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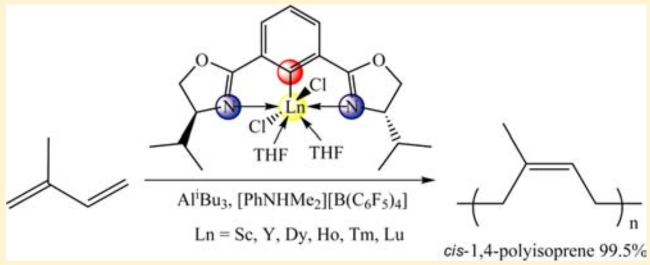
Bis(oxazolinyl)phenyl-Ligated Rare-Earth-Metal Complexes: Highly Regioselective Catalysts for *cis*-1,4-Polymerization of Isoprene

Yu Pan, Tieqi Xu,* Guan-Wen Yang, Kun Jin, and Xiao-Bing Lu*

State Key Laboratory of Fine Chemicals, College of Chemistry, Dalian University of Technology, Dalian 116024, China

Ⓢ *Supporting Information*

ABSTRACT: NCN-pincer (*S,S*)-2,6-bis(4′-isopropyl-2′-oxazolinyl)phenyl-ligated rare-earth-metal dichlorides [(*S,S*)-Phebox-^{i}Pr]$LnCl_2(THF)_2$ (Ln = Sc (**1**); Y (**2**); Dy (**3**); Ho (**4**); Tm (**5**); Lu (**6**)) were synthesized via transmetalation between [(*S,S*)-Phebox-^{i}Pr]Li and $LnCl_3$ in THF solvent. Interestingly, treatment of $LaCl_3$ by the same method generated tris(ligand) lanthanum complex [(*S,S*)-Phebox-^{i}Pr]$_3$La (**7**). Molecular structures of complexes **1**, **2**, **3**, and **7** were established by single-crystal X-ray diffraction study. Pincer ligand (*S,S*)-Phebox-^{i}Pr adopts a κC:κN:κN′ tridentate coordination mode to the central metal ion. Upon activation with $[PhNHMe_2][B(C_6F_5)_4]$ and Al^iBu_3, complexes **2**−**5** exhibited highly catalytic activities and more than 98% *cis*-1,4-selectivity for isoprene polymerization while complexes **1** and **6** were inactive for this reaction. When use of the catalyst system consisted of complex **2**, $[PhNHMe_2][B(C_6F_5)_4]$, and Al^iBu_3 for isoprene polymerization, the resultant polymer has a high *cis*-1,4-selectivity up to 99.5%. The reaction temperature had little effect on the regioselectivity, and high *cis*-1,4-selectivity almost remained even at 80 °C.



■ INTRODUCTION

With advances in the synthetic rubber industry, regioselective polymerization of 1,3-conjugated dienes has attracted much attention in recent decades. It is generally known that high *cis*-1,4-regioselectivity for isoprene polymerization is a prerequisite for obtaining polymers with excellent properties, comparable to natural rubber with nearly 100% *cis*-1,4-regularity.[1] Therefore, much effort has been devoted to develop privileged catalysts to produce polyisoprene with high *cis*-1,4-regularity as well as controlled molecular weight.[2] In particular, some catalyst systems based on rare-earth-metal complexes have been reported to be highly active and *cis*-1,4-selective for isoprene polymerization with less gel formation.[3,4] Earlier reports mainly concerned heterogeneous Ziegler−Natta ternary catalyst systems based on rare-earth-metal chlorides.[5] Subsequently, modified catalyst systems composed of lanthanide carboxylates (or alkoxides) and cocatalysts (aluminum alkyls or aluminum alkyl chlorides) were extensively investigated and further applied to industrial production.[6] Contrary to heterogeneous catalysts with the lack of active-site control, the well-defined structures of single-site homogeneous catalysts are beneficial to mechanistic investigations. It propelled the design of various discrete rare-earth-metal catalysts.[7−15] Representative catalysts are the dialkyl rare-earth-metal complexes bearing an ancillary tridentate ligand bis(phosphinophenyl)amido (PNP) reported by Hou et al.[15] By treating the complexes with one equivalent of borates, the formed cationic alkyl rare-earth-metal species could catalyze not only the living polymerization of isoprene with over 99% *cis*-1,4-selectivity but also the living *cis*-1,4-copolymerization of isoprene and butadiene.

Being different from the difficult handleability of alkyl rare-earth-metal catalysts due to ligand redistribution or thermal instability, rare-earth-metal chloride complexes are more conveniently treated. More recently, Cui et al. reported rare-earth-metal dichlorides stabilized by aryldiimine NCN-pincer ligands,[16a] bis(carbene) CCC-pincer ligands,[16b,c] and β-diketiminato ligands.[16d] These complexes in combination with aluminum alkyls and borates generated the homogeneous Ziegler−Natta catalyst systems, which displayed high activities and distinguished *cis*-1,4-selectivities for polymerization of conjugated dienes. The excellent catalytic performance significantly contributed to the C_2-symmetric geometry of the ligands.[16c,d]

2,6-Bis(2′-oxazolinyl)phenyl (Phebox)[17] as a C_2-geometric NCN-pincer trident ligand has been extensively used in coordination chemistry because of its easy preparation and modification by simple group substitution. To date, numerous Phebox complexes of late transition metals have been widely applied to asymmetric catalysis reactions.[18] Also, transition-metal (Ti, Cr, V, Zr, Hf, Nb) complexes with the Phebox ligand were successfully synthesized via a transmetalation reaction of the corresponding transition-metal chlorides with a Phebox−gold compound.[19] Some of these complexes showed activity for ethylene polymerization by immobilization on $MgCl_2$-based supports.[19] Moreover, rare-earth-metal complexes of oxazoline ligands were found to be active in olefin polymerization.[20] In particular, Gade et al. described that tris(oxazoline)-chelated

