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Cis-1,4-Polymerization of Isoprene by 1,3-Bis(oxazolinymethylidene)isoindoline Ligated Rare Earth Metal Dialkyl Complexes

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Abstract: A series of novel chiral nonmetallocene pincer-type rare earth metal dialkyl complexes bearing the chiral monoanionic tridentate C_2-symmetric 1,3-bis(oxazolinymethylidene)isoindoline (BOXMI) ligand (BOXMI)Ln(CH_2SiMe_3)$_2$ **1–3** (**1**: Ln = Sc, yield = 57%; **2**: Ln = Lu, yield = 55%; **3**: Ln = Y, yield = 62%) have been prepared in moderate yields via the acid-base reaction between the BOXMI ligand and rare earth metal tri(trimethylsilylmethyl) complexes. The X-ray diffractions show that both of the complexes **1** and **2** contain one BOXMI ligand and two trimethylsilylmethyl ligands, adopting a distorted-trigonal-bipyramidal configuration. In the presence of cocatalyst such as borate and AlR_3, these complexes **1–3** exhibit high activities up to 6.8×10^4 (g of polymer)/(mol$_{Ln}$ h) and high *cis*-1,4-selectivities up to 97%) in the polymerization of isoprene in toluene, yielding the *cis*-1,4-polyisoprenes with high molecular weights (M_n up to 710000 g/mol) and bimodal molecular weight distributions (M_w/M_n = 2.0–4.5).

Keywords: rare earth metal complexes; 1,3-bis(oxazolinymethylidene)isoindoline ligand; polymerization; isoprene; *cis*-1,4-selectivity.

1. Introduction

The development of highly efficient and selective organometallic catalysts is a permanent topic for the olefin polymerization, which brings new opportunities for the synthesis of high-performance (co)polymers with precisely controlled structures and excellent properties [1–6]. Recently, *cis*-1,4-polyisoprene (CPIP) has attracted much attentions from the academia and industry in view that it is the principal component of natural rubber and serves as strategically important elastomer used for pneumatic tires [7–12]. In general, the practical and most used synthesis method of CPIP is the coordinative-insertive polymerization of IP by using the homogeneous organometallic catalysts based on rare earth metals [13–19]. So far, a large number of the rare earth metal catalyst precursors bearing different chelating ligand have been reported for the *cis*-1,4-polymerization of IP [20–28]. Among them, the nonmetallocene pincer-type rare earth metal complexes bearing the monoanionic tridentate C_2-symmetric ligands usually exhibit both high activities and high *cis*-1,4-selectivities in the polymerization of IP [29–30] (Chart 1). In 2007, the rare earth metal alkyl complexes bearing a bis(phosphinophenyl)amido (PNP) ligand were reported by Hou et al., which showed high activities up to 4.9 × 10^5 (g of polymer)/(mol_{Ln} h) and high *cis*-1,4-selectivities up to 99% in the living *cis*-1,4-polymerization of isoprene [31]. In 2008, the aryldiimine (NCN) ligated rare earth metal dichlorides were developed by Cui et al. These complexes can serve as catalyst precursors in the *cis*-1,4-polymerization of isoprene with high activities up to 4.1 × 10^5 (g of polymer)/(mol_{Ln} h) and high *cis*-1,4 selectivities ca. 98.8% [32]. Subsequently, Cui also reported the *cis*-1,4-polymerization of isoprene by using the bis(carbene)phenyl (CCC) rare earth metal dibromides (activities up to 1.3 × 10^5 (g of polymer)/(mol_{Ln} h) and *cis*-1,4-selectivities up to 99.6%) [33], the bis(phosphino)carbazolide (PNP) chelated rare earth metal complexes (activities up to 8.2 × 10^5 (g of polymer)/(mol_{Ln} h), *cis*-1,4-selectivities up to 99%) [34], and the bis(pyrrolidin-1-yl)pyrrolyl or bis(piperidino)methylene) pyrrolyl [NNN] ligated rare earth metal complexes (activities ca. 2.7 × 10^4 (g of polymer)/(mol_{Ln} h) and *cis*-1,4-selectivities ca. 94.1%) [35]. In 2013, Lv described the *cis*-1,4-polymerization of isoprene by use of the bis(oxazolinyl)phenyl (NCN) ligated rare earth metal dichlorides with the activities up to 4.1 × 10^5 (g of polymer)/(mol_{Ln} h) and *cis*-1,4-selectivities up to 99.5% [36]. By contrast, the rare earth metal complexes bearing pincer-type NNN ligand exhibited unsatisfactory activity (< 10^5 (g of polymer)/(mol_{Ln} h)) and *cis*-1,4-selectivity (< 94%) in the polymerization of IP [37]. Therefore, it is of great interest to develop higher efficient and selective NNN chelated rare earth metal complexes for the *cis*-1,4-polymerization of IP.

