 54.47 (NC(CH_{3})_{3}), 36.51 (NC(CH_{3})_{3}), 30.59 (d, J = 45.4 Hz, ScC_{2}H_{5}Si(CH_{3})_{3}), 25.02 (β-THF), 5.94 (Si(CH_{3})_{2}), 4.62 (CH_{2}Si(CH_{3})_{3}). Anal. Calcd (%) for C_{3}H_{50}NO_{2}ScSi_{2}: C, 65.45; H, 8.68; N, 2.46. Found: C, 65.40; H, 8.61; N, 2.53.

1H NMR of complex 2 (400 MHz, C6D6): δ 8.21 (d, J = 7.7 Hz, 2H, Flu), 8.07 (d, J = 7.7 Hz, 2H, Flu), 7.52 (t, J = 7.1 Hz, 2H, Flu), 7.22 (t, J = 7.2 Hz, 2H, Flu), 2.94 (br, 8H, THF-). 13C NMR of complex 2 (100 MHz, C6D6): δ 144.20, 132.67, 125.73, 120.34, 117.47, 116.83 (C1), 69.77 (α-THF), 54.40 (NC(CH_{3})_{3}), 36.22 (NC(CH_{3})_{3}), 31.98 (LuC_{2}H_{5}Si(CH_{3})_{3}), 25.22 (β-THF), 5.55 (Si(CH_{3})_{2}), 4.76 (CH_{2}Si(CH_{3})_{3}). Anal. Calcd (%) for C_{3}H_{50}NO_{2}LuSi_{2}: C, 53.28; H, 7.07; N, 2.00. Found: C, 53.21; H, 7.01; N, 2.04.

1H NMR of complex 3 (400 MHz, Tol-d8): δ 8.16 (d, J = 7.8 Hz, 2H, Flu), 8.09 (d, J = 8.1 Hz, 2H, Flu), 7.47 (t, J = 7.5 Hz, 2H, Flu), 7.19 (s, 2H, Flu), 3.05 (br, 8H, THF-). 13C NMR of complex 3 (100 MHz, C6D6): δ 142.51, 131.62, 124.59, 120.16, 117.53, 116.66, 83.57 (C1), 69.75 (α-THF), 53.97 (NC(CH_{3})_{3}), 36.41 (NC(CH_{3})_{3}), 35.62 (YCH_{2}Si(CH_{3})_{3}), 24.74 (β-THF), 5.34 (Si(CH_{3})_{2}), 4.38 (CH_{2}Si(CH_{3})_{3}). Anal. Calcd (%) for C_{3}H_{50}NO_{2}YSi_{2}: C, 60.76; H, 8.06; N, 2.29. Found: C, 60.72; H, 8.00; N, 2.34.

2.5. A Typical Procedure for IP Polymerization in Table 2 Entry 4

In a glovebox at 25 °C, toluene solution (3.5 mL), Al^3Bu_{3} (100 µL, 1.0 M, 100 µmol), complex 1 (0.0057 g, 10 µmol), a toluene solution (1.5 mL) of [Ph_{3}C][B(C_{6}F_{5})_{4}] (0.0093 g, 10 µmol), and IP (0.34 g, 5 mmol) were added into a 50 mL round bottom flask in succession. The reaction system became sticky rapidly. After 2 min, the flask was taken outside and then quenched by addition of ethanol (50 mL, containing 5% butyldihydroxytoluene (BHT) as stabilizing agent). The mixture was washed with ethanol and then dried under vacuum at 45 °C to a constant weight (0.34 g, yield = 100%). The resulting polymer was soluble in THF and chloroform at room temperature. The isomer contents of the polyisoprene was calculated from the $^1$H and $^{13}$C NMR spectra according to the following Formulas (1)–(5):

$$\text{Mol 1,4-IP\%} = \left[\frac{I_{H1}}{I_{H1} + 0.5I_{H2}}\right] \times 100\%$$

(1)
Mol 3,4-IP% = \[0.5I_{12}/(I_{11} + 0.5I_{12})\] × 100% (2)
in which \(I_{11}\) represents the resonance integration of the one vinyl proton of the 1,4-isoprene unit at 5.13 ppm in the \(^{1}\text{H}\) NMR spectrum; and \(I_{12}\) represents the resonance integration of the two vinyl protons of the 3,4-isoprene unit at 4.72 ppm in the \(^{1}\text{H}\) NMR spectrum.

\[
\text{Mol cis-1,4-IP%} = [I_{C1}/(I_{C1} + I_{C2} + I_{C3})] \times 100\% \\
\text{Mol trans-1,4-IP%} = [I_{C3}/(I_{C1} + I_{C2} + I_{C3})] \times 100\% \\
\text{Mol 3,4-IP%} = [I_{C2}/(I_{C1} + I_{C2} + I_{C3})] \times 100\%
\]
in which \(I_{C1}\) is the integration of 23.2 ppm signals of the cis-1,4-isoprene unit methyl carbon, and \(I_{C2}\) is the integration of 18.5 ppm signals of the 3,4-isoprene unit methyl carbon, while \(I_{C3}\) is the integration of 15.9 ppm signals of the trans-1,4-isoprene unit methyl carbon in the \(^{13}\text{C}\) NMR spectrum.

### 2.6. A Typical Procedure for MY Polymerization in Table 3 Entry 3

In a glovebox at 25 °C, toluene solution (3.5 mL), Al\(^{1}\)Bu\(_3\) (100 µL, 1.0 M, 100 µmol), complex \(3\) (0.0063 g, 10 µmol), a toluene solution (1.5 mL) of B(C\(_6\)F\(_5\))\(_3\) (0.0052 g, 10 µmol), and MY (0.68 g, 5 mmol) were added into a 50 mL round bottom flask in succession. The reaction system became sticky rapidly. After 1 h, the flask was taken outside and then quenched by addition of ethanol (50 mL, containing 5% butylhydroxytoluene (BHT) as stabilizing agent). The mixture was washed with ethanol and then dried under vacuum at 45 °C to a constant weight (0.49 g, yield = 72%). The resulting polymer was soluble in THF and chloroform at room temperature. The isomer contents of the PMY products were calculated from the \(^{1}\text{H}\) NMR spectra (Formulas (6)–(8) and \(^{13}\text{C}\) NMR spectra (Formulas (9)–(12)).

\[
\text{Mol 1,2-MY%} = [I_{5,30}/(I_{5,11} + 0.5I_{4,76})] \times 100\% \\
\text{Mol 3,4-MY%} = [I_{4,76} - 2I_{5,30}/(I_{5,11} + 0.5I_{4,76})] \times 100\% \\
\text{Mol 1,4-MY%} = [(I_{5,11} - 0.5I_{4,76})/(I_{5,11} + 0.5I_{4,76})] \times 100\% \\
\text{Mol 1,2-MY%} = [I_{29,07}/(I_{29,07} + I_{37,09} + I_{37,51} + I_{42,18})] \times 100\% \\
\text{Mol 3,4-MY%} = [I_{42,18}/(I_{29,07} + I_{37,09} + I_{37,51} + I_{42,18})] \times 100\% \\
\text{Mol cis-1,4-MY%} = [I_{37,09}/(I_{29,07} + I_{37,09} + I_{37,51} + I_{42,18})] \times 100\% \\
\text{Mol trans-1,4-MY%} = [I_{37,51}/(I_{29,07} + I_{37,09} + I_{37,51} + I_{42,18})] \times 100\% 
\]

