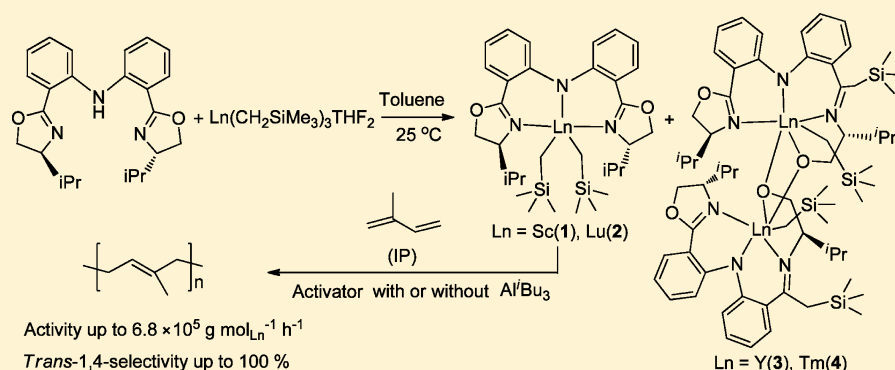


Quasi-Living *trans*-1,4-Polymerization of Isoprene by Cationic Rare Earth Metal Alkyl Species Bearing a Chiral (*S,S*)-Bis(oxazolinyphenyl)amido LigandHui Liu,[†] Jianyun He,[†] Zhanxiong Liu, Zhengguo Lin, Gaixia Du, Shaowen Zhang,* and Xiaofang Li*

Key Laboratory of Cluster Science of Ministry of Education, Department of Chemistry, Beijing Institute of Technology, 5 South Zhongguancun Street, Haidian District, Beijing 100081, China

S Supporting Information



ABSTRACT: A series of chiral mononuclear dialkyl complexes $[(S,S)\text{-BOPA}]\text{Ln}(\text{CH}_2\text{SiMe}_3)_2$ (**1**, **2**) (BOPA = (*S,S*)-bis(oxazolinyphenyl)amido; Ln = Sc (**1**); Ln = Lu (**2**)) and binuclear alkyl complexes $[o\text{-(}S\text{)-OPA-C}_6\text{H}_4\text{-(CH}_2\text{SiMe}_3\text{)C}\equiv\text{N-CH}(\text{iPr})\text{CH}_2\text{-O}]\text{Ln}(\text{CH}_2\text{SiMe}_3)_2$ (**3**, **4**) (OPA = (oxazolinyphenyl)amine; Ln = Y (**3**); Ln = Tm (**4**)) have been synthesized in moderate yields via one-pot acid–base reactions by use of the tris(trimethylsilylmethyl) rare earth metal complexes with the chiral tridentate (*S,S*)-bis(oxazolinyphenyl)amine ligand. In the presence of activator with or without a small amount of Al^iBu_3 , the dialkyl complexes **1** and **2** exhibit very high activities (up to $6.8 \times 10^5 \text{ g mol}^{-1} \text{ h}^{-1}$) and *trans*-1,4-selectivity (up to 100%) in the quasi-living polymerization of isoprene, yielding the *trans*-1,4-PIPs with moderate molecular weights ($M_n = (0.2\text{--}1.0) \times 10^5 \text{ g/mol}$) and narrow molecular weight distributions ($M_w/M_n = 1.02\text{--}2.66$).

■ INTRODUCTION

The stereospecific polymerization (i.e., *cis*-1,4, *trans*-1,4, 1,2-, and/or 3,4-isotactic) of conjugated dienes (butadiene, isoprene) is an attractive research subject and has drawn much attention from both academic and industrial researchers for more than half a century because of the limited supply of natural rubber and the increasing demands for high-performance synthetic rubbers.¹ *trans*-1,4-Polyisoprene (TPIP) produced naturally as gutta-percha rubber or balata rubber (>99% *trans*-1,4, $M_n = (1.4\text{--}1.7) \times 10^5 \text{ g/mol}$) is a thermoplastic crystalline polymer and shows excellent dynamic mechanical properties including long fatigue life, good abrasion resistance, and low heat buildup for myriad applications such as high-performance green tires, medical materials, golf ball covers, electrical insulated materials, and heat-simulated shape-memory materials.² In contrast with the more studies of *cis*-1,4-polyisoprene natural rubber,³ however, the *trans*-1,4-polyisoprene has attracted less research efforts.⁴ Until now, only few rare earth metal catalytic systems consisted of mixed organo-Ln/Mg combinations such as $\text{Cp}^*\text{Nd}(\text{BH}_4)_2(\text{THF})_2/\text{Mg-}(\text{i}^n\text{Bu})_2$ (98.5% *trans*-1,4, activity $>2.9 \times 10^3 \text{ g mol}^{-1} \text{ h}^{-1}$)^{4e} and Ln/ AlMe_4 trinuclear systems (e.g., $(\text{C}_5\text{Me}_4\text{SiMe}_3)\text{Ln-}$

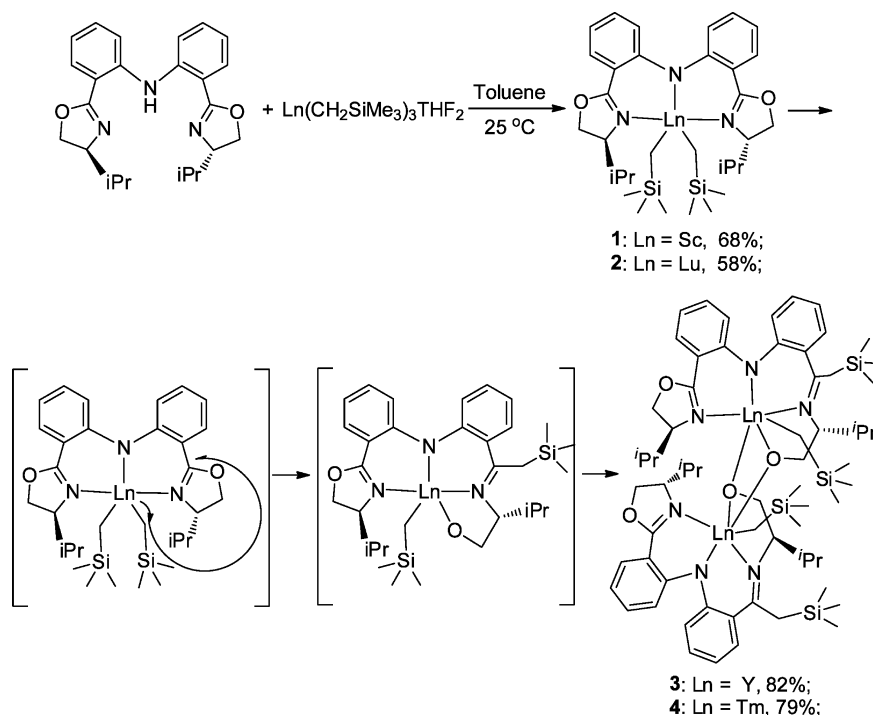
$(\text{AlMe}_4)_2$ (99.5% *trans*-1,4, activity $>3.8 \times 10^3 \text{ g mol}^{-1} \text{ h}^{-1}$)^{4h} can serve as highly stereospecific catalysts to afford TPIP. A drawback that may limit the application scope of these catalysts in industry, however, is their low activities. Therefore, the development of highly efficient catalyst based on rare earth metals in the *trans*-1,4-polymerization of isoprene remains a challenge to date.

It is well-known that the suitably designed chiral organo-metallic catalyst increases the possibility to induce the coordination polymerization of olefin in a regular fashion,⁵ while the structure of chiral chelating ligand determines the selectivity of chiral catalyst. Although various discrete chiral rare earth metal complexes have been investigated so far,⁶ none of them can promote the specific polymerization of conjugated dienes. Recently, chiral C_2 -symmetric tridentate (*S,S*)-bis-(oxazolinyphenyl)amine ((*S,S*)-BOPA) ligand provides a unique scaffold for the synthesis and isolation of organometallic reagent based on transition metal,⁷ exhibiting active in the

Received: March 15, 2013

Revised: April 9, 2013

Published: April 17, 2013

Scheme 1. Synthesis of Chiral Rare Earth Metal Complexes by Using a Chiral (*S,S*)-Bis(oxazolinylphenyl)amine Ligand

asymmetric reaction, including transformation, bond formation, and catalysis.⁸ However, such well-defined organometallic complex based on rare earth metal has not been reported previously. Its catalytic potential for the olefin polymerization has remained unexplored to date, as far as we are aware.