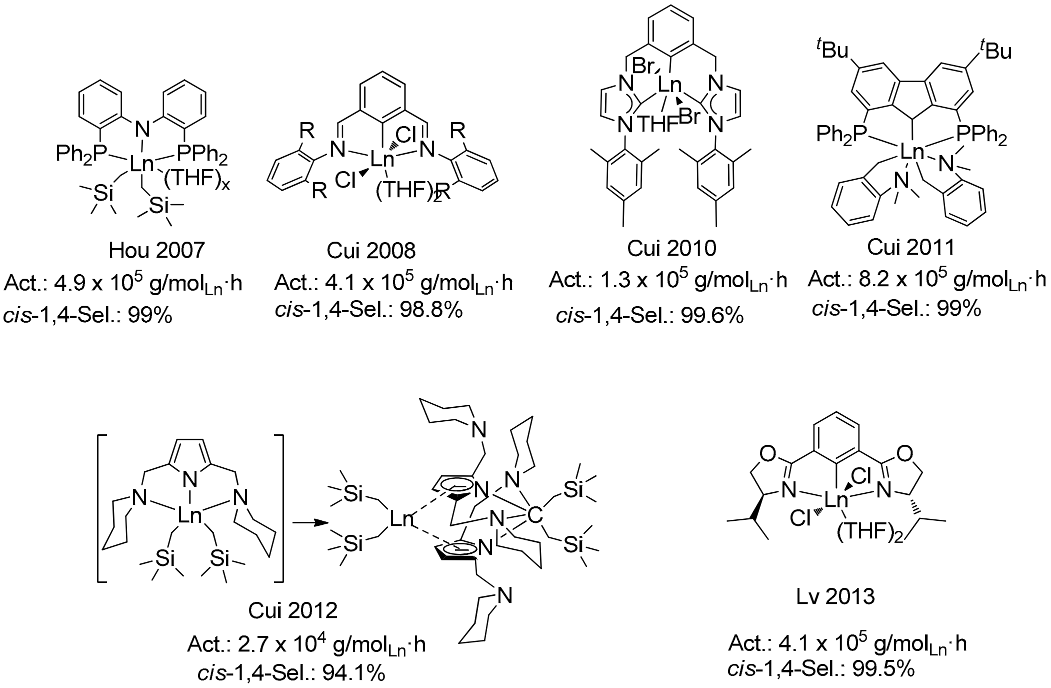

Chart 1. The previous pincer-type rare earth metal catalysts bearing tridentate C_2-symmetric chelating ligand.

Recently, we have paid attention to the synthesis of the NNN-ligated rare earth metal dialkyl complexes and their applications in the IP polymerization. In 2013, we reported the synthesis of a series of chiral (S,S)-bis(oxazolinylphenyl)amine ((S,S)-BOPA) ligated rare earth metal dialkyl complexes [(S,S)-BOPA]Ln(CH_2SiMe_3)$_2$ (**1**–**2**) (**1**: Ln = Sc; **2**: Ln = Lu). In the presence of activator with or without a small amount of Al^{i}Bu$_3$, the dialkyl complexes **1** and **2** exhibited very high activities up to 6.8 × 10^5 (g of polymer)/(mol_{Ln} h) and *trans*-1,4-selectivities up to 100% in the quasi-living polymerization of isoprene, yielding the *trans*-1,4-PIPs with moderate molecular weights (M_n = (0.2–

1.0) × 10^5 g/mol) and narrow molecular weight distributions (M_w/M_n = 1.02–2.66) [38]. Recently, we also reported that the 1,3-bis(2-pyridylimino)isoindoline ligated rare earth metal dialkyl complexes showed very high activities up to 1.9 × 10^6 (g of polymer)/(mol_{Ln} h) and high *cis*-1,4-selectivities > 99% in the polymerization of isoprene in the presence of activator and AlR_3, affording the CPIP with high molecular weights (M_n up to 610000 g/mol) and narrow to moderate molecular weight distributions (M_w/M_n = 1.26–2.08) [39]. These results demonstrated that the effective adjustment of the skeleton of the pincer-type NNN ligand have an important impact on the catalyst performance of these rare earth metal complexes in the IP polymerization, which arouse our interests to explore more NNN-ligated rare earth metal dialkyl complexes and detect their catalytic performance in the selective polymerization of IP. 1,3-Bis(oxazolinymethylidene)isoindoline (BOXMI) ligand which have both structural characteristics of the (S,S)-bis(oxazolinylphenyl)amine and 1,3-bis(2-pyridylimino)isoindoline ligands is an interesting chiral tridentate C_2-symmetric NNN ligand for the organometallic complex based on transition metals for the asymmetric reaction [40–43]. Until now, the BOXMI ligated rare earth metal complexes have never been reported and their applications for the coordinative-insertive polymerization of olefin have never been investigated as far as we are aware. Herein, we report the synthesis of three pincer-type BOXMI-ligated rare earth metal dialkyl complexes (BOXMI)Ln$(CH_2SiMe_3)_2$ **1–3** (**1**: Ln = Sc; **2**: Ln = Lu; **3**: Ln = Y) via the acid−base reaction between the BOXMI ligand and rare earth metal trialkyl complexes. These complexes **1–3** exhibited high activities up to 6.8 × 10^4 (g of polymer)/(mol_{Ln} h) and high *cis*-1,4-selectivities up to 97% in the IP polymerization in toluene, affording the *cis*-1,4-polyisoprenes with high molecular weights (M_n up to 710000 g/mol) and bimodal molecular weight distributions (M_w/M_n = 2.0–4.5).