### 2.7. A Typical Procedure for ST Polymerization in Table 4 Entry 9

In a glovebox at 25 °C, toluene solution (3.5 mL), Al\(^{1}\)Bu\(_3\) (100 µL, 1.0 M, 100 µmol), complex \(1\) (0.0057 g, 10 µmol), a toluene solution (1.5 mL) of [PhNHMe\(_2\)][B(C\(_6\)F\(_5\))\(_3\)] (0.0081 g, 10 µmol), and ST (0.52 g, 5 mmol) were added into a 50 mL round bottom flask in succession. Some solids were gradually precipitated from the reaction system. After 20 h, the flask was taken outside and then quenched by addition of ethanol (50 mL, containing 5% butylhydroxytoluene (BHT) as stabilizing agent). The mixture was washed with ethanol and then dried under vacuum at 45 °C to a constant weight (0.22 g, yield = 43%). The resulting polymer is soluble in CHCl\(_3\) and 1,2,4-trichlorobenzene at high temperature. The isomer contents of the polystyrene products were calculated from the \(^{1}\text{H}\) and \(^{13}\text{C}\) NMR spectra according to the following Formulas (13) and (14):

\[
\text{Mol isotactic PST%} = [I_{C1}/I_{C1}] \times 100\% \\
\text{Mol syndiotactic PST%} = [I_{C2}/I_{C3}] \times 100\% 
\]
in which $I_{C1}$ is the integration of the resonance at 146.8 ppm (mmm) and $I_{C2}$ is the integration of the resonance at 145.4 ppm (rrrr) in the $^{13}$C NMR spectrum.

3. Results and Discussion

3.1. Synthesis of Flu-Based CGC Allyl-Type Rare Earth Metal Monoalkyl Complexes 1–3

The FluSiMe$_2$N$^t$Bu ligand was synthesized according to the literature [33]. The alkane elimination reaction between the FluSiMe$_2$N$^t$Bu ligand and 1 equivalent unit of the rare earth metal tri(trimethylsilylmethyl) complexes Ln(CH$_2$SiMe$_3$)$_3$(THF)$_n$ straightforwardly yielded the Flu-based CGC allyl-type rare earth metal monoalkyl complexes (η$^3$η$^1$-FluSiMe$_2$N$^t$Bu)Ln(CH$_2$SiMe$_3$)(THF)$_2$ 1–3 (1: Ln = Sc, 63%; 2: Ln = Lu, 67%; 3: Ln = Y, 84%) with moderate to high yields in 2–3 h (Scheme 1). In comparison with the slow synthesis speed of previous similar results [η$^3$-η$^1$-(3,6-$^t$Bu$_2$Flu)SiR$_2$N$^t$Bu]Y(CH$_2$SiMe$_3$)(THF)$_2$ (37% yield after 1 h and 90% yield after a few days) [27], the rapid synthesis speed of these complexes might be attributed to the lesser bulk of the FluSiMe$_2$NH$^t$Bu ligand than that of the (3,6-$^t$Bu$_2$-FluH)SiR$_2$NH$^t$Bu ligand.

![Scheme 1. Synthesis of the Flu-based CGC allyl-type rare earth metal monoalkyl complexes 1–3.](image)

3.2. Structural Characterization of Flu-Based CGC Allyl-Type Rare Earth Metal Monoalkyl Complexes 1–3

These complexes 1–3 have good solubilities in common organic solvents such as hexane, toluene and THF. In the $^1$H NMR spectra of the complexes 1–3 in C$_7$D$_8$ and C$_6$D$_6$, the disappearance of the proton signals attributed to the Flu–H and N–H group of the FluHSiMe$_2$NH$^t$Bu ligand suggests the generation of a dianionic chelating ligand in these complexes. Moreover, the eight Flu protons are divided into four peaks, indicating an asymmetric coordination mode of the Flu ligand around the metal center [29]. In each case, the molar ratio of the integral areas of the signals for the FluSiMe$_2$N$^t$Bu ligand, the CH$_2$SiMe$_3$ ligand, and THF molecules is 1:1:2. Similar to the flexible [(3,6-$^t$Bu$_2$C$_{13}$H$_6$)SiR$_2$N$^t$Bu]Y(CH$_2$SiMe$_3$)(THF)$_2$ at room temperature [27], these complexes also have a flexible structure and the CH$_2$SiMe$_3$ group in these complexes can not be fixed at the NMR time scale at room temperature since the two methylene protons of the Ln-CH$_2$SiMe$_3$ groups show only a singlet at high field for 1 at –1.09 ppm, for 2 at –0.82 ppm, and for 3 at –1.06 ppm, respectively.

In a mixed toluene/hexane solution at –30 °C, single crystals of the complexes 1–3 were cultivated for an X-ray determination. The ORTEP (Oak Ridge Thermal-Ellipsoid Plot Program) drawings of the complexes 1–3 are shown in Figure 1 and the representative bond distances and angles are summarized in Table 1. The X-ray diffraction study reveals that these complexes 1–3 are isomorphous and isostructural. Similar to the previous Flu-based CGC allyl-type complex [η$^3$-η$^1$-(3,6-$^t$Bu$_2$C$_{13}$H$_6$)SiR$_2$N$^t$Bu]Y(CH$_2$SiMe$_3$)(THF)$_2$ [27], each of them contains one dianionic FluSiMe$_2$N$^t$Bu ligand, one CH$_2$SiMe$_3$ group, and two coordinated THF molecules and adopts a distorted-trigonal-bipyramidal configuration. Moreover, the 9-position carbon atom (C1) and the two adjacent carbon atoms (C2, C3) of one phenyl (Ph) ring of the Flu ligand are bound to the metal center in an asymmetric η$^3$-allyl mode. The distance of Ln–C1 (2.395(3)–2.566(3) Å) is shorter than those of
Ln–C2 (2.730(3)–2.769(3) Å) and Ln–C3 (3.036(4)–3.067(3) Å), implying the more possible presence of –C1–C2=C3 than –C3–C2=C1 in such asymmetric η3-Flu ligands. By comparison, the bond distances of Ln–N1, Ln–O1, Ln–O2, Ln–C1 as well as Ln–C2 increase in the order of 1 < 2 < 3, which are consistent with the trend of the increased ionic radius of the metal centers (Sc < Lu < Y).

Figure 1. ORTEP (Oak Ridge Thermal-Ellipsoid Plot Program) drawings of complexes 1–3 with thermal ellipsoids with a 30% probability. Hydrogen atoms are omitted for clarity.