We report herein the synthesis and structural characterization of chiral non-metallocene rare earth metal complexes (**1–4**) based on the chiral *C*₂-symmetric tridentate (*S,S*)-bis(oxazolinylphenyl)amine ligand. In the presence of 1 equiv of activator such as borate [Ph₃C][B(C₆F₅)₄] (**A**), [PhMe₂NH][B(C₆F₅)₄] (**B**), or borane B(C₆F₅)₃ (**C**) with or without 2 equiv of Al^{*i*}Bu₃, the dialkyl complexes **1** and **2** serve as highly efficient catalysts in the quasi-living *trans*-1,4-polymerization of isoprene (activity >6.8 × 10⁵ g mol⁻¹ h⁻¹), affording pure *trans*-1,4-polyisoprenes (*trans*-1,4-selectivity: 99–100%) with moderate molecular weights (*M*_n = (0.2–1.0) × 10⁵ g mol⁻¹).

RESULTS AND DISCUSSION

Synthesis and Characterization of Complexes **1–4**.

The chiral *C*₂-symmetric tridentate (*S,S*)-bis(oxazolinylphenyl)amine ligand was synthesized according to the literature.^{8a} The acid–base reaction between the rare earth metal trialkyl complex Ln(CH₂SiMe₃)₃(THF)₂ and the (*S,S*)-bis(oxazolinylphenyl)amine ligand in toluene at 25 °C afforded the chiral *C*₂-symmetric (*S,S*)-bis(oxazolinylphenyl)amido rare earth metal dialkyl complexes [(*S,S*)-BOPA]Ln(CH₂SiMe₃)₂ (**1**, **2**) (**1**: Ln = Sc, 68%; **2**: Ln = Lu, 58%) in moderate yields (Scheme 1). If the larger rare earth metal was used as metal center, however, such a dialkyl complex was unstable. Instead, the complexes (**3**, **4**) (**3**: Ln = Y, 82%; **4**: Ln = Tm, 79%) adopting a relatively robust binuclear structure through the oxygen bridges, in which each of the two metal centers bore a terminal alkyl ligand, were formed probably through the alkyl migration of one trimethylsilylmethyl group in the dialkyl complex from metal to one oxazoline ring (Scheme 1).¹⁰ At

first, one of the trimethylsilylmethyl groups as the nucleophilic species attacked the imine carbon atom of one oxazoline ring, which resulted in opening this oxazoline ring and generating an oxygen anion. Such oxygen anion coordinated not only with intramolecular metal center but also with other intermolecular metal center to form the binuclear complex. Such an alkyl shift is first observed in the organometallic complex bearing the same chiral ligands.⁷

Complexes **1–4** are soluble in common organic solvents such as THF, toluene, and hexane and gave well-resolved NMR spectra in C₆D₆. ¹H NMR spectra of the chiral *C*₂-symmetric dialkyl complexes **1** and **2** indicated that four similar singlets for the isopropyl–methyl group between 0.56 and 0.61 ppm integrating for 12 protons were observed, suggesting a symmetry in the chelating (*S,S*)-BOPA ligand. No THF molecule which showed signals at 1.70 and 3.50 ppm was found. The signals at high field assigned for the methylene protons of the Ln–CH₂SiMe₃ groups were observed for **1** at –0.04 ppm (s, 4H) and for **2** at –0.60 ppm (d, 2H, *J* = 12.0 Hz) and –0.55 ppm (d, 2H, *J* = 12.0 Hz), respectively, suggesting the existence of two similar trimethylsilylmethyl groups. By contrast, the complicated ¹H NMR spectrum of the binuclear yttrium complex **3** implied a loss of symmetry in the chelating (*S,S*)-BOPA ligand. There were two kinds of isopropyl groups in the complex **3**. The isopropyl group belonging the oxazoline ring showed multiplets at 0.56–0.69 ppm (m, 12H) similar to those in the dialkyl complexes **1** and **2**, while the isopropyl group in the new forming five-membered ring gave multiplets at 1.19–1.40 ppm (m, 12H). Similarly, the methylene and methine groups in the oxazoline ring and the new forming five-membered ring also appeared at the different positions. Moreover, two kinds of trimethylsilylmethyl groups (CH₂SiMe₃) were also observed. Multiplets at –0.96 to –0.83 ppm (m, 4H) for the methylene protons and double peaks at –0.18 to –0.15 ppm (d, 18H) for the methyl groups were assigned for the Ln–CH₂SiMe₃ group. Whereas, the other

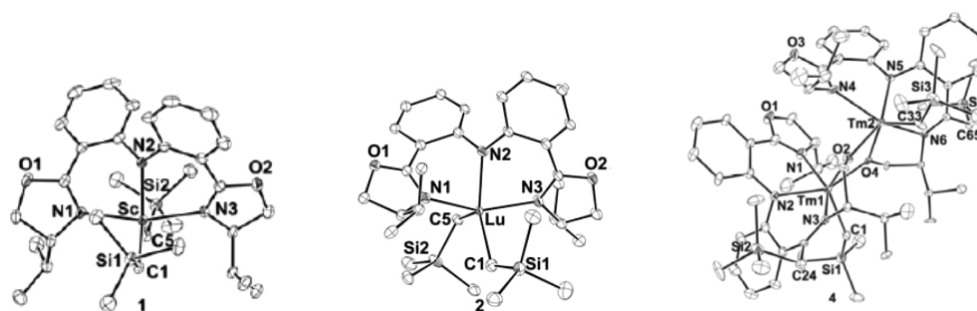


Figure 1. ORTEP drawings of **1**, **2**, and **4** with 30% thermal ellipsoids. The hydrogen atoms in **1**, **2**, and **4**, the isomers in **1** and **2**, and hexane solvent molecule in **4** are omitted for clarity. Selected bond distances (Å) and angles (deg): **1** (Sc), Ln1–N1 2.256(3), Ln1–N2 2.154(3), Ln1–N3 2.259(3), Ln1–C1 2.256(4), Ln1–C5 2.248(4), \angle N1–Ln1–N2 81.6(1), \angle N2–Ln1–N3 81.6(1), \angle N1–Ln1–N3 162.5(1); **2** (Lu), Ln1–N1 2.346(13), Ln1–N2 2.294(14), Ln1–N3 2.291(13), Ln1–C1 2.292(16), Ln1–C5 2.297(16), \angle N1–Ln1–N2 80.1(5), \angle N2–Ln1–N3 76.8(5), \angle N1–Ln1–N3 154.2(5); **4** (Tm), Ln1–N1 2.389(8), Ln1–N2 2.315(9), Ln1–N3 2.417(8), Ln1–C1 2.378(10), Ln1–O2 2.239(7), Ln1–O4 2.263(6), \angle N1–Ln1–N2 73.8(1), \angle N2–Ln1–N3 74.6(1), \angle N1–Ln1–N3 147.2(1).

Table 1. *trans*-1,4-Polymerization of Isoprene by Complexes **1**, **2**/Activator Binary Systems^a

entry	cat.(Ln)	IP (mmol)	cocat. ^b	[IP]/[Ln]	t (h)	T (°C)	yield (%)	activity (kg/(mol _{Ln} h))	<i>trans</i> -1,4 ^c (mol %)	<i>M_n</i> ^d (10 ³)	<i>M_w</i> / <i>M_n</i> ^d	<i>T_m</i> ^e (°C)	efficiency ^f
1	1(Sc)	8	A	400	4	25	100	6.8	>99.5	34	1.39	51	0.80
2	1(Sc)	10	A	500	6	25	80	4.5	>99.5	33	1.25	49	0.83
3	1(Sc)	10	B	500	6	25	73	4.1	>99.5	48	1.23	51	0.52
4	1(Sc)	10	C	500	24	25	38	0.5	>99.5	46	1.29	48	0.28
5	2(Lu)	10	A	500	0.5	25	27	18.4	99.5	30	1.18	44	0.31
6	2(Lu)	10	A	500	1	25	39	13.3	99.5	36	1.20	43	0.37
7	2(Lu)	10	A	500	1.5	25	54	12.2	99.5	43	1.27	40	0.43
8	2(Lu)	10	A	500	2	25	70	11.9	99.5	49	1.30	42	0.49
9	2(Lu)	10	A	500	3	25	100	11.4	99.5	64	1.38	44	0.53
10 ^g	2(Lu)	10	A	1000	6	25	100	11.4	99.5	98	1.32	44	0.70
11	2(Lu)	16	A	800	4	25	100	13.6	99.5	87	1.29	41	0.63
12	2(Lu)	18	A	900	5	25	100	12.3	99.5	103	1.14	39	0.60
13	2(Lu)	20	A	1000	6	25	100	11.4	99.5	92	1.26	41	0.74
14	2(Lu)	30	A	1500	6	25	79	13.5	99.5	76	1.50	41	1.06
15	2(Lu)	30	B	1500	6	25	60	10.2	99.5	31	2.66	44	1.98
16	2(Lu)	30	C	1500	6	25	23	3.9	99.5	30	1.38	39	0.78
17	2(Lu)	30	A	1500	72	−20	19	0.3	100	12	1.24	40	1.62
18	2(Lu)	30	A	1500	24	0	30	1.3	>99.5	15	1.33	44	2.04
19	2(Lu)	30	A	1500	4	50	100	25.5	99	53	1.39	39	1.93
20	2(Lu)	30	A	1500	3	70	100	34.1	99	64	1.38	39	1.60
21	2(Lu)	30	A	1500	0.5	90	100	204.4	99	37	2.18	40	2.76