2. Materials and Methods

2.1 Materials

All catalysts and the polymerization Procedure were carried out in a nitrogen-filled MBraun glovebox. $[Ph_3C][B(C_6F_5)_4]$, $[PhMe_2NH][B(C_6F_5)_4]$, and $B(C_6F_5)_3$ were purchased from Tosoh Finechem Corporation. $LiCH_2SiMe_3$ (1.0 M solution in pentane) and $LnCl_3$ were purchased from Aldrich. Al^iBu_3 (1.1 M solution in hexane), $AlMe_3$ (1.0 M solution in Toluene), $AlEt_3$ (0.6 M solution in heptane), Phthalimides, (Carbethoxymethylene)triphenylphosphorane, (*S*)-amino alcohol, NaH, , PPh_3, Et_3N, CCl_4, Na_2SO_4, CaH_2, dichloromethane, petroleum ether, and methanol were obtained from Energy Chemistry. The 1,3-bis(oxazolinymethylidene)isoindolines (Boxmi) ligand [40] and $Ln(CH_2SiMe_3)_3(THF)_2$ [44] were prepared according to the literature. Isoprene were purchased form Aldrich and TCI, and dried through CaH_2. Toluene, THF, and hexane were purified by a solvent purification system (SPS-800, Mbraun), and dried over Na in the glovebox. The deuterated solvents C_6D_6 (99.6 atom% D) and $CDCl_3$ (99.8 atom% D) were purchased from Cambridge Isotope.

2.2 Method

The Samples of rare earth metal complexes were prepared in the glovebox using J. Young valve NMR tubes for NMR spectroscopic measurements. ^1H, ^{13}C NMR spectra of catalyst precursors were tested on an AVANCE 400 spectrometer in C_6D_6 at room temperature. ^1H, ^{13}C NMR spectra of polyisoprene samples obtained in this paper were tested on an AVANCE 400 spectrometer at room temperature with $CDCl_3$ as a solvent. Elemental analyses were performed on an Elementary Vario MICRO CUBE (Germany). The molecular weights and the molecular weight distributions (*PDI* =

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M_w/M_n) of the polyisoprene samples were performed at 40 °C by gel permeation chromatography (GPC) on a WATERS 1515 apparatus. THF was employed as the eluent at a flow rate of 1 mL/min. The calibration was made by polystyrene standard EasiCal PS-1 (PL Ltd). Differential scanning calorimetry (DSC) measurements were conducted on a TA 60 (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.

2.3 X-ray Crystallographic Analysis.

The crystals of complex **1** and **2** were sealed in oil under a microscope in the glove box. Data collections were performed on a Bruker Smart-Apex CCD diffractometer with a CCD area detector using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at –100 °C. The determination of crystal class and unit cell parameters was carried out by the SMART program package [45]. The raw frame data were processed using SAINT [46] and SADABS [47] to yield the reflection data file. The structures were solved by using SHELXTL-97 program [48]. Refinements were performed on F2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. All non-hydrogen atoms were refined anisotropically, 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-1539945 (**1**), 1536645 (**2**) contain 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 Chiral BOXMI-Ligated Rare Earth Metal Dialkyl Complexes.

Synthesis of BOXMI-ligated rare earth metal dialkyl complex (BOXMI)Sc($CH_2SiMe_3)_2$ (1). To a colorless toluene solution (8 mL) of Sc($CH_2SiMe_3)_3(THF)_2$ (208 mg, 0.461 mmol) was added a solution of the 1,3-bis(oxazolinymethylidene)isoindolines (BOXMI) ligand (200 mg, 0.461 mmol) in toluene (10.0 mL) at room temperature. The mixture was stirred at room temperature for 4 h. After removal of all volatiles in vacuo, the residue was recrystallized from toluene/hexane at –30 °C to give **1** (171 mg, yield as 57%). ^{1}H NMR (400 MHz, C_6D_6) δ: 7.25–7.23 (m, 6H,), 7.18–7.14 (m, 4H), 7.11–7.09 (m, 2H), 5.79 (s, 2H), 5.56 (dd, 2H, J = 4 Hz, 8 Hz), 4.27 (t, 2H, J = 8 Hz), 3.91 (dd, 2H, J = 4 Hz, 8 Hz), 0.17 (d, 2H, J = 12 Hz,), 0.02 (s, 18H, $CH_2Si(CH_3)_3$), –0.54 (d, 2H, J = 12 Hz,). ^{13}C NMR (100 MHz, C_6D_6) δ 173.71, 162.61, 142.62, 138.31, 130.10, 129.41, 128.63, 127.93, 121.10, 82.76, 75.81, 69.71 3.46. Anal. Calcd (%) for $C_{36}H_{44}N_3O_2ScSi_2$: C, 60.33; H, 6.80; N, 6.45. Found: C, 60.31; H, 6.78; N, 6.46.