Table 1. Selected bond distances (Å) and angles (deg) of complexes 1–3.

|                  | 1    | 2    | 3    |
|------------------|------|------|------|
| Ln–N1            | 2.065(3) | 2.180(3) | 2.213(3) |
| Ln–C1            | 2.395(3) | 2.504(4) | 2.566(3) |
| Ln–C2            | 2.730(3) | 2.746(4) | 2.769(3) |
| Ln–C3            | 3.067(3) | 3.044(4) | 3.036(4) |
| Ln–C20           | 2.226(4) | 2.338(4) | 2.392(4) |
| N1–Ln–C20        | 109.34(13) | 111.36(14) | 112.29(13) |
| N1–Ln–C1         | 75.05(11) | 71.80(13) | 70.57(11) |
| C20–Ln–C1        | 144.95(13) | 148.23(15) | 149.02(13) |
| N1–Ln–C2         | 91.58(11) | 88.71(12) | 87.82(11) |
| C20–Ln–C2        | 113.15(12) | 117.13(14) | 118.56(13) |
| C1–Ln–C2         | 32.52(11) | 31.92(13) | 31.58(11) |
| N1–Ln–C3         | 86.93(11) | 85.21(13) | 84.56(11) |
| C20–Ln–C3        | 89.52(11) | 93.24(14) | 94.39(12) |
| C1–Ln–C3         | 55.57(11) | 55.06(13) | 54.68(11) |
| C2–Ln–C3         | 27.22(10) | 27.32(12) | 27.47(11) |

3.3. Cis-1,4-Polymerization of Ip by the Complexes 1–3/Activator/AlR3 Ternary Systems

The complexes 1–3 alone, the complexes 1–3/AlR3 binary systems, and the complexes 1–3/activator binary systems were inactive in IP polymerization. In the presence of both activator and AlR3, however, these complexes 1–3 unprecedentedly exhibited high activities and regio-/stereoselectivities in IP polymerization under mild conditions as shown by 1H and 13C NMR analysis (Table 2 and supporting information). At the very beginning, the best catalytic system was investigated for IP polymerization. In the presence of borate A and 10 equivalent units of Al iBu3, high activity approximately 1.1 × 103 (g of polymer)/(mol Ln h) and moderate cis-1,4-selectivity of approximately 83% in 30 min. (Table 2, entry 1), while anilinium borate [PhNHMe2][B(C6F5)4] (B) displayed moderate activity, approximately 18 × 103 (g of polymer)/(mol Ln h) and low cis-1,4-selectivity of approximately 65% under the same condition (Table 2, entry 2). By contrast, neutral borane B(C6F5)3 (C) was inert for the polymerization of IP even in a long polymerization time (Table 2, entry 3). In order to prepare PIPs with high cis-1,4-selectivities, the borate A was chosen as an optimum activator in the following IP polymerization. In the presence of borate A and 10 equivalent units of Al iBu3, high activity approximately 1.1 × 106 (g of polymer)/(mol Ln h) and high cis-1,4-selectivity of approximately 90% were obtained in IP polymerization catalyzed by...
the Sc complex 1 only in 2 min, affording main cis-1,4-PIP with high molecular weight and moderate molecular weight distribution (\(M_n = 700 \text{ kg/mol}\), \(M_w/M_n = 2.26\)) (Table 2, entry 4). In comparison, the Lu complex 2 and the Y complex 3 had moderate activities (\(1.6 \times 10^4\)–\(1.7 \times 10^4\) (g of polymer)/(mol\(\text{Ln}\) h)) and similar or slightly lower cis-1,4-selectivities (86%–90%) under the same conditions to prepare main cis-1,4-PIPs with lower molecular weights and broader molecular weight distributions (\(M_n: 100\)–300 kg/mol, \(M_w/M_n: 3.17\)–3.26) (Table 2, entries 5–6). Therefore, the Sc complex 1 served as an optimized catalyst in the following polymerization of IP.

### Table 2. Cis-1,4-polymerization of isoprene by complexes 1–3/activator/AlR₃ ternary systems.

| entry | Cat. | A | AlR₃ | [Al]/[Ln] | [IP]/[Ln] | Sol. | t (h) | T (°C) | Y (%) | A² | \(M_n\)e (10⁴) | \(M_w/M_n\)e | Microstructure |
|-------|------|---|------|----------|---------|-----|------|-------|-------|----|-------------|-------------|----------------|
| 1     | 3    | A | AlBu₃ | 2.5      | 500     | Tol  | 0.5  | 25    | 6     | 4   | 83          | 0            | 17             | 3.23         | 55             |
| 2     | 3    | B | AlBu₃ | 2.5      | 500     | Tol  | 0.5  | 25    | 6     | 4   | 83          | 0            | 17             | 3.23         | 55             |
| 3     | 3    | C | AlBu₃ | 2.5      | 500     | Tol  | 0.5  | 25    | 6     | 4   | 83          | 0            | 17             | 3.23         | 55             |
| 4     | 1    | A | AlBu₃ | 10      | 500     | Tol  | 0.03 | 25    | 100   | 1135 | 90          | 1            | 9              | 2.26         | 56             |
| 5     | 2    | A | AlBu₃ | 10      | 500     | Tol  | 1    | 25    | 51    | 17   | 90          | 0            | 10             | 3.17         | 57             |
| 6     | 3    | A | AlBu₃ | 10      | 500     | Tol  | 1    | 25    | 47    | 16   | 86          | 0            | 14             | 3.26         | 55             |
| 7     | 1    | A | AlMe₃ | 10      | 500     | Tol  | 2    | 25    | 76    | 13   | 94          | 1            | 5              | 2.55         | 62             |
| 8     | 1    | A | AlEt₃ | 10      | 500     | Tol  | 0.08 | 25    | 99    | 421  | 92          | 0            | 8              | 1.78         | 59             |
| 9     | 1    | A | AlBu₃ | 10      | 500     | PhCl | 18   | 25    | 14    | 0.3  | 91          | 4            | 5              | 2.58         | 57             |
| 10    | 1    | A | AlMe₃ | 10      | 500     | PhCl | 2    | 25    | 100   | 17   | 94          | 1            | 5              | 2.79         | 58             |
| 11    | 1    | A | AlMe₃ | 5       | 500     | PhCl | 2    | 25    | 100   | 17   | 94          | 1            | 5              | 2.63         | 60             |
| 12    | 1    | A | AlMe₃ | 20      | 500     | PhCl | 2    | 25    | 76    | 13   | 94          | 1            | 5              | 2.67         | 58             |
| 13    | 1    | A | AlEt₃ | 10      | 500     | PhCl | 2    | 5    | 100   | 50  | 96          | 0            | 4              | 1.80         | 66             |
| 14    | 1    | A | AlMe₃ | 10      | 500     | PhCl | 2    | 0    | 44    | 7    | 95          | 1            | 4              | 2.10         | 62             |
| 15    | 1    | A | AlMe₃ | 10      | 500     | PhCl | 0.5  | 50    | 100   | 68   | 93          | 1            | 6              | 2.36         | 60             |
| 16    | 1    | A | AlMe₃ | 10      | 500     | PhCl | 0.5  | 70    | 94    | 64   | 90          | 3            | 7              | 3.71         | 55             |
| 17    | 1    | A | AlMe₃ | 10      | 100     | PhCl | 1    | 25    | 13    | 0.9  | 94          | 2            | 4              | 2.23         | 59             |
| 18    | 1    | A | AlMe₃ | 10      | 300     | PhCl | 1    | 25    | 51    | 10   | 95          | 1            | 4              | 2.05         | 62             |
| 19    | 1    | A | AlMe₃ | 10      | 800     | PhCl | 0.5  | 25    | 100   | 109  | 94          | 3            | 3              | 2.10         | 58             |
| 20    | Sc² | A | AlMe₃ | 10      | 500     | PhCl | 2    | 25    | 21    | 4    | 93          | 4            | 3              | 0.9          | 2.18–60        |
| 21    | Sc² | A | AlMe₃ | 10      | 500     | PhCl | 2    | 25    | 89    | 15   | 94          | 2            | 4              | 3.70         | 60             |

*Conditions unless specified otherwise: 10 μmol of Ln complex, 10 μmol of activator, 5 mL of solvent. A²: Activator: A¹ = [Ph₃C][B(C₆F₅)₄]; B = [PhNHMe₂][B(C₆F₅)₄]; C = B(C₆F₅)₃. Activity in 10⁵ g of polymer/(mol Ln h). Determined by ¹H and ¹³C NMR spectrum: c1,4: cis-1,4-selectivity; t1,4: trans-1,4-selectivity; 3,4: 3,4-selectivity. Determined by GPC in THF at 40 °C against polystyrene standard. Measured by DSC. Sc² = Sc(THF)₃SiMe₃. ²20 μmol of activator.