^aConditions: 20 μmol of Ln, 20 μmol of activator, 5 mL of toluene, unless otherwise noted. ^bActivator: A = [Ph₃C][B(C₆F₅)₄], B = [PhMe₂NH][B(C₆F₅)₄], C = B(C₆F₅)₃. ^cDetermined by ¹H, ¹³C NMR. ^dDetermined by GPC in THF at 35 °C using polystyrene standard. ^eMeasured by DSC. ^fInitiation efficiency = *M_n* (calculated)/*M_n* (measured). ^gPolymerization of 500 equiv of IP in 5 mL of toluene for 3 h followed by the addition of 500 equiv of IP for another 3 h.

trimethylsilylmethyl group which connected with the imine carbon atom showed a doublet at 0.01–0.03 ppm (d, 18H) for methyl groups and triplet at 0.86–0.90 ppm (t, 4H) for methylene group.

Single crystals of complexes **1**, **2**, and **4** suitable for an X-ray determination were grown from a concentrated hexane solution at −30 °C. The X-ray diffraction study revealed that the dialkyl

complexes **1** and **2** are isomorphous but not isostructural (Figure 1 and Supporting Information). Both of complexes **1** and **2** consist of one C₂-symmetric tridentate (*S,S*)-bis-(oxazolinyphenyl)amido unit and two trimethylsilylmethyl groups. Based on τ data, however, the complex **1** (τ = 0.62, 0.63) adopts a distorted trigonal-bipyramidal geometry, while the complex **2** (τ = 0.17, 0.37) chooses a distorted square-

pyramidal geometry. Each of the metal centers in the binuclear complex **4** is bonded with one tetradentate dianionic [NNNO] unit and one trimethylsilylmethyl group. The Tm–O2 bond with the negatively charged oxygen atom is significantly shorter at 2.239(7) Å than the Tm–O4 bonds with the neutral oxygen atom at 2.263(6) Å. Because of the ionic radius of the metal center in a trend of Sc (0.89 Å) < Lu (1.00 Å) < Tm (1.02 Å), the bond distances of the chelating Ln–N(1), Ln–N(2), Ln–N(3), Ln–C(1) as well as Ln–C(5) bond increase in the order of $1 < 2 < 4$. The Ln–N(2) bonds of complexes **1**, **2**, and **4** divide the angles of N(1)–Ln–N(3) ($147.2(1)^\circ$ – $162.5(1)^\circ$) into two almost equal parts N(1)–Ln–N(2) and N(2)–Ln–N(3) ($73.8(1)^\circ$ – $81.6(1)^\circ$), suggesting the N(1), N(2), N(3), and Ln atom are almost planar. These angles decrease in order of $1 > 2 > 4$.

Quasi-Living *trans*-1,4-Polymerization of Isoprene by Complexes **1, **2**/Activator Binary Systems.** Addition of 1 equiv of activator such as $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ to the scandium complex **1** [$(S,S)\text{-BOPA}\text{Sc}(\text{CH}_2\text{SiMe}_3)_2$] in THF- d_8 at 25 °C yielded quantitatively the cationic scandium alkyl complexes $[\{(S,S)\text{-BOPA}\text{Sc}(\text{CH}_2\text{SiMe}_3)(\text{THF})\}[\text{B}(\text{C}_6\text{F}_5)_4]]$ with release of $\text{Ph}_3\text{CCH}_2\text{SiMe}_3$ as monitored by ^1H NMR spectrum (see Supporting Information). The cationic (*S,S*)-bis-(oxazolinyphenyl)amido rare earth metal alkyl species in situ generated by the reaction of complexes **1**, **2** and 1 equiv of activator ($[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (**A**), $[\text{PhMe}_2\text{NH}][\text{B}(\text{C}_6\text{F}_5)_4]$ (**B**), or $\text{B}(\text{C}_6\text{F}_5)_3$ (**C**)) exhibited high activities for the quasi-living *trans*-1,4-polymerization of isoprene, yielding the pure *trans*-1,4-polyisoprene materials (TPIP) with the moderate molecular weights. Some representative results are summarized in Table 1. In the presence of 1 equiv of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, the scandium complex **1** showed low activity (up to 6.8×10^3 g/(mol_{Ln} h)), whereas almost complete *trans*-1,4-selectivity (*trans*-1,4-selectivities >99.5%), affording pure *trans*-1,4-PIPs with moderate molecular weights ($M_n = 33\,000$ – $34\,000$ g/mol) and narrow molecular weight distributions ($M_w/M_n = 1.25$ – 1.39) (Table 1, entries 1, 2). As an activator, $[\text{PhMe}_2\text{NH}][\text{B}(\text{C}_6\text{F}_5)_4]$ was also effective for this *trans*-1,4-polymerization of isoprene (activity ca. 4.1×10^3 g/(mol_{Ln} h)), whereas the use of $\text{B}(\text{C}_6\text{F}_5)_3$ led to only a small amount of TPIP product (Table 1, entries 3, 4). By contrast, the lutetium complex **2** showed both high activities (up to 2.0×10^5 g/(mol_{Ln} h)) and high *trans*-1,4-selectivities (>99.5%) under the similar condition (Table 1, entries 5–21). With an increase in the monomer conversion, the molecular weight of the resultant TPIP increased linearly from 30 000 to 64 000 g/mol, whereas the molecular weight distribution remained very narrow ($M_w/M_n = 1.18$ – 1.38) (Table 1, entries 5–9, Figures 2 and 3). Moreover, after complete consumption of the first 500 equiv of IP in 3 h, the polymer chain ends were still active and continually concerted the second 500 equiv of IP to TPIP in another 3 h (Table 1, entry 10). The molecular weight of the resulting TPIP increased from 60 000 g/mol ($M_w/M_n = 1.30$) to 98 000 g/mol ($M_w/M_n = 1.32$), whereas the molecular weight distributions remained unchanged (see Supporting Information). These results demonstrated that the lutetium complex **2** indeed has the quasi-living character. With the increased monomer concentration, the complex **2** could completely convert up to 1000 equiv of IP less than 6 h at room temperature, yielding high molecular weight TPIPs ($M_n = 87\,000$ – $103\,000$ g/mol) with narrow molecular weight distributions ($M_w/M_n = 1.14$ – 1.29) (Table 1, entries 11–13). The trityl and anilinium borate activators **A** and **B** showed similar influences on the polymerization activities, while the neutral

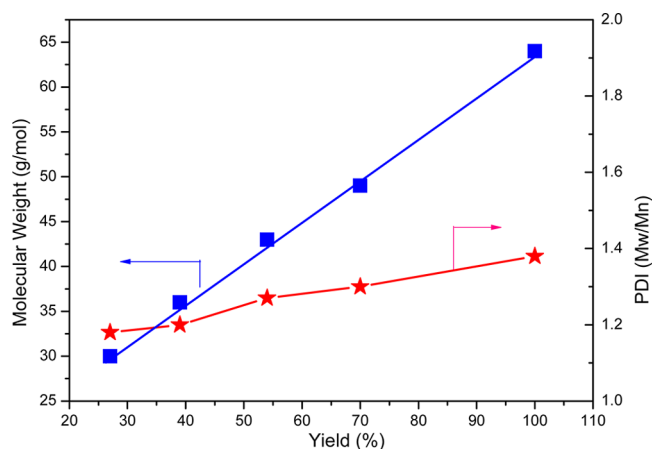


Figure 2. Plot of monomer conversions vs molecular weights and molecular weight distributions of the TPIPs obtained in Table 1, entries 5–9.