Synthesis of BOXMI-ligated rare earth metal dialkyl complex (BOXMI)Lu($CH_2SiMe_3)_2$ (2). To a colorless toluene solution (5 mL) of Lu($CH_2SiMe_3)_3(THF)_2$ (268 mg, 0.461 mmol) was added a solution of 1,3-bis(oxazolinymethylidene)isoindoline (BOXMI) ligand (200 mg, 0.461 mmol) in toluene (10.0 mL) at room temperature. The mixture was stirred at room temperature for 4 h. After removal of all volatiles in vacuo, the residue was recrystallized from toluene/hexane at –30 °C to give **2** (198 mg, yield ca. 55%). ^{1}H NMR (400 MHz, C_6D_6) δ: 7.17–7.12 (m, 10H), 7.09–7.07 (m, 2H), 6.92–6.90 (m, 2H), 5.72 (s, 2H), 5.41 (dd, 2H, J = 4 Hz, 8Hz), 4.19 (t, 2H, J = 8 Hz), 3.84 (dd, 2H, J = 4 Hz, 8Hz), 0.05 (s, 18H), –0.62 (d, 2H, J = 12 Hz), –1.44 (d, 2H, J = 12 Hz). ^{13}C NMR (100 MHz, C_6D_6) δ: 170.81,

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163.41, 141.92, 138.85, 130.06, 129.48, 128.81, 127.97, 121.08, 82.50, 75.65, 68.91, 43.56, 4.00. Anal. Calcd (%) for $C_{36}H_{44}N_3O_2LuSi_2$: C, 55.30; H, 5.67; N, 5.37. Found: C, 55.32; H, 5.71; N, 5.41.

Synthesis of BOXMI-ligated rare earth metal dialkyl complex (BOXMI)Y(CH_2SiMe_3)$_2$ (3). To a colorless toluene solution (5 mL) of Y(CH_2SiMe_3)$_3$(THF)$_2$ (228 mg, 0.461 mmol) was added a solution of the 1,3–bis(oxazolinymethylidene)isoindoline (BOXMI) ligand (200 mg, 0.461 mmol) in toluene (10.0 mL) at room temperature. The mixture was stirred at room temperature for 4 h. After removal of all volatiles in vacuo, the residue was recrystallized from toluene/hexane at –30 °C to give **3** (199 mg, yield ca. 62%). ^{1}H NMR (400 MHz, C_6D_6) δ 7.18–7.12 (m, 12H), 7.09–7.07 (m, 2H), 6.92–6.89 (m, 2H), 5.72 (s, 2H), 5.40 (dd, 2H, *J* = 4 Hz, 8Hz), 4.17 (t, 2H, *J* = 8 Hz), 3.81 (dd, 2H, *J* = 4 Hz, 8Hz), 0.05 (s, 18H), –0.41 (d, 2H, *J* = 12 Hz), –1.30 (d, 2H, *J* = 12 Hz). ^{13}C NMR (100 MHz, C_6D_6) δ 170.80, 163.13, 141.73, 138.9, 129.97, 129.56, , 127.97, 121.00, 82.26, 75.35, 68.85, 37.29, 37.08, 3.88. Anal. Calcd (%) for $C_{36}H_{44}N_3O_2YSi_2$: C, 62.14; H, 6.37; N, 6.04. Found: C, 62.10; H, 6.35; N, 6.01.

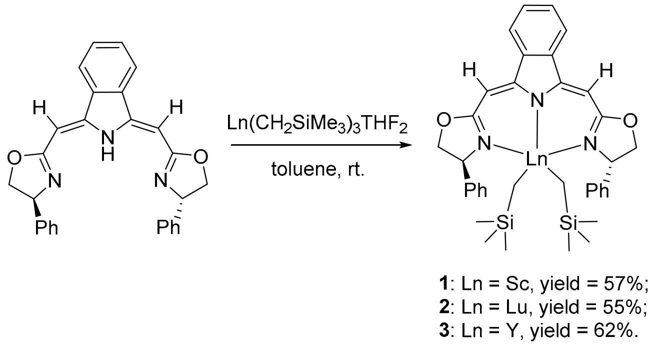
2.5 A Typical Procedure for Isoprene (IP) Polymerization