Then, the influence of alkyln aluminum on the catalytic performance of the Sc complex 1/A system was studied (Table 2, entries 4, 7–8). In comparison with PIP obtained by Al¹Bu₃ in entry 4, PIP obtained by AlEt₃ had lower yield in long polymerization time (99% in 5 min), but higher molecular weight (\(M_n = 1000 \text{ kg/mol}\)), narrower molecular weight distribution (\(M_w/M_n = 1.78\)), and higher cis-1,4-selectivity (92%) (Table 2, entry 8). While PIP obtained by AlMe₃ had the highest cis-1,4-selectivity, up to 94%, its yield, molecular weight, and molecular weight distribution were lower than those obtained in the above two cases (Table 2, entry 7). Therefore, the complex 1/A/AlMe₃ ternary system was identified as the optimum catalytic system for IP polymerization and was used for choosing the optimized polymerization conditions. Solvent, [Al]:[1] molar ratio, polymerization temperature, and [IP]:[1] molar ratio had an effect on yield, regio-/stereoselectivity, molecular weight, and molecular weight distribution of the resulting PIPs (Table 2, entries 7, 9–19). When the IP polymerization catalyzed by the Sc complex 1/A/AlMe₃ ternary system was carried out in different solvents such as Tol, PhCl, and PhCl₂, the catalytic activity obtained in PhCl₂ (1.7 × 10⁴ (g of polymer)/(mol\(\text{Ln}\) h)) was higher than those obtained in Tol and PhCl (0.3 × 10³–1.3 × 10⁴ (g of polymer)/(mol\(\text{Ln}\) h)), while the cis-1,4-selectivities of PIPs obtained in Tol and PhCl₂ (94%) were higher than that obtained in PhCl (91%). When the
[Al][I] molar ratio was decreased to 5:1, the catalytic activity and the PIP’s cis-1,4-selectivity and molecular weight did not change practically (Table 2, entries 10–11). In contrast, with the increasing [Al][I] molar ratio to 20:1, the catalytic activity and the PIP’s molecular weight slightly decreased, while the PIP’s cis-1,4-selectivity was still retained (Table 2, entries 10, 12). The PIPs obtained in low polymerization temperatures approximately −10 °C and 0 °C had higher cis-1,4-selectivities (95%–96%), higher molecular weights (Mn: 700–1000 kg/mol), narrower molecular weight distributions (Mw/Mn: 1.80–2.10), but resulted in lower yields (Table 2, entries 10, 13–14). Moreover, the complex I/A/AlMe₃ ternary system had a certain tolerance to the high polymerization temperatures of approximately 50 and 70 °C with increasing catalytic activities but decreasing cis-1,4-selectivity (Table 2, entries 10, 15–16). With the increasing [IP]:[I] molar ratio from 100:1 to 800:1, the catalytic activities gradually increased from 0.9 × 10³ (g of polymer)/(mol AlMe₃ h) to 1.1 × 10⁵ (g of polymer)/(mol AlMe₃ h), and the cis-1,4-selectivities of the resulting PIPs remained almost unchanged (Table 2, entries 10, 17–19). For comparison, IP polymerization was also carried out by use of the Sc(CH₂SiMe₃)₃(THF)/₂/A/AlMe₃ ternary system with molar ratios of 1:1:10 and 1:2:10 (Table 2, entries 20, 21). The commonality of these three catalytic systems was the similar cis-1,4-selectivities of the resulting PIPs, but the catalytic activities of these three catalytic systems were different in decreasing order of the Sc complex I/A/AlMe₃ ternary system, the Sc(CH₂SiMe₃)₃(THF)/₂/A/AlMe₃ ternary system with a molar ratio of 1:2:10, and the Sc(CH₂SiMe₃)₃(THF)/₂/A/AlMe₃ ternary system with a molar ratio of 1:1:10.

All of the resulting PIPs have good solubilities in THF and CHCl₃. The ¹H NMR spectra of these PIPs in CDCl₃ indicate the presence of main 1,4-PIP unit and a trace amount of 3,4-PIP unit. The ¹³C NMR spectra of these PIPs give diagnostic signals assigned as main cis-1,4 configuration (δ = 23.6, 26.6, 32.4, 125.2, and 135.4 ppm) and a small amount of 3,4-configuration (δ = 18.8, 26.6, 32.4, 125.2, and 135.4 ppm) with or without a trace amount of trans-1,4-configuration (δ = 16.1, 26.6, 32.4, 125.2, and 135.4 ppm) (see supporting information). The GPC curves reveal that these main cis-1,4-PIP’s have moderate to high molecular weights in the range of 100–1000 kg/mol and bimodal molecular weight distributions (Mw/Mn = 1.78–3.71) similar to natural rubber. The DSC curves of these PIPs show the glass transition temperature (T_g) in the range of −52 to −66 °C, consistent with the thermoplasticity of the CPIP (see Supporting Information).