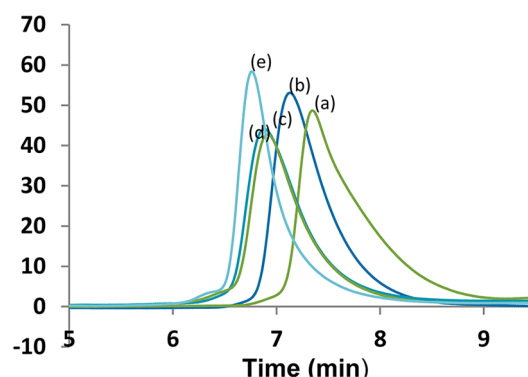


Figure 3. DSC curves for *trans*-1,4-PIPs obtained in Table 1 (a: entry 5; b: entry 6; c: entry 7; d: entry 8; e: entry 9).

borane compound **C** showed lower activity (Table 1, entries 14–16). In addition, the temperature has significant influence on the activity and selectivity. When the isoprene polymerization by the complex **2**/[$\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ system was carried out at low temperature ca. -20 °C, the complete *trans*-1,4-selectivity (100%) was observed as shown by the ^1H and ^{13}C NMR analyses (Table 1, entry 17). It is noteworthy that the complex **2** exhibited very high activities up to 2.0×10^5 g/(mol_{Ln} h) when the temperature increased to 90 °C (Table 1, entry 21). Only 0.5 h was needed to completely convert 1500 equiv of monomer, producing moderate molecular weight TPIP (*trans*-1,4-selectivity = 99%, $M_n = 37\,000$ g mol^{−1}) with moderate molecular weight distribution ($M_w/M_n = 2.18$). In contrast, the binuclear complexes **3** and **4** showed very low activity under the same conditions, affording PIP with mixture microstructures. The neutral complexes **1**–**4** alone were inactive, suggesting that the generation of a cationic metal alkyl species is essential for the present polymerization.

The resulting *trans*-1,4-poly(isoprene)s all showed good solubility in THF and CHCl_3 . The ^1H NMR spectra of the TPIP obtained by complexes **1**–**3**/borane system in CDCl_3 indicates almost complete *trans*-1,4-microstructure (*trans*-1,4-PIP selectivity >99%), and the ^{13}C NMR spectra showed diagnostic signals for a *trans* configuration (δ 16.2, 26.9, 39.9, 124.4, and 135.1 ppm) (Figure 4). GPC curves reveal that these TPIPs have moderate molecular weights in the range of 12 000–103 000 g/mol and the unimodal molecular weight

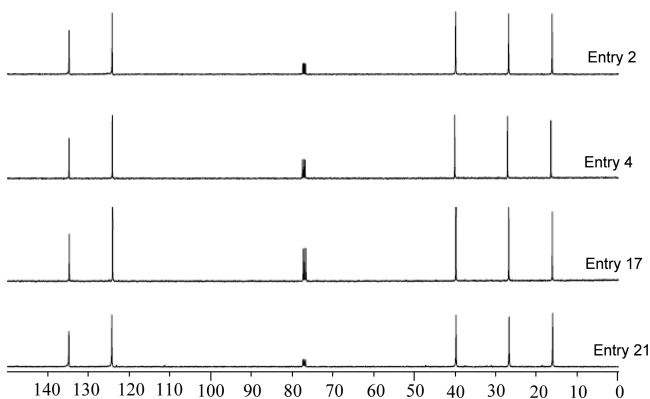


Figure 4. ^{13}C NMR spectra of *trans*-1,4-polyisoprenes obtained by the complex 1/activator binary system in Table 1.

distributions (1.14–2.66), consistent with the predominance of a homogeneous single-site catalytic species. Endo peaks in the range 39–51 °C were observed in the curves of the resulting TPIPs characterized by differential scanning calorimetry (DSC), consistent with the thermoplastic crystalline character of the TPIP.

***trans*-1,4-Polymerization of Isoprene by Complexes 1, 2/Activator/ Al^iBu_3 Ternary Systems.** To thoroughly investigate the structure–reactivity relationship of these chiral cationic (*S,S*)-bis(oxazolinylphenyl)amido rare earth metal dialkyl catalyst-promoted isoprene polymerization, 2 equiv of Al^iBu_3 was added to the complexes 1, 2/activator binary system in the isoprene polymerization under the similar conditions. In contrast with the complexes 1, 2/activator binary systems, the presence of 2 equiv of Al^iBu_3 dramatically increased catalytic activities in keeping the *trans*-1,4-selectivity under the similar conditions (Figure 5). Representative results are summarized in Table 2. It need only 4 h for the scandium complex 1/ $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{Al}^i\text{Bu}_3$ ternary systems to convert quantitatively 500 equiv of isoprene into TPIP at room temperature (Table 2, entry 3), which is much faster than that of the complex 1/activator binary system. Similar to the complex 1/

activator binary system, the ternary systems containing the trityl or anilinium borate activators **A** and **B** showed similar influences on the polymerization activities, while the ternary system consisting of neutral borane compound **C** showed lower activity (Table 2, entries 6–8). Moreover, the small amount of aluminum compounds has less effect on the quasi-living nature of the scandium complex 1/activator binary systems in the isoprene polymerization under the low monomer concentrations (Table 2, entries 1–5). In contrast, the lutetium complex 2 showed higher activity, converting quantitatively 2000 equiv of isoprene into TPIP ca. 6 h in the presence of 1 equiv of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ and 2 equiv of Al^iBu_3 at room temperature (Table 2, entry 12). When the isoprene polymerization was carried out at lower temperature, almost complete TPIP (*trans*-1,4-selectivity: 100%) was obtained as shown by the ^{13}C NMR analyses (Table 2, entry 15, Figure 5). When the temperature was raised to 90 °C, exceptional activity ca. $6.8 \times 10^5 \text{ g}/(\text{mol}_{\text{Ln}} \text{ h})$ was achieved, while the *trans*-1,4-selectivity was remained (*trans*-1,4-selectivities = 99%) (Table 2, entry 19, Figure 5). The GPC curves of these polymers are all unimodal with moderate molecular weight distributions ($M_w/M_n = 1.02$ –2.26), suggesting the predominance of a homogeneous single-site catalytic species. In comparison with those produced by the binary system, these TPIPs have lower molecular weights, revealing that the presence of 2 equiv of Al^iBu_3 compound results in the chain transfer reaction in the polymer chain in some cases (Table 2, entries 9–19).

CONCLUSION

In summary, a series of chiral mononuclear dialkyl and binuclear alkyl complexes based on different rare earth metals (1–4) could be easily prepared in moderate yields via one-pot acid–base reactions by use of the tris(trimethylsilylmethyl) rare earth metal complexes with the chiral tridentate (*S,S*)-bis(oxazolinylphenyl)amine ligand. Activated by an activator such as borate $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, the scandium and lutetium dialkyl complexes 1, 2 showed highly catalytic activities (up to $2.0 \times 10^5 \text{ g}/(\text{mol}_{\text{Ln}} \text{ h})$) and complete *trans*-1,4-selectivities for the quasi-living polymerization of isoprene to afford the pure

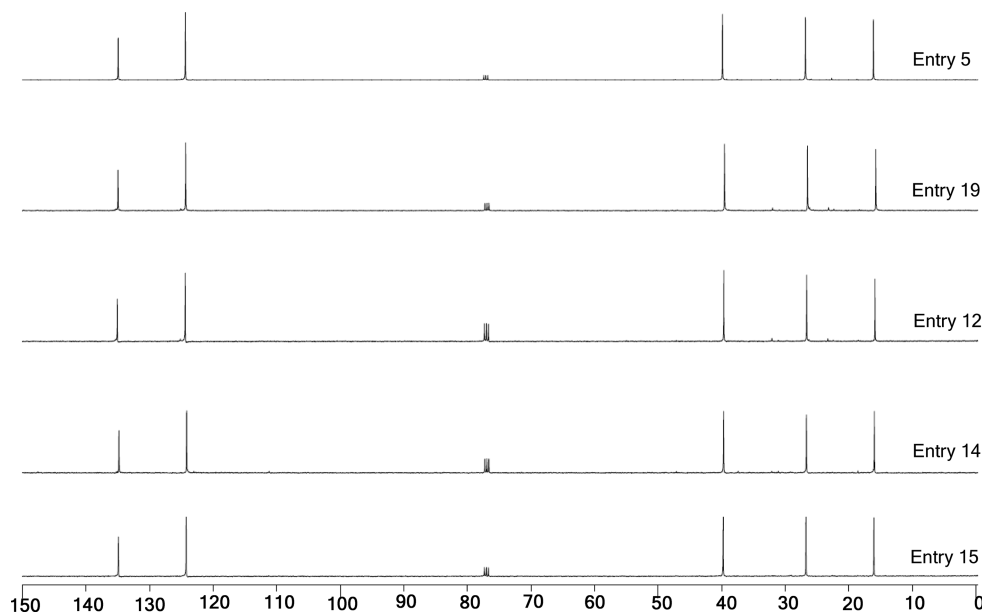
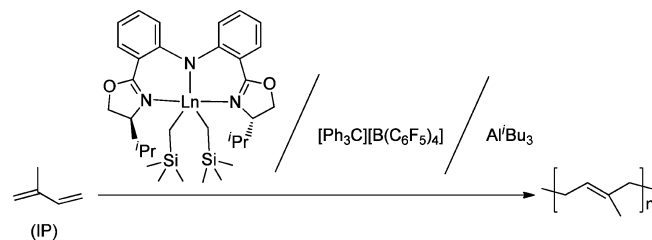


Figure 5. ^{13}C NMR spectra of *trans*-1,4-polyisoprenes obtained by complexes 1, 2/activator/ Al^iBu_3 ternary systems in Table 2.