A detailed polymerization procedure of Entry 1 in Table 2 is described here as a typical example. In a glovebox at 25°C, Al^iBu_3 (181 μL, 1.1 M, 200 μmol) was added to a well-stirred toluene solution (8 mL) in a 50 mL round bottom flask, then complex **1** (0.013 g, 20 μmol), a toluene solution (2.5 mL) of [Ph_3C][$B(C_6F_5)_4$] (0.018 g, 20 μmol), and isoprene (0.27 g, 4 mmol) were added in succession. The reaction mixture became viscous rapidly. After 0.5 h, the flask was taken outside and the polymerization was quenched by addition of ethanol (50 mL, containing 5% butylhydroxytoluene (BHT) as a stabilizing agent). The precipitated polymer was washed with ethanol and dried under vacuum at 40 °C to a constant weight (0.23 g, yield as 85%). The resulting polymer is soluble in THF and chloroform at room temperature. The isomer contents of the polyisoprene products were calculated from the ^{1}H and ^{13}C NMR spectra according to the literature [49].

3. Results and Discussion

*3.1. Synthesis and Structural Characterization of BOXMI-Ligated Rare Earth Metal Dialkyl Complexes **1**–**3**.*

The acid-base reactions of the rare earth metal trialkyl complexes Ln(CH_2SiMe_3)$_3$(THF)$_2$ and 1 equiv. of 1,3-bis(oxazolinymethylidene)isoindoline ligand (BOXMI) straightforwardly yielded the pincer-type NNN-ligated rare earth metal dialkyl complexes (BOXMI)Ln(CH_2SiMe_3)$_2$ **1**–**3** (**1**: Ln = Sc, yield = 57%; **2**: Ln = Lu, yield = 55%; **3**: Ln = Y, yield = 62%) with the moderate yields (Scheme 1).



Scheme 1. Synthesis of BOXMI-ligated rare earth metal dialkyl complexes **1**–**3**.

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These complexes **1–3** have good solubilities in common organic solvents such as hexane, toluene, and THF. In the ^1H NMR spectra of the complexes **1–3** in C_6D_6, all of the proton signals attributed to the NNN ligand except for the proton signal assigned to the N−H group were observed, suggesting the generation of a monoanionic NNN chelating ligand in these complexes. The molar ratio of the integral areas of the signals for the NNN ligand and trimethylsilylmethyl ligand was 1:2 in each case. No THF molecule was detected in either case. Similar to the rigid (S,S)-bis(oxazolinylphenyl)amine ligated rare earth metal dialkyl complexes, all of the methylene protons of the $Ln{-}CH_2SiMe_3$ groups showed two doublets at high field for **1** at 0.16 (d, 2H) and –0.56 ppm (d, 2H), for **2** at –0.62 ppm (d, 2H) and –1.44 (d, 2H), and for **3** at –0.41 ppm (d, 2H) and –1.30 (d, 2H) with a germinal H-H coupling constant of 12 Hz, respectively. These results may suggest that these complexes also have a rigid structure and the CH_2SiMe_3 groups in these complexes are fixed to some extent at the NMR time scale.

*3.2. Single Crystals of Complexes **1** and **2***

In the glovebox, single crystals of the complexes **1** and **2** suitable for an X-ray determination were grown from a mixed toluene/hexane solution at −30 °C. The ORTEP drawings of the complexes **1–2** are shown in Figure 1. The selected bond distances and angles of these complexes **1–2** are summarized in Table 1. The X-ray diffraction study revealed that the dialkyl complexes **1** and **2** are isomorphous and isostructural. Both of these complexes contain one C_2-symmetric monoanionic tridentate NNN ligand and two trimethylsilylmethyl groups, adopting a distorted-trigonal-bipyramidal geometry. Because of the ionic radius of the metal center in a trend of Sc (0.89 Å) < Lu (1.00 Å), the bond distances of the chelating Ln−N(1), Ln−N(2), Ln−N(3), Ln−C(29) as well as Ln−C(33) bond increase in the order of **1** < **2**. The Ln−N(2) bonds of complexes **1** and **2** divide the angles of N(1)−Ln−N(3) (161.8(1)°−166.9(1)°) into two almost equal parts N(1)−Ln−N(2) and N(2)−Ln−N(3) (81.1(1)°−83.9(1)°), implying the N(1), N(2), N(3), and Ln atoms are almost planar.

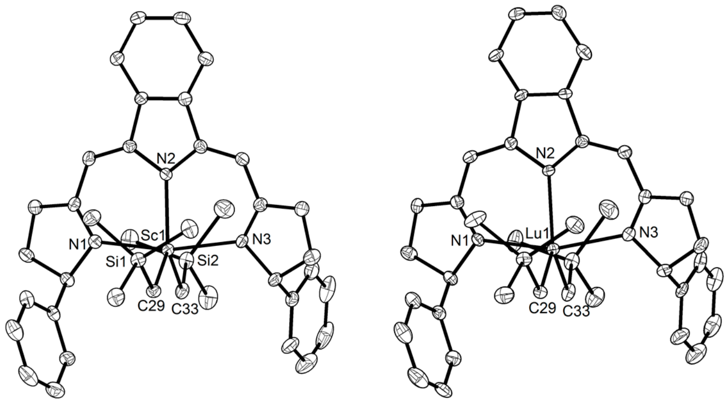


Figure 1. ORTEP drawings of complexes **1**–**2** with thermal ellipsoids with a 30% probability. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) of Complexes **1**–**2**.