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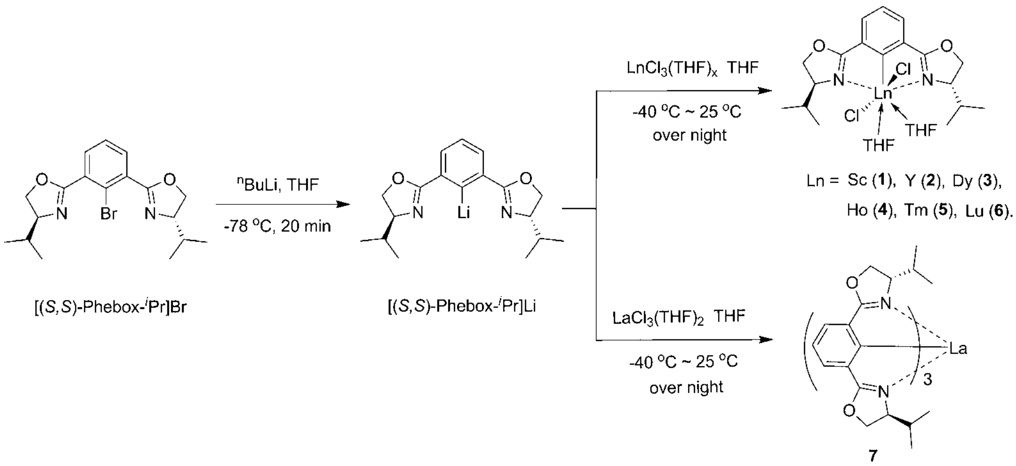
Scheme 1. Synthetic Procedures for Complexes 1−7



rare-earth-metal complexes gave highly isotactic poly(1-hexene).[20a] Herein, we report the synthesis and characterization of a new family of Phebox rare-earth-metal complexes as well as their performance for highly *cis*-1,4-selective polymerization of isoprene.

RESULTS AND DISCUSSION

Synthesis and Characterization. The organolithium species (*S*,*S*)-2,6-bis(4′-isopropyl-2′-oxazolinyl)phenyllithium ([(*S*,*S*)-Phebox-^{i}Pr]Li) was synthesized in situ in THF solution via selective Li−Br exchange of [(*S*,*S*)-Phebox-^{i}Pr]Br.[21,22] Then the lithium salt was added to a THF suspension of rare-earth-metal trichlorides $LnCl_3(THF)_x$, and transmetalation took place. After evaporation, extraction, and filtration, the THF/CH_2Cl_2 mixture solution of raw products was cooled to −30 °C to afford colorless crystals of [(*S*,*S*)-Phebox-^{i}Pr]$LnCl_2(THF)_2$ (Ln = Sc (**1**); Y (**2**); Dy (**3**); Ho (**4**); Tm (**5**); Lu (**6**)) in moderate yields (30−60%) within 24 h, Scheme 1. Application of this method to preparation of the corresponding lanthanum congener was proved to be infeasible. Reaction gave tris(ligand) lanthanum complex **7**, which might be attributed to the larger ionic radius of La^{3+}, which makes the bulkier coordination environment.[23]

The complexes were well characterized by IR spectroscopy analysis. IR spectra show absorption bands of the imine C═N at 1618−1636 cm^{-1}, an obvious red shift in comparison with the pro-ligand.[24a] Complexes **1**, **2**, **6**, and **7** were also characterized by NMR spectra. Resonances of the sp^2 carbon in oxazoline ring are within δ 175.84−176.80 ppm in ^{13}C NMR, indicating that the C═N bonds are not destroyed. In addition, these resonances of C═N bonds move obviously downfield, in comparison with the resonance of [(*S*,*S*)-Phebox-^{i}Pr]Br.[24b] This might be attributed to the nitrogen atoms of oxazoline coordinated to the central metal as donors. ^{13}C NMR spectra of complexes **1**, **2**, **6**, and **7** show typical downfield shifts at δ 193.65, 194.04, 197.4-, and 199.82 ppm, respectively, illustrating formation of the Ln−C bond.[16,25] Due to its instability, complex **7** was characterized by NMR spectra in C_6D_6. NMR spectra revealed the three ligands are magnetically equivalent in the complex. This means formation of a homoleptic rare-earth-metal complex.[26] The solid-state structures of complexes **1**, **2**, **3**, and **7** were further determined by single-crystal X-ray diffraction analysis. Complexes **1**, **2**, and **3** are isostructural monomers with two nitrogen atoms of the oxazolinyl groups, two chlorine atoms, one carbon atom of the benzene ring, and two coordinating THF molecules (Figure 1 for **2**, Figure S4, Supporting Information, for **1**, and Figure S5, Supporting Information, for **3**). The NCN-pincer trident ligand coordinates to the central metal ion in a κC:κN:κN′ tridentate mode to form a meridional conformation. Selected bond lengths and angles of complexes **1**−**3** are listed in Table 1. Cl−Ln−Cl angles of complexes **1**−**3** (172.42−173.95°) are smaller than 176.15° (av) in the aryldiimine NCN-pincer rare-earth-metal complexes,[16a] while the N−Ln−N angles (132.47−137.99°) are larger than 131.07° (av) in those complexes. The Ln^{3+} ion is essentially coplanar with the NCN plane. The solid-state complexes have C_2 symmetry, adopting pentagonal bipyramidal geometry around the central metal. In complexes **1**−**3**, the Ln−C bond lengths vary in a reasonable range from 2.261 to 2.414 Å due to the linkage between a lanthanide ion and a carbon atom. In complex **7**, the lanthanum center is chelated by three ligands, which is nine coordinated by the three carbon atoms of the benzene ring and six nitrogen atoms of the oxazolinyl groups (Figure 2). As a result, complex **7** demonstrates an inner coordination sphere with local C_2 symmetry.

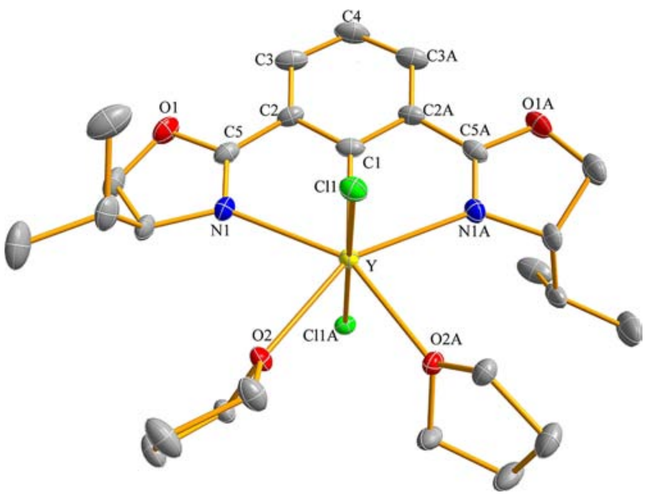


Figure 1. Structure of complex **2** (thermal ellipsoids are drawn at the 30% probability level). Hydrogen atoms and uncoordinated solvent are omitted for clarity.