Table 2. *trans*-1,4-Polymerization of Isoprene by Complexes 1, 2/Activator/ Al^iBu_3 Ternary Systems^a


entry	cat. (Ln)	IP (mmol)	cocat. ^b	[IP]/[Ln]	t (h)	T (°C)	yield (%)	activity (kg/(mol _{Ln} h))	<i>trans</i> -1,4 ^c (mol %)	M_n^d (10 ³)	M_w/M_n^d	T_m^e (°C)	efficiency ^f
1	1(Sc)	4	A	200	2	25	100	6.8	99	20	1.06	52	0.68
2	1(Sc)	8	A	400	3	25	100	9.1	99	24	1.29	52	1.14
3	1(Sc)	10	A	500	4	25	100	8.5	99	27	1.33	52	1.26
4	1(Sc)	16	A	800	5	25	100	10.9	99	29	1.45	50	1.88
5	1(Sc)	20	A	1000	6	25	100	11.3	99	31	1.47	51	2.20
6	1(Sc)	24	A	1200	6	25	77	10.5	99	30	1.70	51	2.10
7	1(Sc)	24	B	1200	6	25	50	6.8	99	25	1.59	51	1.63
8	1(Sc)	24	C	1200	6	25	21	2.9	99	20	1.31	51	0.86
9	2(Lu)	20	A	1000	6	25	100	11.3	99	37	1.45	45	1.84
10	2(Lu)	30	A	1500	5	25	100	20.4	99	48	1.52	43	2.13
11	2(Lu)	36	A	1800	6	25	100	20.4	99	41	2.25	43	2.99
12	2(Lu)	40	A	2000	6	25	93	21.1	99	41	1.79	43	3.09
13	2(Lu)	40	B	2000	6	25	69	15.7	99	21	1.56	46	4.48
14	2(Lu)	40	C	2000	6	25	23	5.2	99	33	1.25	44	0.95
15	2(Lu)	40	A	2000	72	-20	27	0.5	100	25	1.02	45	1.47
16	2(Lu)	40	A	2000	12	0	36	4.1	>99.5	27	1.22	46	1.82
17	2(Lu)	40	A	2000	3	50	100	45.4	99	21	2.24	43	6.49
18	2(Lu)	40	A	2000	2	70	100	68.1	99	25	2.10	40	5.45
19	2(Lu)	40	A	2000	0.2	90	100	681.5	99	21	2.26	40	6.49

^aConditions: 20 μmol of cat., 20 μmol of activator, 40 μmol of Al^iBu_3 , 5 mL of toluene, unless otherwise noted. ^bActivator: A = $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, B = $[\text{PhMe}_2\text{NH}][\text{B}(\text{C}_6\text{F}_5)_4]$, C = $\text{B}(\text{C}_6\text{F}_5)_3$. ^cDetermined by ^1H , ^{13}C NMR. ^dDetermined by GPC in THF at 35 °C using polystyrene standard. ^eMeasured by DSC. ^fInitiation efficiency = M_n (calculated)/ M_n (measured).

trans-1,4-PIPs (*trans*-1,4-selectivity: 99–100%) with the narrow molecular weight distributions. In the presence of 2 equiv of Al^iBu_3 , the complexes 1, 2/activator systems exhibited higher activities (up to 6.8×10^5 g/(mol_{Ln} h)) and almost complete *trans*-1,4-selectivities in the quasi-living polymerization of isoprene. Significant influences of the metal center and temperature on the polymerization activity and selectivity are also observed in these cationic catalytic systems. This is the first chiral catalyst used in the *trans*-1,4-polymerization of isoprene, to our knowledge. Studies on the polymerization mechanism based on DFT calculation and the monocationic (*S,S*)-bis(oxazolinyphenyl)amido complexes with other substituents and other transition metals are in progress.

EXPERIMENTAL SECTION

Materials. All manipulations of air- and moisture-sensitive compounds were performed under a dry nitrogen atmosphere by use of standard Schlenk techniques or a nitrogen-filled MBraun glovebox. Nitrogen (Beijing AP Beifen Gases Industrial Co., Ltd.) was purified by being passed through a Dryclean column (4 A molecular sieves, Dalian Replete Science and Technology Co., LTD) and a Gasclean CC-XR column (Dalian Replete Science and Technology Co., Ltd.). Anhydrous toluene, THF, and hexane were purified by use of a SPS-800 solvent purification system (MBraun) and dried over fresh Na chips in the glovebox. Isoprene was purchased from TCI, dried over CaH_2 , vacuum-transferred, and degassed by two freeze–pump–thaw cycles prior to polymerization experiments. ScCl_3 was purchased from Strem. $\text{LiCH}_2\text{SiMe}_3$ (1.0 M solution in pentane) and Al^iBu_3 (1.1 M solution in toluene) were purchased from Aldrich and

used as received. The chiral C_2 -symmetric tridentate (*S,S*)-bis-(oxazolinyphenyl)amine ligand and $\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ were synthesized according to the literature.⁹ $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, $[\text{PhMe}_2\text{NH}][\text{B}(\text{C}_6\text{F}_5)_4]$, and $\text{B}(\text{C}_6\text{F}_5)_3$ were purchased from Tosoh Finechem Corporation and used without purification. The deuterated solvents benzene- d_6 (99.6 atom % D) and CDCl_3 - d (99.8 atom % D) were obtained from Cambridge Isotope.

General Methods. Samples of rare earth metal complexes for NMR spectroscopic measurements were prepared in the glovebox using J. Young valve NMR tubes. The NMR (^1H , ^{13}C) spectra of catalyst precursors were recorded on an AVANCE 400 spectrometer at room temperature with C_6D_6 as a solvent. ^1H , ^{13}C NMR spectra of polyisoprene samples obtained by cationic chiral (*S,S*)-bis-(oxazolinyphenyl)amido rare earth metal species were recorded on an AVANCE 400 spectrometer in CDCl_3 at room temperature. Elemental analyses were performed on an Elementary Vario MICRO CUBE (Germany). The molecular weights and the molecular weight distributions of the polyisoprene samples were determined at 35 °C by gel permeation chromatography (GPC) on a HLC-8320GPC. THF was employed as the eluent at a flow rate of 0.35 mL/min. The calibration was made by polystyrene standard EasiCal PS-1 (PL Ltd.). The DSC measurements were performed on a TA60 (TA Co.) at a rate of 10 °C/min. Any thermal history difference in the polymers 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.