### 3.4. Cis-1,4-Polymerization of MY by the Complexes 1–3/Activator/AlR₃ Ternary Systems

Similarly, the complexes 1–3/activator/AlR₃ ternary systems also served as highly efficient and regio-/stereoselective catalyst for the cis-1,4-polymerization of MY (Table 3). In pursuit of high cis-1,4-selectivity, the Y complex 3/borane C/AlBu₃ ternary system was chosen as the optimum catalytic system for MY polymerization since it showed the highest cis-1,4-selectivity up to 99% among these different ternary systems under similar condition in toluene (Table 3, entries 1–5). In comparison with MY polymerization in toluene, the Y complex 3/C/AlBu₃ ternary system demonstrated low activities, approximately 8 × 10³–1.1 × 10⁴ (g of polymer)/(mol Al₃ h) and low cis-1,4-selectivities of approximately 95%–96% in MY polymerization in PhCl and PhCl₂ (Table 3, entries 3,6,7). The amount of AlBu₃ had an impact on the catalytic activity (Table 3, entries 3, 8–10). With an increase of the molar ratio of [Al][3] from 5:1 to 40:1, the activity first increased from 2 × 10³ (g of polymer)/(mol Al₃ h) to 4.9 × 10⁴ (g of polymer)/(mol Al₃ h), then decreased to 3.2 × 10⁴ (g of polymer)/(mol Al₃ h) (Table 3, entries 3, 8–10). The cis-1,4-selectivities, molecular weights, and molecular weight distributions of the resulting PMYs remained constant or made small changes. In low polymerization temperature, approximately 0 °C, the complete cis-1,4-PMY (cis-1,4-selectivity of approximately 100%) was obtained with the highest molecular weight (Mn = 700 kg/mol) and the narrowest molecular weight distribution (Mw/Mn = 1.66) (Table 3, entry 11). In high polymerization temperature, approximately 50 °C or 70 °C, the catalytic activities and the cis-1,4-selectivities gradually decreased, implying the instability of this catalyst in high temperatures (Table 3, entries 12–13). The concentration of MY monomer also affected the catalytic activity (Table 3, entries 3, 14–17). With a gradually increasing [MY]:[3] molar ratio from 250:1 to 4000:1, the activity gradually increased from 1.3 × 10⁴ (g of polymer)/(mol Al₃ h) to 1.2 × 10⁵.
(g of polymer)/(mol Ln h), but at the same time the cis-1,4-selectivity of PMYs were retained (Table 3, entries 3, 14–17). By contrast, low activities approximately 0.2–1 (g of polymer)/(mol Ln h) and low cis-1,4-selectivities of approximately 95% were obtained by the Y(CH2SiMe3)3(THF)/C/Al’Bu3 ternary system with different molar ratios as 1:1:10 and 1:2:10 under similar conditions (Table 3, entries 18, 19).

Table 3. Cis-1,4-polymerization of myrcene by complexes 1–3/activator/AlRe3 ternary systems.a

| entry | Cat. | A | [Al]/[Ln] | [MY]/[Ln] | Sol. | t (h) | T (°C) | Y (%) | Microstructure (%) | Mw/Mn | Mw | Tg (°C) |
|-------|------|---|-----------|-----------|------|------|-------|------|------------------|------|-----|---------|
| 1     | 3    | A | 10        | 500       | Tol  | 1    | 25    | 100  | 68  | 68  | 0  | 24 | 0 | 3 | 3.47 | 60 |
| 2     | 3    | B | 10        | 500       | Tol  | 1    | 25    | 100  | 68  | 80  | 0  | 20 | 0 | 3 | 2.56 | 60 |
| 3     | 3    | C | 10        | 500       | Tol  | 1    | 25    | 72   | 49  | >99 | 0  | 0  | 4  | 1.93 | 65 |
| 4     | 1    | C | 10        | 500       | Tol  | 2    | 25    | 72   | 24  | 88  | 0  | 12 | 9  | 1.97 | 66 |
| 5     | 2    | C | 10        | 500       | Tol  | 48   | 25    | 56   | 0.002 | 93 | 0  | 7  | 0  | 2  | 2.51 | 60 |
| 6     | 3    | C | 10        | 500       | PhCl  | 8   | 25    | 99   | 8   | 95  | 0  | 5  | 0  | 4  | 2.24 | 61 |
| 7     | 3    | C | 10        | 500       | PhCl2 | 6   | 25    | 99   | 11  | 96  | 0  | 4  | 0  | 5  | 2.73 | 61 |
| 8     | 3    | C | 5        | 500       | Tol  | 2    | 25    | 7    | 2   | 99  | 0  | 1  | 0  | 6  | 2.58 | 63 |
| 9     | 3    | C | 20        | 500       | Tol  | 2    | 25    | 99   | 34  | 99  | 0  | 1  | 0  | 5  | 2.61 | 63 |
| 10    | 3    | C | 40        | 500       | Tol  | 2    | 25    | 94   | 32  | 98  | 0  | 2  | 0  | 3  | 4.26 | 62 |
| 11    | 3    | C | 10        | 500       | Tol  | 2    | 25    | 11   | 100  | 0  | 0  | 7  | 1  | 3.16 | 67 |
| 12    | 3    | C | 10        | 500       | Tol  | 2    | 50    | 78   | 27  | 98  | 0  | 2  | 0  | 5  | 3.01 | 66 |
| 13    | 3    | C | 10        | 500       | Tol  | 2    | 70    | 77   | 96  | 0  | 4  | 0  | 1  | 3.31 | 60 |
| 14    | 3    | C | 10        | 500       | Tol  | 2    | 25    | 75   | 13  | 99  | 0  | 1  | 0  | 6  | 2.71 | 62 |
| 15    | 3    | C | 10        | 1000      | Tol  | 2    | 25    | 75   | 51  | 100  | 0  | 0  | 5  | 1.5 | 7  | 63 |
| 16    | 3    | C | 10        | 2000      | Tol  | 2    | 25    | 61   | 93  | 99  | 0  | 1  | 0  | 7  | 1.96 | 66 |
| 17    | 3    | C | 10        | 4000      | Tol  | 3    | 25    | 65   | 118 | 99  | 0  | 1  | 0  | 9  | 1.76 | 64 |
| 18    | Y1   | C | 10        | 500       | Tol  | 48   | 25    | 20   | 0.23 | 95  | 0  | 5  | 0  | 0.1 | 7.01 | 60 |
| 19    | Y2   | C | 10        | 500       | Tol  | 12   | 25    | 22   | 1   | 95  | 2  | 3  | 0  | 1  | 7.19 | 60 |

a Conditions unless specified otherwise: 10 μmol of Ln complex, 10 μmol of activator, only Al’Bu3 as AlRe3, 5 mL of solvent. b Activator: A = [Ph3C][B(C6F5)4]; B = [PhNHMe][B(C6F5)4]; C = (C6SiMe3)3. c Activity in 10^3 g of polymer/(mol Ln h). d Determined by 1H and 13C NMR spectrum: c-1,4: cis-1,4-selectivity; t-1,4: trans-1,4-selectivity; 3,4: 3,4-selectivity; 1,2: 1,2-selectivity. e Determined by GPC in THF at 40 °C against polystyrene standard. f Measured by DSC. g Y = (CH2SiMe3)3(THF). h 20 μmol of activator.

All of the PMYs obtained by the complexes 1–3/activator/Al’Bu3 systems were also soluble in THF and CHCl3. The 1H NMR spectra in CDC13 demonstrated that these PMYs contained mainly 1,4-microstructure and a trace amount of 3,4-microstructure (see supporting information). The 13C NMR spectra display that these PMYs had mainly cis-1,4 configuration (δ = 17.86, 25.84, 26.96, 27.14, 30.79, 37.09, 124.63, 124.82, 131.34, and 139.16 ppm) and trace amount of 3,4-configuration (δ = 17.81, 25.81, 26.61, 32.32, 37.08, 47.55, 109.28, 124.63, 131.34, and 151.77 ppm) (see supporting information). By GPC analysis, these cis-1,4-PMYs had high molecular weights in the range of 100–900 kg/mol and bimodal molecular weight distributions (Mw/Mn = 1.66–4.26). The glass transition temperature (Tg) in the range of –60 °C to –67 °C was obtained for these cis-1,4-PMYs by DSC.