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Table 1. Selected Bond Lengths (Angstroms) and Angles (degrees) for Complexes 1−3[a]

	1	2	3
Ln−C(1)	2.261(3)	2.414(3)	2.397(11)
Ln−O(2)	2.3758(16)	2.4580(15)	2.469(5)
Ln−N(1)	2.4455(19)	2.5351(18)	2.542(5)
Ln−Cl(1)	2.4644(5)	2.6047(5)	2.6233(17)
C(5)−N(1)	1.280(3)	1.280(3)	1.270(11)
C(5)−C(2)	1.458(4)	1.457(4)	1.476(12)
C(1)−C(2)	1.398(3)	1.397(3)	1.406(10)
C(1)−Ln−O(2)	143.49(4)	143.14(4)	143.26(11)
C(1)−Ln−N(1)	69.00(5)	66.23(5)	66.35(15)
O(2)−Ln−N(1)	74.53(6)	76.95(6)	76.95(18)
C(1)−Ln−Cl(1)	93.023(18)	93.731(17)	93.79(8)
O(2)−Ln−Cl(1)	88.45(4)	86.82(6)	87.64(13)
N(1)−Ln−Cl(1)	90.05(5)	89.70(4)	93.04(15)
Cl(1)−Ln−Cl(1A)	173.95(4)	172.54(3)	172.42(15)
N(1)−Ln−N(1A)	137.99(9)	132.47(9)	132.7(3)

[a]Ln = Sc for **1**, Ln = Y for **2**, Ln = Dy for **3**.

Polymerization of Isoprene. Rare-earth-metal complexes **1−6** were tested for isoprene polymerization under activation with alkylaluminum ($AlMe_3$, $AlEt_3$, Al^iBu_3) and borates ($[Ph_3C][B(C_6F_5)_4]$, $[PhNHMe_2][B(C_6F_5)_4]$, $B(C_6F_5)_3$). Selected polymerization data are summarized in Table 2. These complexes all exhibited excellent *cis*-1,4-selectivity (>98%), while their catalytic activities were strongly dependent on the central metal ion (Table 2, runs 1−6). When activated by Al^iBu_3 and $[PhNHMe_2][B(C_6F_5)_4]$, the Dy complex exhibited the highest activity and finished polymerization within 15 min at 30 °C (Table 2, run 3). Under the same conditions, Y and Ho analogues showed slightly lower activities, giving complete conversion within 30 min (Table 2, runs 2 and 4). In contrast, complexes based on the smaller metals (Sc, Lu) exhibited very low polymerization activities (Table 2, runs 1 and 6). On the basis of the experimental data shown in Table 2, a catalyst activity order was established as follows: **3** (Dy) > **2** (Y) ≈ **4** (Ho) > **5** (Tm) ≫ **6** (Lu) > **1** (Sc). The order is in agreement with the size of the metal ionic radii (Dy (102.7 pm) > Y (101.9 pm) ≈ Ho (101.5 pm) > Tm (99.4 pm) > Lu (97.9 pm) > Sc (87.0 pm)).[23] When complex **2** was chosen as the precursor and $[PhNHMe_2][B(C_6F_5)_4]$ was selected as the cationizing agent, the highest activity was observed by combining $AlEt_3$ (Table 2, run 8)[27] with the relatively poor *cis*-1,4-selectivity (90.7%). In addition, under the same conditions, the activities for polymerization were almost the same as employing $[PhNHMe_2][B(C_6F_5)_4]$ or $[Ph_3C][B(C_6F_5)_4]$ as the cationizing agent, but an obvious decrease was found in the system regarding $B(C_6F_5)_3$ (Table 2, runs 2, 9, and 10). However, no obvious effect on the *cis*-1,4-selectivity was observed,[16d] similar to the conventional Ziegler−Natta system.[28,29]

The catalyst system **2**/$[PhNHMe_2][B(C_6F_5)_4]$/Al^iBu_3 could conduct isoprene polymerization under various monomer to initiator ratios. When the ratio was increased from 500 to 4000, the molecular weights of the resultant polymers increased linearly from 11.7 × 10^4 to 49.9 × 10^4. Meanwhile, the molecular weight distribution and *cis*-1,4-selectivity were almost constant (Table 2, runs 2 and 11−13). Furthermore, this system showed a tolerance of change in the polymerization temperature. While polymerization was performed at elevated temperature, the catalytic activity increased strikingly[30] and the *cis*-1,4-selectivity decreased slightly (96.4%, at 80 °C) (Table 2, runs 2, 15, 16). Lowering the temperature to −8 °C, polymerization had medium activity and up to 99.5% *cis*-1,4-selectivity (Table 2, run 14). It might be reasonably thought that the isomerization reaction of the propagating chain is significantly suppressed at lower temperature.[31] The effect of Al to catalyst ratio on isoprene polymerization was investigated using the system **2**/$[PhNHMe_2][B(C_6F_5)_4]$/Al^iBu_3. The increase of the Al to catalyst ratio significantly reduced the molecular weight of the polymerization products and obviously broadened the molecular weight distribution (Table 2, runs 2

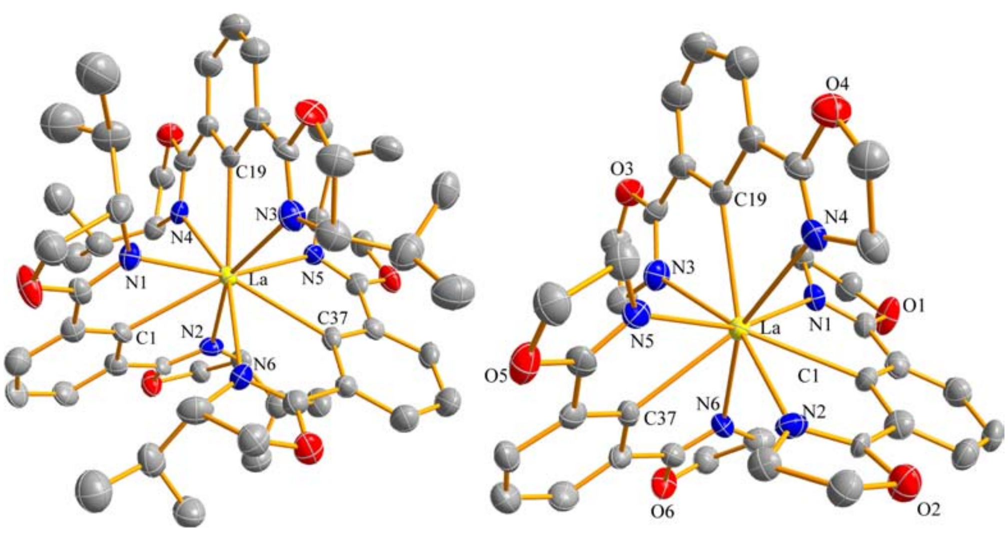

Figure 2. Structure of complex **7** (hydrogen atoms are omitted for clarity; in the right view, ^{i}Pr groups are also omitted; thermal ellipsoids are drawn at the 30% probability level). Selected bond lengths (Angstroms) and angles (degrees): La−C(1) 2.700(6), La−C(19) 2.643(16), La−C37(3) 2.686(16), La−N(1) 2.852(11), La−N(2) 2.815(12), La−N(3) 2.807(13), La−N(4) 2.871(13), La−N(5) 2.872(13), La−N(6) 2.853(14), N(1)−La−N(2) 121.9(4), N(1)−La−N(3) 74.0(4), N(3)−La−N(6) 75.1(4), N(2)−La−N(6) 96.0(4), N(1)−La−N(6) 72.0(4), N(3)−La−N(5) 96.1(4), N(2)−La−N(5) 72.1(4), N(1)−La−N(5) 161.4(4), N(5)−La−N(6) 121.4(4), N(3)−La−N(4) 121.6(4), N(2)−La−N(4) 72.2(4), N(1)−La−N(4) 98.7(3), N(6)−La−N(4) 158.7(4), N(5)−La−N(4) 72.8(3).