Synthesis of [(*S,S*)-BOPA]Sc(CH_2SiMe_3)₂ (1). To a colorless THF solution (5 mL) of $\text{Sc}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ (1.15 g, 2.56 mmol) was added a solution of chiral C_2 -symmetric tridentate (*S,S*)-bis(oxazolinyphenyl)amine ligand (1.00 g, 2.56 mmol) in THF (5.0 mL) at room temperature. The mixture was stirred at room temperature for 3 h. After removal of all volatiles in vacuo, the

residue was recrystallized from hexane at $-30\text{ }^{\circ}\text{C}$ to give **1** as light yellow crystals (1.07 g, 1.75 mmol, 68% yield). ^1H NMR (C_6D_6 , $25\text{ }^{\circ}\text{C}$, δ/ppm): -0.04 (s, 4H, CH_2SiMe_3), 0.08 (s, 18H, CH_2SiMe_3), $0.56\text{--}0.61$ (q, 12H, CHMe_2), $2.40\text{--}2.44$ (m, 2H, CHMe_2), $3.96\text{--}4.04$ (m, 4H, CH_2 in oxazoline), $4.63\text{--}4.67$ (m, 2H, CH in oxazoline), $6.58\text{--}8.00$ (m, 8H, ArH). ^{13}C NMR (C_6D_6 , $25\text{ }^{\circ}\text{C}$, δ/ppm): 3.6 (CH_2SiMe_3), $13.8\text{--}14.2$ (CHMe_2), $18.6\text{--}19.6$ (CHMe_2), 30.8 (CH_2SiMe_3), 67.6 ($\text{CHMe}_2 + \text{CH}_2$ in oxazoline), 70.1 (CH in oxazoline), 114.7 , 118.8 , 119.0 , 124.6 , 126.0 , 129.8 , 131.2 , 133.7 , 134.2 (ArC), 155.0 , 168.0 (C in oxazoline). Anal. Calcd for $\text{C}_{32}\text{H}_{50}\text{ScN}_3\text{O}_2\text{Si}_2$: C, 63.02; H, 8.26; N, 6.89. Found: C, 63.28; H, 8.75; N, 7.25.

Synthesis of [(S,S)-BOPA]Lu(CH_2SiMe_3)₂ (2**).** To a colorless THF solution (5 mL) of $\text{Lu}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ (1.49 g, 2.56 mmol) was added a solution of chiral C_2 -symmetric tridentate (S,S)-bis(oxazolinyphenyl)amine ligand (1.00 g, 2.56 mmol) in THF (5.0 mL) at room temperature. The mixture was stirred at room temperature for 3 h. After removal of all volatiles in vacuo, the residue was recrystallized from hexane at $-30\text{ }^{\circ}\text{C}$ to give **2** as yellow crystals (1.09 g, 1.47 mmol, 58% yield). ^1H NMR (C_6D_6 , $25\text{ }^{\circ}\text{C}$, δ/ppm): -0.62 to -0.59 (d, 2H, $J = 12.0\text{ Hz}$, CH_2SiMe_3), -0.57 to -0.54 (d, 2H, $J = 12.0\text{ Hz}$, CH_2SiMe_3), 0.16 (s, 18H, CH_2SiMe_3), $0.52\text{--}0.56$ (q, 12H, CHMe_2), $2.30\text{--}2.34$ (m, 2H, CHMe_2), $3.89\text{--}3.91$ (m, 4H, CH_2 in oxazoline), $4.49\text{--}4.54$ (m, 2H, CH in oxazoline), $6.56\text{--}7.97$ (m, 8H, ArH). ^{13}C NMR (C_6D_6 , $25\text{ }^{\circ}\text{C}$, δ/ppm): 3.2 (CH_2SiMe_3), $13.8\text{--}14.3$ (CHMe_2), $18.5\text{--}19.4$ (CHMe_2), 31.2 (CH_2SiMe_3), 43.3 (CHMe_2), 67.6 (CH_2 in oxazoline), 70.1 (CH in oxazoline), 114.4 , 118.5 , 125.4 , 127.0 , 130.1 , 131.6 , 133.8 , 134.4 (m, ArC), 155.7 , 168.7 (C in oxazoline). Anal. Calcd for $\text{C}_{32}\text{H}_{50}\text{LuN}_3\text{O}_2\text{Si}_2$: C, 51.95; H, 6.81; N, 5.68. Found: C, 52.28; H, 6.25; N, 5.08.

Synthesis of [*o*-(S)-OPA- C_6H_4 -(CH_2SiMe_3) $\text{C}\equiv\text{N}$ -CH(*i*Pr)- CH_2 -O]Y(CH_2SiMe_3)₂ (3**).** To a colorless THF solution (5 mL) of $\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ (1.27 g, 2.56 mmol) was added a solution of chiral C_2 -symmetric tridentate (S,S)-bis(oxazolinyphenyl)amine ligand (1.00 g, 2.56 mmol) in THF (5.0 mL) at room temperature. The mixture was stirred at room temperature for 3 h. After removal of all volatiles in vacuo, the residue was recrystallized from hexane at $-30\text{ }^{\circ}\text{C}$ to give **3** as yellow crystals (1.55 g, 1.05 mmol, 82% yield). ^1H NMR (400 MHz, C_6D_6 , $22\text{ }^{\circ}\text{C}$, δ/ppm): -0.96 to -0.83 (m, 4H, $\text{YCH}_2\text{SiMe}_3$), -0.18 to -0.15 (d, 18H, $\text{YCH}_2\text{SiMe}_3$), $0.01\text{--}0.03$ (d, 18H, CH_2SiMe_3), $0.56\text{--}0.69$ (m, 12H, CHMe_2 in oxazoline), $0.86\text{--}0.90$ (t, 4H, CH_2SiMe_3), $1.19\text{--}1.40$ (m, 12H, CHMe_2 in new five ring), 2.39 (m, 4H, CHMe_2), $3.17\text{--}3.45$ (m, 4H, CH_2 in new five ring), $3.66\text{--}3.75$ (m, 2H, CH in new five ring), $3.95\text{--}4.28$ (m, 4H, CH_2 in oxazoline), $4.81\text{--}4.93$ (m, 2H, CH in oxazoline), $6.58\text{--}8.17$ (m, 16H, ArH). ^{13}C NMR (C_6D_6 , $25\text{ }^{\circ}\text{C}$, δ/ppm): -0.8 (CH_2SiMe_3), 4.5 ($\text{YCH}_2\text{SiMe}_3$), 14.3 (CHMe_2), 18.6 (CHMe_2), 20.7 , 21.4 , 23.0 , 27.4 (CH_2SiMe_3), 30.0 , 30.2 , 31.4 , 31.9 ($\text{YCH}_2\text{SiMe}_3$), 65.6 , 67.8 , 68.6 ($\text{CHMe}_2 + \text{CH}_2$ in oxazoline and new forming five ring), 70.3 , 72.6 (CH in oxazoline and new forming five ring), 115.1 , 115.8 , 119.6 , 124.9 , 129.8 , 130.5 , 131.8 , 133.0 (ArC), 167.2 , 170.7 (C in oxazoline). Anal. Calcd for $\text{C}_{76}\text{H}_{128}\text{N}_6\text{O}_4\text{Si}_4\text{Y}_2$: C, 61.68; H, 8.72; N, 5.68. Found: C, 62.07; H, 9.27; N, 5.99.

Synthesis of [*o*-(S)-OPA- C_6H_4 -(CH_2SiMe_3) $\text{C}\equiv\text{N}$ -CH(*i*Pr)- CH_2 -O]Tm(CH_2SiMe_3)₂ (4**).** To a colorless THF solution (5 mL) of $\text{Tm}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ (1.47 g, 2.56 mmol) was added a solution of chiral C_2 -symmetric tridentate (S,S)-bis(oxazolinyphenyl)amine ligand (1.00 g, 2.56 mmol) in THF (5.0 mL) at room temperature. The mixture was stirred at room temperature for 3 h. After removal of all volatiles in vacuo, the residue was recrystallized from hexane at $-30\text{ }^{\circ}\text{C}$ to give **4** as yellow crystals (1.66 g, 1.01 mmol, 79% yield). Anal. Calcd for $\text{C}_{76}\text{H}_{128}\text{N}_6\text{O}_4\text{Si}_4\text{Tm}_2$: C, 55.66; H, 7.78; N, 5.12. Found: C, 56.07; H, 7.27; N, 5.02.

Synthesis of [(S,S)-BOPA]Sc(CH_2SiMe_3)]₂[B(C_6F_5)₄] (5**).** To a 3 mL of THF-*d*₈ solution of complex **1** [(S,S)-BOPA]Sc(CH_2SiMe_3)₂ (0.015 g, 25 μmol) was added 1 equiv of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (0.020 g, 25 μmol) in THF-*d*₈ (4 mL) at room temperature. ^1H NMR (400 MHz, THF-*d*₈, $23\text{ }^{\circ}\text{C}$, δ/ppm): -0.53 to -0.38 (m, 2H, $\text{ScCH}_2\text{SiMe}_3$), -0.07 (s, 18H, SiMe_3), $0.74\text{--}0.76$ (d, 6H, CHMe_2),

$0.94\text{--}0.96$ (d, 6H, CHMe_2), 1.65 (s, 2H, $\text{Ph}_3\text{CCH}_2\text{SiMe}_3$), $1.94\text{--}1.98$ (m, 4H, THF- β - CH_2), 3.51 (m, 4H, THF- α - CH_2), $4.45\text{--}4.50$ (t, 2H, CHMe_2), $4.59\text{--}4.61$ (m, 2H, CH in oxazoline), $4.72\text{--}4.76$ (m, 4H, CH_2 in oxazoline), $6.71\text{--}6.73$, $6.79\text{--}6.83$, $6.97\text{--}6.70$, $7.22\text{--}7.26$, $7.86\text{--}7.89$ (m, 8H, ArH), $7.02\text{--}7.03$, $7.06\text{--}7.10$, $7.14\text{--}7.18$ (m, 15H, $\text{Ph}_3\text{CCH}_2\text{SiMe}_3$).