3.5. Syndiotactic Polymerization of ST by the Complexes 1–3/Activator/AlRe3 Ternary Systems

The complexes 1–3/activator/AlRe3 ternary systems could also promote the syndiotactic polymerization of ST (Table 4). By contrast, the Sc complex 1/B/Al’Bu3 ternary system was the best catalytic system for ST polymerization since such a catalyst exhibited the highest catalytic activity, approximately 2.8 × 10^3 (g of polymer)/(mol Ln h) and the highest syndiotacticity up to 99% in PhCl2, affording SPST with the highest molecular weight and moderate molecular weight distribution (Mw = 900 kg/mol, Mw/Mn = 2.38) (Table 4, entries 1–6). The solvent had a significant effect on syndiotacticity. When the ST polymerization was carried out in PhCl2 or Tol, the syndiotactic PSTs (SPSTs) with high syndiotacticities (rrrr up to 99%) were obtained (Table 4, entries 2, 9). While the PSTs
with moderate syndiotacticities (rrrr in the range of 61% to 65%) were prepared in ST polymerization in PhCl and C₄H₂Cl₄ (Table 4, entries 7,8,10). Different from the polymerization of conjugated dienes, the amount of Al'Bu₃, polymerization temperature, and the concentration of ST monomer only had influence on catalytic activity instead of syndiotacticity of the Sc complex 1/B/Al'Bu₃ ternary system (Table 4, entries 2, 11–18). With the increasing molar ratio of [Al]/[Ln] from 5:1 to 15:1, the activity first increased from 0.2 × 10³ (g of polymer)/(mol Ln h) to 2.8 × 10³ (g of polymer)/(mol Ln h) then decreased to 1.8 × 10³ (g of polymer)/(mol Ln h). When the polymerization temperature rose from 25 °C to 90 °C, the activity slightly dropped from 2.8 × 10³ (g of polymer)/(mol Ln h) to 2.6 × 10³ (g of polymer)/(mol Ln h), suggesting that such catalyst is very stable in high polymerization temperatures (Table 4, entries 2, 13–15). Moreover, the activity went up from 0.7 × 10³ (g of polymer)/(mol Ln h) to 2.8 × 10³ (g of polymer)/(mol Ln h) with the gradually increasing [St]/[Al] molar ratio from 200:1 to 700:1 (Table 4, entries 2, 16–18). In the above cases, the resulting SPSTs always had complete syndiotacticities up to 99%. In comparison, the Sc(CH₃SiMe₃)₃(THF)₂/Al'Bu₃ ternary system with the molar ratio of 1:10 produced PST with complete syndioselectivity (rrrr > 99%) similar to the Sc complex 1/B/Al'Bu₃ ternary system, while the Sc(CH₃SiMe₃)₃(THF)₂/Al'Bu₃ ternary system with the molar ratio of 1:1:10 only afforded PST with moderate syndioselectivity (rrrr = 78%) under similar conditions (Table 4, entries 19–20).

Table 4. Syndiotactic polymerization of styrene by complexes 1–3/activator/AlR₃ ternary systems.

| entry | Cat. | AlR₃ | [Al]/[Ln] | [Al]/[Ln] | Sol. | t (h) | T (°C) | Y (%) | Aₙ | rrr (%) | Mₙ (g/mol) | Mₘ/Mₙ (%) | T_m/°C |
|-------|------|------|-----------|-----------|------|-------|--------|-------|-------|-----------|------------|-------------|-------|
| 1     | 1 A  | Al'Bu₃ | 10   | 500     | PhCl₂ | 12   | 25     | 18    | 781   | >99       | 7        | 2.05        | 272  |
| 2     | 1 B  | Al'Bu₃ | 10   | 500     | PhCl₂ | 6    | 25     | 32    | 2777  | >99       | 9        | 2.38        | 271  |
| 3     | 1 C  | Al'Bu₃ | 10   | 500     | PhCl₂ | 24   | 25     | 7     | 152   | >99       | 3        | 2.36        | 274  |
| 4     | 2 B  | Al'Bu₃ | 10   | 500     | PhCl₂ | 24   | 25     | 6     | 130   | 54        | n.d.      | n.d.        | 260  |
| 5     | 3 B  | Al'Bu₃ | 10   | 500     | PhCl₂ | 24   | 25     | 23    | 499   | >99       | 9        | 2.21        | 277  |
| 6     | 3 A  | Al'Bu₃ | 10   | 500     | PhCl₂ | 24   | 25     | 10    | 217   | >99       | 0.1       | 6.42        | 271  |
| 7     | 3 B  | Al'Bu₃ | 10   | 500     | PhCl₂ | 24   | 25     | 17    | 369   | 65        | n.d.      | n.d.        | 265  |
| 8     | 3 B  | Al'Bu₃ | 10   | 500     | PhCl₂ | 24   | 25     | 17    | 369   | 65        | n.d.      | n.d.        | 267  |
| 9     | 3 B  | Al'Bu₃ | 10   | 500     | PhCl₂ | 24   | 25     | 17    | 369   | 65        | n.d.      | n.d.        | 267  |
| 10    | 3 B  | Al'Bu₃ | 10   | 500     | PhCl₂ | 24   | 25     | 17    | 369   | 65        | n.d.      | n.d.        | 267  |
| 11    | 1 B  | Al'Bu₃ | 5    | 500     | PhCl₂ | 12   | 25     | 5     | 217   | >99       | n.d.      | n.d.        | 272  |
| 12    | 1 B  | Al'Bu₃ | 15   | 500     | PhCl₂ | 12   | 25     | 42    | 1822  | >99       | 6        | 2.09        | 277  |
| 13    | 1 B  | Al'Bu₃ | 10   | 500     | PhCl₂ | 12   | 50     | 60    | 2604  | >99       | 5        | 2.09        | 273  |
| 14    | 1 B  | Al'Bu₃ | 10   | 500     | PhCl₂ | 12   | 70     | 59    | 2561  | >99       | 4        | 1.98        | 272  |
| 15    | 1 B  | Al'Bu₃ | 10   | 500     | PhCl₂ | 12   | 90     | 61    | 2647  | >99       | 0.1       | 18.78       | 271  |
| 16    | 1 B  | Al'Bu₃ | 10   | 500     | PhCl₂ | 12   | 25     | 41    | 712   | >99       | 5        | 2.02        | 275  |
| 17    | 1 B  | Al'Bu₃ | 10   | 400     | PhCl₂ | 12   | 25     | 35    | 1215  | >99       | 8        | 2.02        | 273  |
| 18    | 1 B  | Al'Bu₃ | 10   | 700     | PhCl₂ | 12   | 25     | 35    | 2126  | >99       | 13       | 1.49        | 271  |
| 19    | Se²  | B    | 10   | 500     | PhCl₂ | 48   | 25     | 7     | 76    | 78        | n.d.      | n.d.        | 268  |
| 20    | Se²  | B    | 10   | 500     | PhCl₂ | 12   | 25     | 9     | 390   | >99       | n.d.      | n.d.        | 272  |

*Conditions unless specified otherwise: 10 µmol of Ln complex, 10 µmol of activator, 5 mL of solvent. ⁵Activator: A = [Ph(C₅H₅)₂]COMe; B = [PhNHMe₂][B(C₆H₅)₃]; C = B(C₆H₅)₃. ⁶Activity in (g of polymer)/(mol Ln h). ⁷ Determined by ¹H and ¹³C NMR spectrum. ⁸ Determined by GPC in 1,2,4-trichlorobenzene at 150 °C against polystyrene standard. ⁹ Measured by DSC. ¹ Sc = Sc(THF₂)₃(THF). ¹² 20 µmol of activator.