Table 2. Polymerization of Isoprene under Various Conditions[a]

run	complex	borate[b]	AlR_3	temp. (°C)	time (min)	yield (%)	M_n[c] ($\times10^4$)	M_w/M_w[c]	microstructure (%)[d] cis- 1,4	trans-1,4	3,4	eff.[e](%)
1	**1** (Sc)	A	^{i}Bu	30	60	trace	nd[f]	nd	nd	nd	nd	nd
2	**2** (Y)	A	^{i}Bu	30	30	100	11.6	2.12	98.6	0.8	0.6	29.3
3	**3** (Dy)	A	^{i}Bu	30	15	100	11.0	2.34	98.9	0.6	0.5	30.9
4	**4** (Ho)	A	^{i}Bu	30	30	100	13.9	3.21	99.2	0.4	0.4	24.5
5	**5** (Tm)	A	^{i}Bu	30	60	78	12.0	3.69	98.3	0.9	0.8	22.1
6	**6** (Lu)	A	^{i}Bu	30	60	7	nd	nd	nd	nd	nd	nd
7	**2** (Y)	A	Me	30	30	100	23.6	1.75	94.8	4.6	0.6	14.4
8	**2** (Y)	A	Et	30	8	100	12.9	1.74	90.7	8.4	0.9	26.3
9	**2** (Y)	B	^{i}Bu	30	30	100	7.4	4.13	97.1	1.6	1.3	45.9
10	**2** (Y)	C	^{i}Bu	30	90	91	8.2	3.14	98.9	0.3	0.8	37.7
11[g]	**2** (Y)	A	^{i}Bu	30	40	100	20.6	1.90	98.1	0.9	1.0	33.0
12[h]	**2** (Y)	A	^{i}Bu	30	40	100	31.1	1.85	98.4	0.7	0.9	43.7
13[i]	**2** (Y)	A	^{i}Bu	30	50	89	49.9	1.78	98.8	0.1	1.1	48.5
14	**2** (Y)	A	^{i}Bu	−8	60	84	57.4	2.26	99.5	0	0.5	5.0
15	**2** (Y)	A	^{i}Bu	50	5	100	10.7	1.65	97.4	1.4	1.2	31.8
16	**2** (Y)	A	^{i}Bu	80	5	86	11.2	2.07	96.4	1.6	2.0	26.1
17[j]	**2** (Y)	A	^{i}Bu	30	30	100	35.5	1.71	99.3	0	0.7	10.0
18[k]	**2** (Y)	A	^{i}Bu	30	30	100	4.9	2.76	96.6	0.9	2.5	69.4
19[l]	**2** (Y)	A	^{i}Bu	30	30	100	2.1	4.65	98.3	0.8	0.9	161.9

[a]Conditions: C_6H_5Cl (3 mL), complex (10 μmol), $[Ln]_0/[B]_0/[AlR_3]_0$ = 1:1:10 (B = borate), [IP]/[Ln] = 500. [b]A: $[PhNHMe_2][B(C_6F_5)_4]$. B: $[Ph_3C][B(C_6F_5)_4]$. C: $B(C_6F_5)_3$. [c]Determined by means of gel permeation chromatography (GPC) against polystyrene standards. [d]Determined by the ^{13}C NMR spectrum of polyisoprene in $CDCl_3$. [e]Catalyst efficiency, calculated by M_n(calcd)/M_n(measd). [f]nd: not determined. [g][IP]/[Ln] = 1000, C_6H_5Cl (5 mL). [h][IP]/[Ln] = 2000, C_6H_5Cl (8 mL). [i][IP]/[Ln] = 4000, C_6H_5Cl (15 mL). [j]$[Ln]_0/[B]_0/[AlR_3]_0$ = 1:1:5. [k]$[Ln]_0/[B]_0/[AlR_3]_0$ = 1:1:20. [l]$[Ln]_0/[B]_0/[AlR_3]_0$ = 1:1:50.

and 17−19). This suggests that Al^iBu_3 plays the role of both cocatalyst to activate the main precursor and chain transfer agent during polymerization.

■ CONCLUSION

We developed highly active and *cis*-1,4-selective isoprene polymerization catalysts with tridentate NCN-pincer ligands. This system provided high activity and excellent *cis*-1,4-selectivity up to 99.5% for polymerization of isoprene. The central metal ion has little effect on the regioselectivity, whereas it has an obvious influence on the catalytic activity. Remarkably, such distinguished catalytic performances remained under broad ranges of monomer to initiator ratios (500−4000) and polymerization temperatures (−8−80 °C).

■ EXPERIMENTAL SECTION

General Methods. All manipulations involving air- and/or water-sensitive compounds were carried out in a glovebox or under dry nitrogen using standard Schlenk techniques. Toluene and tetrahydrofuran (THF) were distilled from sodium/benzophenone under nitrogen, degassed, and stored over fresh Na chips. Monochlorobenzene and *n*-hexane were dried over CaH_2 while stirring for 48 h, distilled before use, and then degassed and stored over 4 Å sieves. Isoprene was dried over CaH_2 while stirring for 48 h and distilled before use. ^{n}BuLi (1.6 M in hexane) was supplied by J&K and used as received. Deuterated benzene (Armar Chem., 99.5 atom % D) was dried over sodium. Deuterated chloroform (J&K, 99.8 Atom % D) was dried over CaH_2. They were all degassed prior to use. $LnCl_3(THF)_x$ (Ln = Sc, Y, La, Dy, Tm, Ho, Lu) were in situ synthesized by adding corresponding $LnCl_3$ to THF and stirring overnight. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX 400 (^{1}H 400 MHz; ^{13}C 101 MHz) or Varian INOVA-400 spectrometer. ^{1}H and ^{13}C NMR chemical shifts were referred to $SiMe_4$ (TMS). NMR assignments were confirmed by ^{1}H−^{13}C HMBC when necessary. The molecular weight and molecular weight distribution of the polymers were measured by Agilent Technologies 1260 Infinity GPC (Column PL gel 5 μm MIXED-C) at 30 °C using THF as an eluent (the flowing rate is 1.0 mL/min) against polystyrene standards. Elemental analyses were performed on an Elementar Vario EL III. IR spectra were recorded with a Nicolet NEXUS FT-IR spectrometer.