A Typical Procedure for Isoprene (IP) Polymerization by Complexes **1, **2**/[Ph₃C][B(C₆F₅)₄] Binary Systems (Table 1, Entry 1).** In a glovebox, a toluene solution (2.5 mL) of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (0.018 g, 20 μmol) was added to a well-stirred toluene solution (2.55 mL) of complex **1** (0.012 g, 20 μmol) and isoprene (0.55 g, 8 mmol) at $25\text{ }^{\circ}\text{C}$ in a 50 mL flask. The reaction mixture became viscous rapidly. After 4 h, the flask was taken outside, and the polymerization was quenched by addition of methanol (50 mL, containing 5% butylhydroxytoluene (BHT) as a stabilizing agent). Then the mixture was poured into methanol (100 mL) to precipitate the polymer product. The precipitated polymer was dried under vacuum at $60\text{ }^{\circ}\text{C}$ to a constant weight (0.55 g, 100% yield). The resulting polymer is soluble in THF and chloroform at room temperature.

The isomer contents of the polyisoprene products were calculated from the ^1H and ^{13}C NMR spectra according to the following formula (eqs 1–5):

$$\text{mol 1, 4-IP\%} = \{I_{\text{H1}}/(I_{\text{H1}} + 0.5I_{\text{H2}})\} \times 100 \quad (1)$$

$$\text{mol 3, 4-IP\%} = \{0.5I_{\text{H2}}/(I_{\text{H1}} + 0.5I_{\text{H2}})\} \times 100 \quad (2)$$

in which I_{H1} is the integration of the resonance at 5.13 ppm (one vinyl proton of the 1,4-isoprene unit) and I_{H2} is the integration of the resonance at 4.72 ppm (two vinyl protons of the 3,4-isoprene unit) in the ^1H NMR spectrum.

$$\text{mol cis-1, 4-IP\%} = \{I_{\text{C1}}/(I_{\text{C1}} + I_{\text{C2}} + I_{\text{C3}})\} \times 100 \quad (3)$$

$$\text{mol trans-1, 4-IP\%} = \{I_{\text{C3}}/(I_{\text{C1}} + I_{\text{C2}} + I_{\text{C3}})\} \times 100 \quad (4)$$

$$\text{mol 3, 4-IP\%} = \{I_{\text{C2}}/(I_{\text{C1}} + I_{\text{C2}} + I_{\text{C3}})\} \times 100 \quad (5)$$

in which I_{C1} is the integration of the signals at 23.2 ppm assigned as the methyl carbon of the *cis*-1,4-isoprene unit and I_{C2} is the integration of the signals at 18.5 ppm assigned as the methyl carbon of the 3,4-isoprene unit, while I_{C3} is the integration of the signals at 15.9 ppm assigned as the methyl carbon of the *trans*-1,4-isoprene unit in the ^{13}C NMR spectrum.

A Typical Procedure for Isoprene (IP) Polymerization by Complexes **1, **2**/[Ph₃C][B(C₆F₅)₄]/Al*i*Bu₃ Ternary Systems (Table 2, Entry 4).** In a glovebox, a toluene solution (2.5 mL) of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (0.018 g, 20 μmol) was added to a well-stirred toluene solution (2.5 mL) of complex **1** (0.012 g, 20 μmol), Al*i*Bu₃ (36 μL , 1.1M, 50 μmol), and isoprene (1.09 g, 16 mmol) at $25\text{ }^{\circ}\text{C}$ in a 50 mL flask. The reaction mixture became viscous rapidly. After 5 h, the flask was taken outside and the polymerization was quenched by addition of methanol (50 mL, containing 5% butylhydroxytoluene (BHT) as a stabilizing agent). Then the mixture was poured into methanol (100 mL) to precipitate the polymer product. The precipitated polymer was dried under vacuum at $60\text{ }^{\circ}\text{C}$ to a constant weight (1.09 g, 100% yield). The resulting polymer is soluble in THF and chloroform at room temperature.

X-ray Crystallographic Analysis. A crystal was sealed in oil under a microscope in the glovebox. Data collections were performed at $-100\text{ }^{\circ}\text{C}$ on a Bruker Smart-Apex CCD diffractometer with a CCD area detector using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structures were solved by using SHELXTL-97 program. Refinements were performed on F₂ anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The analytical scattering factors for neutral atoms were used throughout the analysis. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the

parameters. The residual electron densities were of no chemical significance. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-917207 (1), 917205 (2), and 917206 (4) and contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ ASSOCIATED CONTENT

■ Supporting Information

Figures showing XRD, GPC, DSC, and NMR (^1H and ^{13}C) spectra of representative polymer products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: xfli@bit.edu.cn (X.L.); swzhang@bit.edu.cn (S.Z.); Fax (+) (86)10-68914780.

Author Contributions

[†]H.L. and J.H. contributed equally to this paper.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was partly supported by the National Natural Science Foundation of China (No. 20974014, 21274012) and the 111 project (B07012).