The resulting SPSTs are soluble in PhCl₂ and C₄H₂Cl₄ in high temperatures. The ¹³C NMR spectra in CDCl₃ indicate that these SPSTs have complete syndiotactic-microstructure with only a singlet at 145.35 ppm (see Supporting Information). GPC curves display that these SPSTs have moderate to high molecular weights in the range of 10–900 kg/mol and bimodal molecular weight distributions (Mₘ/Mₚ = 1.98–18.78). As demonstrated by DSC, the melting points (T_m) of these SPSTs are in the range of 260 °C to 275 °C (see Supporting Information).
3.6. Polymerization Mechanism Study

In general, the catalytically active species in the coordination–insertion polymerization of olefin is usually generated from the rare earth metal dialkyl/dihalides complex and activator with or without AlR₃ (Chart 2a,b) [8]. In such catalytic systems, an activator usually eliminates one alkyl group from the metal center to afford cationic species containing a metal–alkyl (Ln–R) bond for the coordination and insertion of olefin monomer to finally give polyolefin with different regio-/stereoselectivity and microstructure. Unlike an activator, AlR₃ can perform a lot of functions in olefin polymerization, such as scavenging impurities, transforming (alkylating and reducing) the cationic species, and/or acting as a chain transfer agent [34–36]. Later, AlR₃, especially AlMe₃, was found to react with the rare earth metal trialkyl/dialkyl complex to form a heterobimetallic tetraalkylaluminate complex as a catalyst precursor. Activated by an activator, the corresponding cationic heterobimetallic tetraalkylaluminate complex was formed as a truly active species in the olefin polymerization (Chart 2b) [37–39]. Recently, AlR₃ was found to remove coordinated solvent molecules such as THF or pyridine from the metal center or transfer the anionic chelating ligand from the rare earth metal center (Chart 2b) [40–43]. But in comparison, the catalytically active species in the coordination–insertion polymerization of olefins by use of rare earth metal monoalkyl complex/activator/AlR₃ ternary system is difficult to calculate and understand (Chart 2c). According to the conventional synthesis method a, the resulting cationic species does not have the alkyl group, which inhibits coordination and insertion of olefin monomer into the Ln–R bond. As a result, the high regio-/stereoselective polymerization of olefins can’t occur. Therefore, some special reaction must be happened during the formation of cationic active species. More recently, we found that in the cis-1,4-polymerization of isoprene catalyzed by the dipyrromethene ligated scandium monoalkyl complex/activator/AlR₃ ternary system, both of two anionic dipyrromethene chelating ligands transferred from the Sc center to the Al center. This was observable by using naked eyes, UV irradiation, fluorescence spectrum, and in situ ¹H NMR spectrum, and affords a catalyst precursor heterobimetallic tetraalkylaluminate complex (Chart 2d) [40]. Then, one alkyl group of such catalyst precursor was removed by an activator to form the cationic heterobimetallic tetraalkylaluminate complex as a truly active species in cis-1,4-polymerization of IP (Chart 2d). In this paper, these Flu-based CGC allyl-type rare earth metal monoalkyl complexes/activator/AlR₃ ternary system also exhibited high regio-/stereoselectivities and/or high activities in the polymerization of olefins such as IP, MY, and ST. The catalytically active species of such ternary systems in the coordination–insertion polymerization of olefins also aroused our interest. Therefore, the polymerization initiation processes by the Y complex 3/activator/AlR₃ ternary systems under different [Ln]/[AlR₃] molar ratios were monitored by use of the in situ ¹H NMR spectrum in d-toluene or d-THF at 25 °C (Figure 2 and supporting information).
Chart 2. Coordination–insertion polymerization of olefin by using the different rare earth metal catalysts.

The analysis of the in situ $^1$H NMR spectra of the active species generated from the Y complex $3\{[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]\}/\text{AlMe}_3$ ternary system in $d$-toluene at 25 °C was taken as an example (Figure 2). Firstly, the reaction between the Y complex 3 and 5 equivalent units of AlMe$_3$ was carried out in a J. Young valve NMR tube for 5 min consistent with polymerization procedure (Figure 2E). The in situ $^1$H NMR spectrum demonstrated that the peaks assigned to the dianionic FluSiMe$_2$NtBu ligand became weak and moved to the high field. Moreover, the position of peaks assigned to the coordinated THF molecules and AlMe$_3$ had obvious changes. It was very interesting that this $^1$H NMR spectrum very much looked like the in situ $^1$H NMR spectrum of the reaction of Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ and 5 equivalent units of AlMe$_3$ after 5 min in $d$-toluene at 25 °C, in which the heterobimetallic tetramethylaluminate complex Y(Me)[(µ-Me)$_2$Al(Me)$_2$]$_2$ was formed with a broad signal at −0.3 ppm for all of the methyl groups (slightly different with AlMe$_3$) in addition with the byproduct Al(CH$_2$SiMe$_3$)$_3$ (Figure 2F).

These results implied that the Y complex 3 had decomposed during this reaction. In view that no free FluHSiMe$_2$NHtBu ligand was observed from the above in situ $^1$H NMR spectrum, the dianionic FluSiMe$_2$NtBu ligand should precipitate from the polymerization solvent. Then 1 equivalent unit of
activator [Ph₃C][B(C₆F₅)₄] was added to the NMR tube in order to generate cationic species. Almost no peaks assigned to the dianionic FluSiMe₂N'Bu ligand were found in the in situ ¹H NMR spectrum, identifying the precipitation of an insoluble complex containing the dianionic FluSiMe₂N'Bu ligand (Figure 2G). Similarly, this ¹H NMR spectrum and the in situ ¹H NMR spectrum of the reaction of Y(Me)[(µ-Me)₂Al(Me)₂]₂ with 2 equivalent units of [Ph₃C][B(C₆F₅)₄] (Figure 2H) were nearly identical. The chemical shift of the main peak at -0.3 ppm was similar to that of the main peak of the cationic heterobimetallic tetramethylaluminate complex [(Me)₂Al(µ-Me)₂Y]⁺[B(C₆F₅)₄]⁻. Meanwhile, a new peak assigned as byproduct Ph₃CCH₃ also appeared at 2.0 ppm. Such results identified the formation of cationic species [(Me)₂Al(µ-Me)₂Y]⁺[B(C₆F₅)₄]⁻ from the Y complex 3/[Ph₃C][B(C₆F₅)₄]/AlMe₃ ternary system. The similar results were also obtained from the in situ ¹H NMR spectra of the Y complex 3/activator/AlR₃ ternary systems in d-THF at 25 °C (Supporting Information). Based on these facts, it is guessed that AlMe₃ firstly removes two coordinated THF molecules from the Y center of complex 3 to give (FluSiMe₂N'Bu)Y(CH₂SiMe₃) as an intermediate. Then the alkyl exchange between the Y center of the above intermediate and the Al center of AlMe₃ forms a new Y complex (FluSiMe₂N'Bu)₃YMe and a byproduct Al complex AlMe₂(CH₂SiMe₃). Similar to the previous (DPM)₂ScR/activator/AlR₃ ternary system [40], the dianionic FluSiMe₂N'Bu ligand of (FluSiMe₂N'Bu)₃LnMe immediately transfers from the Y center to the Al center to produce the heterobimetallic tetramethylaluminate complex (Me)₂Al(µ-Me)₂Y(Me)(µ-Me)₂Al(AlMe)₂ as a catalyst precursor and the insoluble Y-Aluminum salt solid [(Me)₂Al(µ-Me)₂Y(µ-Me)₂Al(Al)₂]Al(Al)₂[(FluSiMe₂N'Bu)₂] as a byproduct. Such a rapid exchange of the FluSiMe₂N'Bu ligand from the Y center to the Al center is also observed in the in situ ¹H NMR spectra when AlEt₃ or Al'Bu₃ was used as AlR₃ (see Supporting Information). Although the transference of monodentate or bidentate ligand from the Al center to the Al center to form the heterobimetallic tetramethylaluminate complex LY[(µ-Me)₂AlMe]ₙ have been reported previously by Anwander [41], Hou [42], and Kempe [43], this is the first discussion of the transference of dianionic CGC allyl-type chelating ligand. Later, in the presence of 2 equivalent units of activator [Ph₃C][B(C₆F₅)₄], a divalent cationic heterobimetallic tetramethylaluminate species [(Me)₂Al(µ-Me)₂Y]⁺[B(C₆F₅)₄]⁻ was obtained, in combination with Ph₃CCH₃ as a byproduct.
Figure 2. In situ $^1$H NMR spectra of active species by using the Y complex $\text{3/[Ph}_3\text{C][B(C}_6\text{F}_5)_4]/\text{AlMe}_3$ ternary system in $d$-$\text{C}_7\text{H}_8$ at 25 °C.