(*S*,*S*)-[2,6-Bis(4′-isopropyl-2′-oxazolinyl)phenyl]$ScCl_2(THF)_2$ (1). Under a nitrogen atmosphere, ^{n}BuLi (1.6 M in hexane, 1.00 mL, 1.60 mmol) was added to a THF solution (25 mL) of (*S*,*S*)-2,6-bis(4′-isopropyl-2′-oxazolinyl)phenyl bromide (0.57 g, 1.50 mmol) by syringe at −78 °C. The reaction solution containing in situ prepared lithium salt was stirred for 20 min. Subsequently, it was warmed and added to a THF suspension (15 mL) of $ScCl_3(THF)_3$ (calculated by $ScCl_3$, 0.31 g, 2.00 mmol) at −40 °C. The reaction mixture was allowed to warm to room temperature gradually and stirred overnight. Removal of volatiles under reduced pressure, extracting the residue with toluene, and evaporating the toluene to dryness afforded brown solid. Crude product was crystallized from a THF/CH_2Cl_2 mixture, affording **1** as colorless crystal (0.51 g, 60.8%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.47 (d, J = 7.6 Hz, 2H, *m*-Sc-C_6H_3), 7.15 (t, J = 7.6 Hz, 1H, *p*-Sc-C_6H_3), 4.66 (t, J = 9.3 Hz, 2H, OCH_2CH), 4.53 (t, J = 8.0 Hz, 2H, OCH_2CH), 4.49−4.38 (m, 2H, $CH_2CH(^iPr)N$), 3.85 (br, 8H, THF), 2.33 (m, 2H, $CH(CH_3)_2$), 1.86 (br, 8H, THF), 1.02 (d, J = 6.9 Hz, 6H, $CH(CH_3)_2$), 0.92 (d, J = 6.7 Hz, 6H, $CH(CH_3)_2$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ 193.65 (s, *C*-Sc), 175.84 (s, C═N), 131.20 (s, *o*-Sc-C_6H_3), 127.24 (s, *m*-Sc-C_6H_3), 126.76 (s, *p*-Sc-C_6H_3), 72.28 (s, OCH_2CH), 69.88 (br, THF), 68.82 (s, $CH_2CH(^iPr)N$), 30.94 (s, $CH(CH_3)_2$), 25.46 (s, THF), 19.75 (s, $CH(CH_3)_2$), 15.90 (s, $CH(CH_3)_2$) ppm. IR (KBr): 2959(s), 2926(s), 2872(m), 1619(s), 1555(s), 1482(m), 1461(m), 1432(m), 1380(s), 1331(m), 1293(m), 1260(m), 1185(m), 1146(m), 1081(m), 1017(w), 969(m), 932(w), 862(m), 804(m),734(w) cm^{-1}. Anal. Calcd for $C_{26}H_{39}Cl_2N_2O_4Sc$: C, 55.82; H, 7.03; N, 5.01. Found: C, 55.69; H, 7.18; N, 4.93.

Synthesis of Complexes 2−6. Following the procedure described for formation of **1**, complexes **2**−**6**, (*S*,*S*)-[2,6-bis(4′-isopropyl-2′-oxazolinyl)phenyl]$LnCl_2(THF)_2$ (Ln = Y, Dy, Ho, Tm, Lu), were synthesized from $LnCl_3(THF)_x$. Y (**2**), colorless crystal,

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Table 3. Crystal Data and Structural Refinement Details for Complexes 1, 2, 3, and 7

	1	2	3	7
mol formula	$C_{26}H_{39}Cl_2N_2O_4Sc$	$C_{26}H_{39}Cl_2N_2O_4Y$	$C_{26}H_{39}Cl_2N_2O_4Dy$	$C_{54}H_{69}N_6O_6La$
mol wt	559.46	603.41	677.00	1037.07
cryst system	monoclinic	monoclinic	monoclinic	monoclinic
space group	C2	C2	C2	P2
a/Å	11.2651(14)	11.2272(3)	11.2404(17)	13.112(2)
b/Å	14.3738(14)	14.6423(3)	14.685(2)	21.904(4)
c/Å	8.4335(10)	8.50860(10)	8.5239(17)	13.254(2)
α/deg	90	90	90	90
β/deg	94.122(2)	94.730(2)	94.719(6)	96.942(3)
γ/deg	90	90	90	90
V/Å^3	1362.0(3)	1393.98(5)	1402.2(4)	3778.6(11)
R_{int}	0.0189	0.0231	0.0375	0.0402
R_1 ($I > 2\delta$)	0.0261	0.0271	0.0258	0.1126
wR_2 ($I > 2\delta$)	0.0697	0.0587	0.0711	0.2993
GOOF	1.056	1.009	1.134	1.114