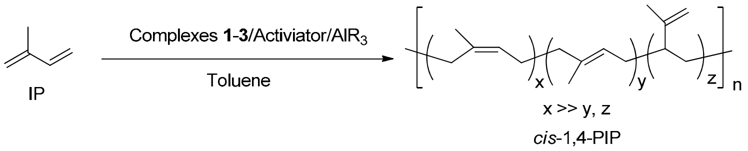
	1	**2**
Ln−N1	2.272(4)	2.345(4)
Ln−N2	2.228(3)	2.313(4)
Ln−N3	2.274(4)	2.351(4)
Ln−C29	2.235(4)	2.329(5)

Ln−C33	2.241(4)	2.333(5)
N1−Ln−N3	166.9(1)	161.8(1)
N2−Ln−N1	83.8(1)	81.1(1)
N2−Ln−N3	83.9(1)	81.4(1)
N2−Ln−C29	118.9(1)	118.9(1)
N2−Ln−C33	126.3(2)	126.3(4)
C29−Ln−N1	98.3(2)	100.5(2)
C29−Ln−N3	91.6(2)	92.2(3)
C29−Ln−C33	114.8(2)	114.7(2)
C33−Ln−N1	88.3(1)	89.1(2)
C33−Ln−N3	95.4(1)	97.4(8)

*3.3. Cis-1,4-Polymerization of Isoprene by the Complexes **1**–**3**/activator/AlR$_3$ Catalytic Systems.*

The neutral complexes **1**–**3** alone and the complexes **1**–**3**/AlR$_3$ binary systems were inactive for the IP polymerization. While the complexes **1**–**3**/activator (such as [Ph$_3$C][B(C$_6$F$_5$)$_4$] (**A**), [PhMe$_2$NH][B(C$_6$F$_5$)$_4$] (**B**), and B(C$_6$F$_5$)$_3$ (**C**)) binary systems showed very low activities in the polymerization of IP. In the presence of both an activator and AlR$_3$, the complexes **1**–**3** could promote the *cis*-1,4-polymerization of IP similar to the 1,3-bis(2-pyridylimino)isoindoline ligated rare earth metal dialkyl complexes [39], affording the *cis*-1,4-polyisoprenes (CPIPs) with high molecular weights (M_n up to 710000 g/mol) and moderate molecular weight distributions (M_w/M_n = 2.0–4.5). Some representative results were summarized in Table 2. As an activator, the trityl borate **A** and the anilinium borate **B** usually exhibited similar activities and *cis*-1,4-selectivities in the IP polymerization, while the neutral borane **C** is inert under the same conditions (Table 2, entries 1–5, 7–10). For the Sc complex **1**, the *cis*-1,4-PIPs obtained by the borate A have higher molecular weights and narrower molecular weight distributions (Table 2, entries 1–2, 4–5). While for the Lu and Y complexes **2**–**3**, the *cis*-1,4-PIPs obtained by the borate **A** also have higher molecular weight but broader molecular weight distribution (Table 2, entries 7–10). Similar to the complex **1**/activator/Al^{i}Bu$_3$ systems, the complex **1**/activator/AlEt$_3$ and the complex **1**/activator/AlMe$_3$ systems also showed moderate activities ca. 3 × 10^3 (g of polymer)/(mol$_{Ln}$ h) and *cis*-1,4-selectivities ca. 88% in the IP polymerization, affording the *cis*-1,4-PIPs with lower molecular weights and broader molecular weight distributions (Table 2, entries 1–6). When the IP polymerization catalyzed by the complex **3**/**A**/Al^{i}Bu$_3$ system was carried out at −20 °C, a PIP with higher *cis*-1,4-selectivity (> 95%), higher molecular weight (M_n = 350000 g/mol), and narrower molecular weight distribution (M_w/M_n = 1.83) could be obtained as shown by the ^{1}H and ^{13}C NMR analysis (Table 2, entry 12). It is noteworthy that the complex **3** exhibited high activities up to 6.8 × 10^4 (g of polymer)/(mol$_{Ln}$ h) when the temperature increased to 70 °C (Table 2, entry 14). Only 0.5 h was needed to completely convert 500 equiv of monomer, producing moderate molecular weight CPIP (*cis*-1,4-selectivity = 85%, M_n = 200000 g/mol) with moderate molecular weight distribution (M_w/M_n = 3.31).