Taking above results into account, a plausible coordination–insertion mechanism is proposed for the regio-/stereoselective polymerization of olefins catalyzed by the Flu-based CGC allyl-type rare earth monoalkyl complexes ($\eta^3:\eta^1$-FluSiMe$_2$N'Bu)Ln(CH$_2$SiMe$_3$)(THF)$_2$ (1–3)/activator/AlR$_3$ ternary systems in Scheme 2. At first, 2 equivalent units of AlR$_3$ abstracts two coordinated THF molecules from the rare earth metal center of these complexes 1–3 to produce intermediate ($\eta^3:\eta^1$-FluSiMe$_2$N'Bu)Ln(CH$_2$SiMe$_3$) (a). Then the exchange of the CH$_2$SiMe$_3$ group of a and
alkyl group of AlR3 gives a new rare earth metal alkyl complex (η3−η1-FluSiMe2NtBu)Ln (c) with the release of AlR2(CH2SiMe3). The continued ligand exchange between metal center of 0.5 equivalent units of the above intermediate c and Al center of AlR3 forms 0.5 equivalent units of a heterobimetallic tetraalkylaluminate complex (R)2Al(µ-R)Ln(R)(µ-R)2Al(R)2 (h) as catalyst precursor and 0.5 equivalent units of (η3−η1-FluSiMe2NtBu)AlR (g). Then the 0.5 equivalent units of g continues to react with the other 0.5 equivalent units of c to finally give an insoluble Y-Aluminum salt solid [(R)2Al(µ-R)Ln(R)(µ-R)2Al(R)2][Al(η3−η1-FluSiMe2NtBu)2]− (k) as a byproduct. Then two alkyl groups of 0.5 equivalent units of the catalyst precursor h are removed from metal center by 1 equivalent unit of activator to finally generate a divalent cationic species Ln[(µ-R)2AlR2]2+ (l) as catalytically active species in the regio-/stereoselective polymerization of olefins. Based on the actual circumstance of syndiotactic polymerization of ST by the Y complex 3/B/AltBu3 ternary system and the Sc(CH2SiMe3)3(THF)2/B/AltBu3 ternary system with different molar ratios as 1:1:20 and 1:1:10 in Table 4, such a divalent cationic active species is quite reasonable. The less steric hindrance around the metal center of this cationic species permits the coordination and insertion of IMY monomers in cis-1,4 mode to form the anti-allyl form intermediate, which finally affords the cis-1,4-PIPs/PMYs with cis-1,4-selectivities up to 96% or 100%. Such high cis-1,4-selectivity in the coordination–insertion polymerization of conjugated dienes is in agreement with the high cis-1,4-selectivity obtained by the heterobimetallic tetraalkylaluminate active species [LLn[(µ-Me)2AlMe2]2+ in the isoprene polymerization [40,41]. Similarly, such a cationic species also promotes the backbiting of the last phenyl group in PST chains with a metal center. As a result, the SPSTs are obtained by such Flu-based CGC allyl-type rare earth metal monoalkyl complexes 1–3/activator/AlR3 ternary systems.

Scheme 2. Possible mechanism process for the coordination–insertion polymerization of olefin by Flu-based CGC allyl-type rare-earth metal complexes 1–3/activator/AlR3 ternary systems.

4. Conclusions

In summary, three Flu-based CGC allyl-type rare earth metal monoalkyl complexes 1–3 have been easily synthesized in moderate to high yields and structural characterization by 1H and 13C NMR spectrum, elemental analyses as well as X-ray diffraction. In the presence of cocatalyst activator borate [Ph3C][B(C6F5)4] (A) and AlMe3, these complexes 1–3 exhibit moderate activities from 0.3 × 103 (g of
polymer)/(mol Ln h) to 1.1 \times 10^6 (g of polymer)/(mol Ln h) and high cis-1,4-selectivities up to 96% in IP polymerization in PhCl, yielding the main cis-1,4-PIPs with high molecular weights (Mn up to 1000 kg/mol) and bimodal molecular weight distributions (Mw/Mn = 1.78–3.71). Activated by the cocatalyst borane B(C6F5)3 (C) and Al′Bu3, these complexes 1–3 display high activities up to 1.2 \times 10^5 (g of polymer)/(mol Ln h) and high cis-1,4-selectivities up to 100% in MY polymerization in Tol, producing the cis-1,4-PMMys with high molecular weights (Mn up to 900 kg/mol) and bimodal molecular weight distributions (Mw/Mn = 1.66–3.47). Moreover, these complexes 1–3/[PhNHMe2][B(C6F5)4] (B)/Al′Bu3 ternary systems also promote the syndiotactic polymerization of ST with moderate activities up to 2.8 \times 10^5 (g of polymer)/(mol Ln h) in PhCl to give SPSTs with high molecular weights (Mn up to 1300 kg/mol) and bimodal molecular weight distributions (Mw/Mn = 1.49–18.78). In comparison with no, or very low activity and regio-/stereoselectivity of the previous CGC allyl type rare earth metal complexes, such results demonstrate that the transfer of the chelating ligand from the rare earth metal center to the Al center to form the heterobimetallic tetraalkylaluminate complex plays a key role on the excellent catalytic performance of these CGC allyl-type rare earth metal monoalkyl complexes in olefin polymerization. These findings will benefit the design of highly efficient and regio-/stereoselective rare earth metal catalysts as well as the precise synthesis of natural rubber. Further studies will be focused on the research of excellent rare earth metal catalysts for the polymerization of olefins.

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