yield 43.0%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.52 (d, J = 6.6 Hz, 2H, m-Y-C_6H_3), 7.14 (t, J = 7.1 Hz, 1H, p-Y-C_6H_3), 4.59 (br, 4H, OCH_2CH), 4.47 (br, 2H, $CH_2CH(^iPr)N$), 3.84 (br, 8H, THF), 2.69 (m, 2H, $CH(CH_3)_2$), 1.84 (br, 8H, THF), 0.95 (d, J = 5.8 Hz, 6H, $CH(CH_3)_2$), 0.79 (d, J = 5.2 Hz, 6H, $CH(CH_3)_2$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ 194.04 (d, J = 36.7 Hz, C-Y), 176.10 (s, C═N), 133.41 (s, o-Y-C_6H_3), 127.13 (s, m-Y-C_6H_3), 125.66 (s, p-Y-C_6H_3), 70.17 (s, OCH_2CH), 69.12 (br, THF), 68.48 (s, CH_2CH-(^{i}Pr)N), 29.95 (s, $CH(CH_3)_2$), 25.50 (s, THF), 19.40 (s, $CH(CH_3)_2$), 14.05 (s, $CH(CH_3)_2$) ppm. IR (KBr): 2959(s), 2927(m), 2871(w), 1620(s), 1557(s), 1482(m), 1463(w), 1369(s), 1331(m), 1292(m), 1247(m), 1179(m), 1145(m), 1104(w), 1080(m), 1021(m), 1000(w), 970(m), 932(w), 871(w), 802(m), 717(m) cm^{-1}. Anal. Calcd for $C_{26}H_{39}Cl_2N_2O_4Y$: C, 51.75; H, 6.51; N, 4.64. Found: C, 51.51; H, 6.71; N, 4.60. Dy (**3**), colorless crystal, yield 31.1%. IR (KBr): 2957(s), 2927(s), 2870(m), 1653(m), 1621(s), 1557(s), 1482(m), 1463(w), 1369(s), 1331(m), 1311(m), 1292(m), 1259(m), 1179(m), 1145(m), 1105(w), 1080(m), 1022(m), 1000(w), 970(m), 933(w), 868(m), 802(m), 771(w), 718(m) cm^{-1}. Anal. Calcd for $C_{26}H_{39}Cl_2N_2O_4Dy$: C, 46.13; H, 5.81; N, 4.14. Found: C, 45.92; H, 6.00; N, 4.11. Ho (**4**), colorless crystal, yield 45.3%. IR (KBr): 2958(s), 2925(s), 2870(m), 1652(m), 1621(s), 1557(s), 1482(m), 1463(m), 1369(s), 1331(w), 1311(w), 1292(m), 1259(m), 1179(w), 1145(m), 1105(w), 1080(m), 1022(m), 1000(w), 970(m), 933(w), 871(w), 801(m), 771(w), 718(m) cm^{-1}. Anal. Calcd for $C_{26}H_{39}Cl_2N_2O_4Ho$: C, 45.96; H, 5.79; N, 4.12. Found: C, 45.70; H, 5.89; N, 4.07. Tm (**5**), colorless crystal, yield 40.4%. IR (KBr): 2958(s), 2931(m), 2871(m), 1653(m), 1622(s), 1558(s), 1482(m), 1463(m), 1370(s), 1331(w), 1312(w), 1292(m), 1259(m), 1179(w), 1145(m), 1106(w), 1080(m), 1022(w), 1000(w), 970(m), 933(w), 865(w), 802(m), 778(w), 718(m) cm^{-1}. Anal. Calcd for $C_{26}H_{39}Cl_2N_2O_4Tm$: C, 45.69; H, 5.75; N, 4.10. Found: C, 45.53; H, 5.88; N, 4.01. NMR spectra of the above three complexes were not available due to their paramagnetism. Lu (**6**), colorless crystal, yield 58.6%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.56 (d, J = 7.3 Hz, 2H, m-Lu-C_6H_3), 7.14 (t, J = 7.3 Hz, 1H, p-Lu-C_6H_3), 4.60 (br, 4H, OCH_2CH), 4.47 (br, 2H, $CH_2CH(^iPr)N$), 3.85 (br, 8H, THF), 2.69 (m, 2H, $CH(CH_3)_2$), 1.84 (br, 8H, THF), 0.94 (d, J = 4.8 Hz, 6H, $CH(CH_3)_2$), 0.78 (d, J = 4.6 Hz, 6H, $CH(CH_3)_2$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ 199.82 (s, C-Lu), 176.80 (s, C═N), 133.41 (s, o-Lu-C_6H_3), 127.23 (s, m-Lu-C_6H_3), 125.54 (s, p-Lu-C_6H_3), 70.41 (s, OCH_2CH), 69.30 (br, THF), 68.45 (s, CH_2CH-(^{i}Pr)N), 29.81 (s, $CH(CH_3)_2$), 25.51 (s, THF), 19.58 (s, $CH(CH_3)_2$), 14.05 (s, $CH(CH_3)_2$) ppm. IR (KBr): 2959(s), 2926(s), 2871(m), 1653(m), 1622(s), 1558(s), 1481(m), 1453(m), 1372(s), 1332(w), 1313(w), 1293(m), 1261(m), 1207(w), 1180(w), 1145(m), 1106(w), 1081(m), 1022(m), 970(m), 923(w), 867(m), 803(s), 734(m), 719(m) cm^{-1}. Anal. Calcd for $C_{26}H_{39}Cl_2N_2O_4Lu$: C, 45.29; H, 5.70; N, 4.06. Found: C, 45.17; H, 5.84; N, 3.98.

(S,S)-[2,6-Bis(4′-isopropyl-2′-oxazolinyl)phenyl]$_3$La (7). Following the same procedure described for formation of **1**, treatment of (S,S)-2,6-bis(4′-isopropyl-2′-oxazolinyl)phenyl bromide (0.57 g, 1.50 mmol in 25 mL of THF) with ^{n}BuLi (1.6 M in hexane, 1.00 mL, 1.60 mmol) and then in situ adding to a THF suspension (15 mL) of $LaCl_3(THF)_2$ (calculated by $LaCl_3$, 0.49 g, 2.00 mmol) gave crude product **7**. Crude product was crystallized from a THF/n-hexane mixture, affording **7** as a beige powder (0.17 g, 32.8%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 8.17 (d, J = 7.6 Hz, 6H, m-La-C_6H_3), 7.25 (t, J = 7.7 Hz, 3H, p-La-C_6H_3), 4.01 (t, J = 9.0 Hz, 6H, OCH_2CH), 3.81 (t, J = 8.3 Hz, 6H, OCH_2CH), 3.69 (m, 6H, $CH_2CH(^iPr)N$), 1.36 (m, 6H, $CH(CH_3)_2$), 0.68 (d, J = 6.7 Hz, 18H, $CH(CH_3)_2$), 0.55 (d, J = 6.8 Hz, 18H, $CH(CH_3)_2$) ppm. ^{13}C NMR (101 MHz, C_6D_6, 25 °C): δ 197.37 (m, C-La), 172.48 (s, C═N), 138.26 (s, o-La-C_6H_3), 126.99 (s, m-La-C_6H_3), 122.75 (s, p-La-C_6H_3), 70.17 (s, OCH_2CH), 69.96 (s, $CH_2CH(^iPr)N$), 32.01 (s, $CH(CH_3)_2$), 17.43 (s, $CH(CH_3)_2$), 17.05 (s, $CH(CH_3)_2$) ppm. IR (KBr): 2959(m), 2924(m), 2870(m), 1637(s), 1561(w), 1541(w), 1465(w), 1360(m), 1350(m), 1303(m), 1260(m), 1243(m), 1127(s), 1095(w), 1078(m), 1035(w), 982(s), 803(m). Anal. Calcd for $C_{54}H_{69}N_6O_6La$: C, 62.54; H, 6.71; N, 8.10. Found: C, 62.86; H, 6.82; N, 8.03.

Polymerization of Isoprene. A typical procedure for polymerization was as follows (Table 2, run 2): in a glovebox, 10 μmol of **2** and equimolar $[PhNHMe_2][B(C_6F_5)_4]$ were added to the chlorobenzene (3 mL) solution of 100 μmol of Al^iBu_3 and isoprene (0.34g, 50 mmol) in a 10 mL flask sequentially. Then polymerization was initiated. After a designated time, the reaction mixture was poured into a large quantity of methanol (50 mL) containing a small amount of hydrochloric acid and butylhydroxytoluene (BHT, 0.1% w/w) to terminate polymerization. Precipitated polymer was washed by methanol and dried under vacuum at 35 °C for 24 h to a constant weight.