Table 2. *Cis*-1,4-Polymerization of Isoprene by Complexes **1**–**3**/Activator/AlR$_3$ Ternary Systems.[a]



entry	Comp.	Borate[b]	AlR$_3$	t (h)	T (°C)	Y (%)	A[c]	Microstructure (%)[d] c-1,4-	t-1,4-	3,4-	M_n[e] (10^4)	M_w/M_n[e]	T_g[f] (°C)
1	**1**	A	Al^{i}Bu$_3$	0.5	25	85	23	87	2	11	71	2.00	−58
2	**1**	B	Al^{i}Bu$_3$	4	25	96	3	87	0	13	32	2.75	−60
3	**1**	C	Al^{i}Bu$_3$	12	25	–	–	–	–	–	–	–	–
4	**1**	A	AlEt$_3$	4	25	93	3	88	0	12	16	3.18	−59
5	**1**	B	AlEt$_3$	4	25	86	3	88	0	12	13	3.21	−62
6	**1**	A	AlMe$_3$	6	25	92	2	89	1	10	8	4.31	−58
7	**2**	A	Al^{i}Bu$_3$	4	25	93	3	87	0	13	11	3.72	−59
8	**2**	B	Al^{i}Bu$_3$	4	25	85	3	88	0	12	8	4.51	–
9	**3**	A	Al^{i}Bu$_3$	2	25	92	6	93	0	7	16	1.87	−63
10	**3**	B	Al^{i}Bu$_3$	4	25	85	3	90	0	10	10	3.36	−61
11	**3**	A	Al^{i}Bu$_3$	2	0	82	6	95	0	5	25	2.32	−62
12	**3**	A	Al^{i}Bu$_3$	2	−20	80	5	97	1	2	35	1.83	−65
13	**3**	A	Al^{i}Bu$_3$	0.5	50	93	25	87	0	13	16	2.87	−61
14[g]	**3**	A	Al^{i}Bu$_3$	0.5	70	99	68	85	0	13	20	3.31	−59

[a] Conditions unless specified otherwise: 20 μmol of Ln complex, 20 μmol of activator, 10 equiv. of AlR$_3$, 4 mmol of isoprene, 8 mL of toluene. [b] Activator: **A** = [Ph$_3$C][B(C$_6$F$_5$)$_4$]; **B** = [PhNHMe$_2$][B(C$_6$F$_5$)$_4$]; **C** = B(C$_6$F$_5$)$_3$. [c] Activity in (kg of polymer)/(mol$_{Ln}$·h). [d] Determined by ^{1}H and ^{13}C NMR spectrum: *c*-1,4, *cis*-1.4 selectivity; *t*-1,4, *trans*-1.4 selectivity; 3,4, 3,4-selectivity. [e] Determined by GPC in THF at 40 °C against polystyrene standard. [f] Measured by DSC. [g] 10 mmol of isoprene.

The resulting PIPs all showed good solubilities in THF and CHCl$_3$. The ^{1}H NMR spectra of the PIPs obtained by the complex **1**–**3**/activator/AlR$_3$ systems in CDCl$_3$ indicated the main 1,4-microstructure and a trace amount of 3,4-microstructure. The ^{13}C NMR spectra showed diagnostic signals for a main *cis*-1,4 configuration (δ = 23.4, 26.4, 32.2, 125.0, and 135.2 ppm) (*cis*-1,4-PIP selectivity > 90%) and a small amount of 3,4-configuration (δ = 18.6, 26.4, 32.2, 125.0, and 135.2 ppm) with or without a trace amount of *trans*-1,4-configuration (δ = 15.9, 26.4, 32.2, 125.0, and 135.2 ppm) (Figure 2). GPC curves revealed that these PIPs had moderate to high molecular weights in the range of 77000–710000 g/mol and the bimodal molecular weight distributions (M_w/M_n = 2.0–4.5) similar to natural rubber. The DSC curves of the resulting *cis*-1,4-PIPs showed the glass transition temperature in the range of −58 to −65 °C, consistent with the thermoplastic character of the CPIP (see Supporting Information).