■ REFERENCES

- (1) Selected reviews on 1,3-diene polymerization: (a) Shen, Z.; Ouyang, J. In *Handbook of the Physics and Chemistry of Rare Earths*; Gschneidner, K., Fleming, L., Eds.; Elsevier: Amsterdam, 1987; p 61. (b) Porri, L.; Giarrusso, A. In *Comprehensive Polymer Science*; Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon: Oxford, 1989; Vol. 4, p 53. (c) Taube, R.; Sylvester, G. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; Wiley-VCH: Weinheim, 1996; Vol. 1, p 280. (d) Hou, Z.; Wakatsuki, Y. *Coord. Chem. Rev.* **2002**, *231*, 1–22. (e) Friebe, L.; Nuyken, O.; Obrecht, W. *Adv. Polym. Sci.* **2006**, *204*, 1–154. (f) Fischbach, A.; Anwender, R. *Adv. Polym. Sci.* **2006**, *204*, 155–281.
- (2) (a) *Biopolymers, Polyisoprenoids*; Koyama, E., Steinbuchel, A., Eds.; Wiley-VCH: Weinheim, 2001; Vol. 2. (b) Song, J.; Huang, B.; Yu, D. *J. Appl. Polym. Sci.* **2001**, *82*, 81–89. (c) Zhao, Y.; Huang, B.; Yao, W.; Cong, H.; Shao, H.; Du, A. *J. Appl. Polym. Sci.* **2008**, *107*, 2986–1993.
- (3) For examples of *cis*-1,4-polymerization of isoprene, see: (a) Scott, K. W. *Rubber Plast. Age* **1961**, *42*, 175. (b) Shen, Z.; Ouyang, J.; Wang, F.; Hu, Z.; Yu, F.; Qian, B. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 3345–3357. (c) Kwag, G.; Lee, H.; Kim, S. *Macromolecules* **2001**, *34*, 5367–5369. (d) Evans, W. J.; Giarikos, D. G. *Organometallics* **2001**, *20*, 5751–5758. (e) Evans, W. J.; Giarikos, D. G. *Macromolecules* **2004**, *37*, 5130–5132. (f) Fischbach, A.; Klimpel, M.; Widenmeyer, M.; Herdtweck, E.; Scherer, W.; Anwender, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 2234–2239. (g) Kaita, S.; Doi, Y.; Kaneko, K.; Horiuchi, A. C.; Wakatsuki, Y. *Macromolecules* **2004**, *37*, 5860–5862. (h) Arndt, S.; Beckerle, K.; Zeimentz, P. M.; Spaniol, T. P.; Okuda, J. *Angew. Chem., Int. Ed.* **2005**, *44*, 7473–7477. (i) Ajellal, N.; Furlan, C. M.; Casagrande, O. L., Jr.; Carpentier, J.-F. *Macromol. Rapid Commun.* **2006**, *27*, 338–343. (j) Meermann, C.; Törnroos, K.; Nerdal, W.; Anwender, R. *Angew. Chem., Int. Ed.* **2007**, *46*, 6508–6513. (k) Zhang, L.; Suzuki, T.; Luo, Y.; Nishiura, M.; Hou, Z. *Angew. Chem., Int. Ed.* **2007**, *46*, 1909–1913. (l) Zhang, L.; Nishiura, M.; Yuki, M.; Luo, Y.; Hou, Z. *Angew. Chem., Int. Ed.* **2008**, *47*, 2642–2645. (m) Gao, W.; Cui, D. *J. Am. Chem. Soc.* **2008**, *130*, 4984–4991.
- (4) For examples of *trans*-1,4-polymerization of isoprene, see: (a) Jenkins, D. K. *Polymer* **1985**, *26*, 147–151. (b) Baudry-Barbier, D.; Andre, N.; Dormond, A.; Pardes, C.; Richard, P.; Visseaux, M.; Zhu, C. *Eur. J. Inorg. Chem.* **1998**, 1721–1727. (c) Bonnet, F.; Visseaux, M.; Pereira, A.; Bouyer, F.; Barbier-Baudry, D. *Macromol. Rapid Commun.* **2004**, *25*, 873–877. (d) Bonnet, F.; Visseaux, M.; Barbier-Baudry, D.; Vigier, E.; Kubicki, M. M. *Chem.—Eur. J.* **2004**, *10*, 2428–2434. (e) Bonnet, F.; Visseaux, M.; Pereira, A.; Barbier-Baudry, D. *Macromolecules* **2005**, *38*, 3162–3169. (f) Visseaux, M.; Terrier, M.; Mortreux, A.; Roussel, P. C. R. *Chim.* **2007**, *10*, 1195–1199. (g) Milione, S.; Cuomo, C.; Capacchione, C.; Zannoni, C.; Grassi, A.; Proto, A. *Macromolecules* **2007**, *40*, 5638–5643. (h) Zimmermann, M.; Törnroos, K. W.; Anwender, R. *Angew. Chem., Int. Ed.* **2008**, *47*, 775–778. (i) Zimmermann, M.; Törnroos, K. W.; Sitzmann, H.; Anwender, R. *Chem.—Eur. J.* **2008**, *14*, 7266–7277. (j) Litlabo, R.; Enders, M.; Törnroos, K. W.; Anwender, R. *Organometallics* **2010**, *29*, 2588–2595. (k) Yang, Y.; Lv, K.; Wang, L.; Wang, Y.; Cui, D. *Chem. Commun.* **2010**, 46, 6150–6152. (l) Liu, D.; Cui, D. *Dalton Trans.* **2011**, 40, 7755–7761. (m) Rong, W.; Liu, D.; Zuo, H.; Pan, Y.; Jian, Z.; Li, S.; Cui, D. *Organometallics* **2013**, *32*, 1166–1175.
- (5) (a) Brintzinger, H. H.; Fischer, D.; Mulhaupt, R.; Riger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed.* **1995**, *34*, 1143–1170. (b) Coats, G. W. *Chem. Rev.* **2000**, *100*, 1223–1252.
- (6) Selected reviews for rare earth metal complex: (a) Asinall, H. C. *Chem. Rev.* **2002**, *102*, 1807–1850. (b) Piers, W. E.; Emslie, D. J. H. *Coord. Chem. Rev.* **2002**, *131*, 233–234. (c) Mountford, P.; Ward, B. D. *Chem. Commun.* **2003**, 1797–1803. (d) Gromada, J.; Carpentier, J. F.; Mortreux, A. *Coord. Chem. Rev.* **2004**, *248*, 397–410. (e) Zeimentz, P. M.; Arndt, S.; Elvidge, B. R.; Okuda, J. *Chem. Rev.* **2006**, *106*, 2404–2433. (f) Nishiura, M.; Hou, Z. *Nat. Chem.* **2012**, *2*, 257–268.
- (7) There are only three well-defined (S,S)-bis(oxazolinylphenyl) amido organometallic complexes based on Pd, Fe, Co. (a) Inagaki, T.; Ito, A.; Ito, J.; Nishiyama, H. *Angew. Chem., Int. Ed.* **2010**, *49*, 9384–9387. (b) Inagaki, T.; Phong, L. T.; Furuta, A.; Ito, J.; Nishiyama, H. *Chem.—Eur. J.* **2010**, *16*, 3090–3096. (c) Kieltisch, L.; Dubinina, G. G.; Hamacher, C.; Kaiser, A.; Torres-Nieto, J.; Hutchison, J. M.; Klein, A.; Budnikova, Y.; Vicić, D. A. *Organometallics* **2010**, *29*, 1451–1456.
- (8) (a) McManus, H. A.; Guiry, P. J. *J. Org. Chem.* **2002**, *67*, 8566–8573. (b) Lu, S.-F.; Du, D.-M.; Zhang, S.-W.; Xu, J. *Tetrahedron: Asymmetry* **2004**, *15*, 3433–3441. (c) Du, D.; Lu, S.; Fang, T.; Xu, J. *J. Org. Chem.* **2005**, *70*, 3712–3715. (d) Lu, S.; Du, D.; Xu, J. *Org. Lett.* **2006**, *8*, 2115–2118. (e) Lu, S.; Du, D.; Xu, J.; Zhang, S. *J. Am. Chem. Soc.* **2006**, *128*, 7418–7419. (f) Nishiyama, H.; Furuta, A. *Chem. Commun.* **2007**, 760–762. (g) Torres-Nieto, J.; Hutchison, J. M.; Klein, A.; Budnikova, Y.; Vicić, D. A. *Organometallics* **2010**, *29*, 1451–1456. (h) Inagaki, T.; Phong, L. T.; Furuta, A.; Ito, J.; Nishiyama, H. *Chem.—Eur. J.* **2010**, *16*, 3090–3096.
- (9) (a) McManus, H. A.; Guiry, P. J. *J. Org. Chem.* **2002**, *67*, 8566–8573. (b) Lu, S. F.; Du, D. M.; Zhang, S. W.; Xu, J. *Tetrahedron: Asymmetry* **2004**, *15*, 3433–3441. (c) Arndt, S.; Spaniol, T. P.; Okuda, J. *Angew. Chem., Int. Ed.* **2003**, *42*, 5075. (d) Luo, Y.; Baldamus, J.; Hou, Z. *J. Am. Chem. Soc.* **2004**, *126*, 13910. (e) Li, X.; Baldamus, J.; Hou, Z. *Angew. Chem., Int. Ed.* **2005**, *44*, 962.
- (10) Such alkyl alkylation was also observed in other alkyl complexes based on rare earth metals, main-group metals Al, Mg, Zn, and the transition metals Zr, Hf, Ni. For examples, see: (a) Klerks, J. M.; Stufkens, D. J.; Van Koten, G.; Vrieze, K. *J. Organomet. Chem.* **1979**, *181*, 271–283. (b) Kaim, W. *Acc. Chem. Res.* **1985**, *18*, 160–166. (c) Kaupp, M.; Stoll, H.; Preuss, H.; Kaim, W.; Stahl, T.; vanKoten, G.; Wissing, E.; Smeets, W. J. J.; Spek, A. L. *J. Am. Chem. Soc.* **1991**, *113*, 5606–5618. (d) Bruce, M.; Gibson, V. C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 18, 2523–2538. (e) Clenthsmith, G. K. B.; Gibson, V. C.; Hitchcock, P. B.; Kimberley, B. S.; Rees, C. W. *Chem. Commun.* **2002**, 14, 1498–1499. (f) Scott, J.; Gambarotta, S.; Korobkov, I.; Budzelaar, P. H. M. *J. Am. Chem. Soc.* **2005**, *127*, 13019–13029. (g) Blackmore, I. J.; Gibson, V. C.; Hitchcock, P. B.; Rees, C. W.; Williams, D. J.; White, A. J. P. *J. Am.*

Chem. Soc. **2005**, *127*, 6012–6020. (h) De Waele, P.; Jazdzewski, B. A.; Klosin, J.; Murray, R. E.; Theriault, C. N.; Vosejka, P. C.; Petersen, J. L. *Organometallics* **2007**, *26*, 3896–3899. (i) Olson, J. A.; Boyd, R.; Quail, J. W.; Foley, S. R. *Organometallics* **2008**, *27*, 5333–5338. (j) Tsurugi, H.; Ohnishi, R.; Kaneko, H.; Panda, T. K.; Mashima, K. *Organometallics* **2009**, *28*, 680–687. (k) Du, G.; Wei, Y.; Ai, L.; Chen, Y.; Xu, Q.; Liu, X.; Zhang, S.; Hou, Z.; Li, X. *Organometallics* **2011**, *30*, 160–170.