Crystal Structure Determination. Single crystals of complexes **1**, **2**, **3**, and **7** for X-ray structural analysis was obtained from a solution of THF/CH_2Cl_2. Diffraction data were collected at 210 K on a Bruker SMART-CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Structures were solved by direct methods[32] and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in idealized position. All calculations were performed using the SHELXTL[33] crystallographic software packages. Details of the crystal data, data collections, and structure refinements are summarized in Table 3.

CCDC-877973 (for **1**), CCDC-877974 (for **2**), CCDC-877971 (for **3**), and CCDC-877972 (for **7**) contain 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.

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■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Discussion of possible active species; ^1H and $^1H-^1H$ COSY NMR spectra of intermediates; mass spectrum of the active species solution hydrolyzed with water; ORTEP drawings for molecular structures of complexes **1** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: tqxu@dlut.edu.cn (T. X.); lxb-1999@163.com (X.-B. L.).

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Kuran, W. *Principle of Coordination Polymerization*; John Wiley and Sons Ltd.: New York, 2001; p 275. (b) Baugh, L. S.; Canich, J. A. M. *Stereoselective Polymerization with Single-Site Catalysts*; Taylor & Francis: New York, 2008; p 447. (c) Wilson, D. *Makromol. Chem. Symp.* **1993**, *66*, 273. (d) Lauretti, E.; Miani, B.; Misttrali, F. *Rubber World* **1994**, *210*, 34. (e) Zhao, J.; Ghebremeskel, G. N. *Rubber Chem. Technol.* **2001**, *74*, 409.

(2) For polymerization of 1,3-diene by transition-metal catalysts, see some reviews: (a) Saltman, W. M.; Link, T. H. *Ind. Eng. Chem., Prod. Res. Dev.* **1964**, *3*, 199. (b) 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. (c) Tobisch, S. *Acc. Chem. Res.* **2002**, *35*, 96. (d) Thiele, S. K.-H.; Wilson, D. R. *J. Macromol. Sci., Polym. Rev.* **2003**, *43*, 581. (e) Monakov, Yu. B.; Mullagaliev, I. R. *Russ. Chem. Bull. Int. Ed.* **2004**, *53*, 1. (f) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283. (g) Gibson, V. C.; Redshaw, C.; Solan, G. A. *Chem. Rev.* **2007**, *107*, 1745.

(3) For *cis*-1,4-polymerization of isoprene by rare-earth-metal catalysts, see some reviews: (a) Hou, Z.; Wakatsuki, Y. *Coord. Chem. Rev.* **2002**, *231*, 1. (b) Zeimentz, P. M.; Arndt, S.; Elvidge, B. R.; Okuda, J. *Chem. Rev.* **2006**, *106*, 2404. (c) Friebe, L.; Nuyken, O.; Obrecht, W. *Adv. Polym. Sci.* **2006**, *204*, 1. (d) Fischbach, A.; Anwander, R. *Adv. Polym. Sci.* **2006**, *204*, 155. (e) Shen, Z. *Front. Chem. China* **2006**, *3*, 247. (f) Luo, Y.; Nishiura, M.; Hou, Z. *J. Organomet. Chem.* **2007**, *692*, 536. (g) Nishiura, M.; Hou, Z. *Nat. Chem.* **2010**, *2*, 257. (h) Li, T.; Jenter, J.; Roesky, P. W. *Struct. Bonding (Berlin)* **2010**, *137*, 165. (i) Carpentier, J.-F.; Guillaume, S. M.; Kirillov, E.; Sarazin, Y. *C. R. Chim.* **2010**, *13*, 608.

(4) Zhang, Z.; Cui, D.; Wang, B.; Liu, B.; Yang, Y. *Struct. Bonding (Berlin)* **2010**, *137*, 49.

(5) (a) Longiave, C.; Castelli, R. *J. Polym. Sci. C* **1963**, *4*, 387. (b) Shen, Z.; Gong, C.; Chung, C.; Ouyang, J. *Sci. Sin. (Engl. Transl.)* **1964**, *13*, 1339. (c) Hsieh, H.; Yeh, H. *Rubber Chem. Technol.* **1985**, *58*, 117.

(6) For some selected examples, see: (a) Shen, Z.; Ouyang, J.; Wang, F.; Hu, Z.; Yu, F.; Qian, B. *J. Polym. Sci. Polym. Chem. Ed.* **1980**, *18*, 3345. (b) Mazzei, A. *Makromol. Chem.* **1981**, *4* (Suppl), 61. (c) Wilson, D.; Jenkins, D. *Polym. Bull.* **1992**, *27*, 407. (d) Kobayashi, E.; Hayashi, N.; Aoshima, S.; Furukawa, J. *J. Polym. Sci., Polym. Chem.* **1998**, *36*, 1707. (e) Barbotin, F.; Monteil, V.; Llauro, M.; Boisson, C.; Spitz, R. *Macromolecules* **2000**, *33*, 8521. (f) Maiwald, S.; Sommer, C.; Müller, G.; Taube, R. *Macromol. Chem. Phys.* **2001**, *202*, 1446. (g) Friebe, L.; Nuyken, O.; Windisch, H.; Obrecht, W. *Macromol. Chem. Phys.* **2002**, *203*, 1055. (h) Dong, W.; Masuda, T. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 1838. (i) Dong, W.; Endo, K.; Masuda, T. *Macromol. Chem. Phys.* **2003**, *204*, 104. (j) Dong, W.; Masuda, T. *Polymer* **2003**, *44*, 1561.

(7) Zimmermann, M.; Frøystein, N. Å.; Fischbach, A.; Sirsch, P.; Dietrich, H. M.; Törnroos, K. W.; Herdtweck, E.; Anwander, R. *Chem.—Eur. J.* **2007**, *13*, 8784.

(8) (a) Kaita, S.; Hou, Z.; Wakatsuki, Y. *Macromolecules* **2001**, *34*, 1539. (b) Boisson, C.; Monteil, V.; Ribour, D.; Spitz, R.; Barbotin, F. *Macromol. Chem. Phys.* **2003**, *204*, 1747. (c) Kaita, S.; Hou, Z.; Nishiura, M.; Doi, Y.; Kurazumi, J.; Horiuchi, A. C.; Wakatsuki, Y. *Macromol. Rapid Commun.* **2003**, *24*, 179. (d) Kaita, S.; Doi, Y.; Kaneko, K.; Horiuchi, A. C.; Wakatsuki, Y. *Macromolecules* **2004**, *37*, 5860. (e) Evans, W. J.; Champagne, T. M.; Ziller, J. W. *Chem. Commun.* **2005**, 5925. (f) Evans, W. J.; Champagne, T. M.; Ziller, J. W. *Organometallics* **2005**, *24*, 4882. (g) Kaita, S.; Yamanaka, M.; Horiuchi, A. C.; Wakatsuki, Y. *Macromolecules* **2006**, *39*, 1359.