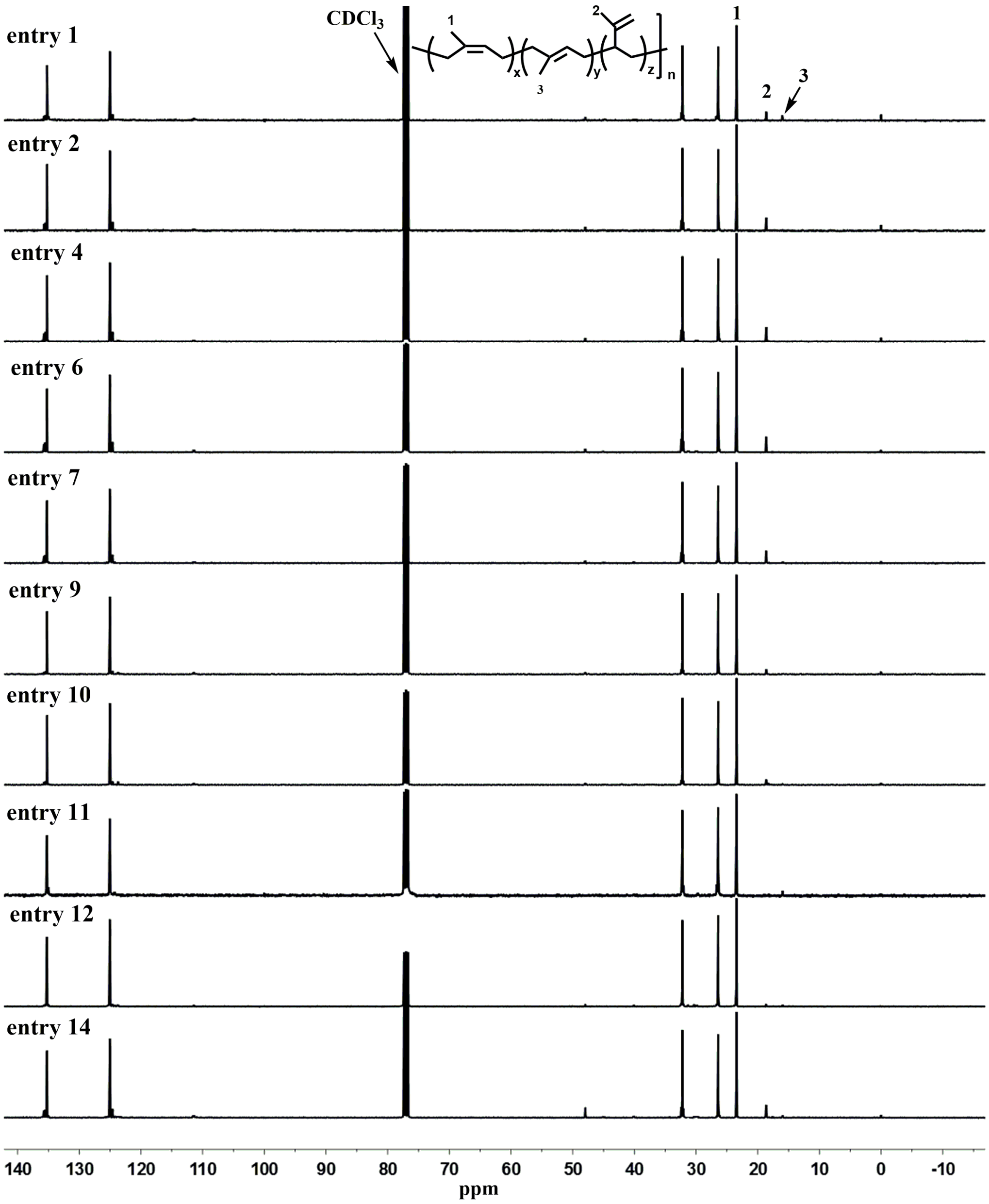


Figure 2. ^{13}C NMR spectra of the polyisoprenes by complexes **1**/AlR$_3$/ Borate systems in Table 2.

4. Conclusions

In summary, the three pincer-type monoanionic tridentate C_2-symmetric BOXMI-ligated rare earth metal dialkyl complexes **1**–**3** have been easily synthesized in moderate yields via one-pot acid-base reaction by using the rare earth metal tris(trimethylsilylmethyl) complexes with the readily available 1,3-bis(oxazolinymethylidene)isoindolines (BOXMI) ligand. The X-ray diffractions demonstrated that the complexes **1** and **2** are isomorphous and isostructural and each of them adopt a distorted-trigonal-bipyramidal configuration. Activated by activator and AlR$_3$ in toluene, these pincer-type BOXMI-ligated complexes **1**–**3** exhibited high activities up to 6.8×10^4 (g of polymer)/(mol$_{\mathrm{Ln}}$ h) and high *cis*-1,4-selectivities up to 97% in the polymerization of isoprene, affording *cis*-1,4-PIPs with high molecular weights (M_n up to 710000 g/mol) and bimodal molecular weight distributions (M_w/M_n = 2.0–4.5). In comparison with the *trans*-1,4-PIPs obtained by the (S,S)-bis(oxazolinylphenyl)amine ligated rare earth metal dialkyl complexes [38] and the *cis*-1,4-PIPs obtained by the 1,3-bis(2-pyridylimino)isoindoline ligated rare earth metal dialkyl complexes [39], such results demonstrate that the main body skeleton of the chelating ligand has more important impact on the catalytic performance of these pincer-type rare earth metal dialkyl complexes in the IP polymerization. Moreover, the rare earth metal dialkyl complexes bearing the pincer-type chelating ligand with the rigid skeleton and the bulky substituents are not good for the *cis*-1,4-polymerization of IP. These findings will benefit the design of the high efficient and selective catalysts as well as the rapid and precise synthesis of natural rubber. Further studies will be focused on the modification of the chelating ligand to improve the selectivity and/or activity of the rare earth metal catalytic system in the *cis*-1,4-polymerization of isoprene.

Supplementary Materials: Supplementary Materials are available online at www.mdpi.com/link

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