(9) (a) Fischbach, A.; Perdih, F.; Sirsch, P.; Scherer, W.; Anwander, R. *Organometallics* **2002**, *21*, 4569. (b) Fischbach, A.; Klimpel, M.; Widenmeyer, M.; Herdtweck, E.; Scherer, W.; Anwander, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 2234. (c) Fischbach, A.; Meermann, C.; Eickerling, G.; Scherer, W.; Anwander, R. *Macromolecules* **2006**, *39*, 6811. (d) Meermann, C.; Törnroos, K.; Nerdal, W.; Anwander, R. *Angew. Chem., Int. Ed.* **2007**, *46*, 6508. (e) Fischbach, A.; Perdih, F.; Herdtweck, E.; Anwander, R. *Organometallics* **2006**, *25*, 1626.

(10) (a) Arndt, S.; Beckerle, K.; Zeimentz, P. M.; Spaniol, T. P.; Okuda, J. *Angew. Chem., Int. Ed.* **2005**, *44*, 7473. (b) Robert, D.; Abinet, E.; Spaniol, T. P.; Okuda, J. *Chem.—Eur. J.* **2009**, *15*, 11937.

(11) (a) Bonnet, F.; Violante, C. D. C.; Roussel, P.; Mortreux, A.; Visseaux, M. *Chem. Commun.* **2009**, 3380. (b) Jian, Z.; Cui, D.; Hou, Z.; Li, X. *Chem. Commun.* **2010**, *46*, 3022.

(12) (a) Yang, Y.; Liu, B.; Lv, K.; Gao, W.; Cui, D.; Chen, X.; Jing, X. *Organometallics* **2007**, *26*, 4575. (b) Yang, Y.; Wang, Q.; Cui, D. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 5251. (c) Yang, Y.; Lv, K.; Wang, L.; Wang, Y.; Cui, D. *Chem. Commun.* **2010**, *46*, 6150.

(13) (a) Kaita, S.; Hou, Z.; Wakatsuki, Y. *Macromolecules* **1999**, *32*, 9078. (b) Gromada, J.; Mortreux, A.; Nowogrocki, G.; Leising, F.; Mathivet, T.; Carpentier, J.-F. *Eur. J. Inorg. Chem.* **2004**, 3247. (c) Ajellal, N.; Furlan, L.; Thomas, C. M.; Casagrande, J. O. L.; Carpentier, J.-F. *Macromol. Rapid Commun.* **2006**, *27*, 338. (d) Tardif, O.; Kaita, S. *Dalton Trans.* **2008**, 2531.

(14) Wang, L.; Cui, D.; Hou, Z.; Li, W.; Li, Y. *Organometallics* **2011**, *30*, 760.

(15) Zhang, L.; Suzuki, T.; Luo, Y.; Nishiura, M.; Hou, Z. *Angew. Chem., Int. Ed.* **2007**, *46*, 1909.

(16) (a) Gao, W.; Cui, D. *J. Am. Chem. Soc.* **2008**, *130*, 4984. (b) Lv, K.; Cui, D. *Organometallics* **2008**, *27*, 5438. (c) Lv, K.; Cui, D. *Organometallics* **2010**, *29*, 2987. (d) Li, D.; Li, S.; Cui, D.; Zhang, X. *Organometallics* **2010**, *29*, 2186.

(17) Bolm, C.; Weickhardt, K.; Zehnder, M.; Ranff, T. *Chem. Ber.* **1991**, *124*, 1173.

(18) For a selected review, see: (a) Nishiyama, H. *Chem. Soc. Rev.* **2007**, *36*, 1133. For some selected examples recently, see: (b) Takemoto, T.; Iwasa, S.; Hiroshi, H.; Shibatomi, K.; Kameyama, M.; Motoyamac, Y.; Nishiyama, H. *Tetrahedron Lett.* **2007**, *48*, 3397. (c) Nishiyama, H.; Ishikawa, J.; Shiomi, T. *Tetrahedron Lett.* **2007**, *48*, 7841. (d) Hashimoto, T.; Shiomi, T.; Ito, J.; Nishiyama, H. *Tetrahedron* **2007**, *63*, 12883. (e) Satake, Y.; Abe, S.; Okazaki, S.; Ban, N.; Hikage, T.; Ueno, T.; Nakajima, H.; Suzuki, A.; Yamane, T.; Nishiyama, H.; Watanabe, Y. *Organometallics* **2007**, *26*, 4904. (f) Ito, J.; Kitase, M.; Nishiyama, H. *Organometallics* **2007**, *26*, 6412. (g) Shiomi, T.; Nishiyama, H. *Org. Lett.* **2007**, *9*, 1651. (h) Inoue, H.; Kikuchi, M.; Ito, J.; Nishiyama, H. *Tetrahedron* **2008**, *64*, 493. (i) Ito, J.; Miyakawa, T.; Nishiyama, H. *Organometallics* **2008**, *27*, 3312. (j) Bugarin, A.; Connell, B. T. *Organometallics* **2008**, *27*, 4357. (k) Kimura, T.; Uozumi, Y. *Organometallics* **2008**, *27*, 5159. (l) Ito, J.; Ujiie, S.; Nishiyama, H. *Organometallics* **2009**, *28*, 630. (m) Shiomi, T.; Adachi, T.; Ito, J.; Nishiyama, H. *Org. Lett.* **2009**, *11*, 1011.

(n) Nishiyama, H.; Ito, J. *Chem. Commun.* **2010**, *46*, 203. (o) Yang, Y.; Shi, T.; Zhang, X.; Tang, Z.; Wen, Z.; Quan, J.; Wu, Y. *Org. Biomol. Chem.* **2011**, *9*, 5845.
(19) Chuchuryukin, A. V.; Huang, R.; Lutz, M.; Chadwick, J. C.; Spek, A. L.; van Koten, G. *Organometallics* **2011**, *30*, 2819.
(20) (a) Ward, B. D.; Bellemin-Laponnaz, S.; Gade, L. H. *Angew. Chem., Int. Ed.* **2005**, *44*, 1668. (b) Lukešová, L.; Ward, B. D.; Bellemin-Laponnaz, S.; Wadepohla, H.; Gade, L. H. *Dalton Trans.* **2007**, 920. (c) Lukešová, L.; Ward, B. D.; Bellemin-Laponnaz, S.; Wadepohl, H.; Gade, L. H. *Organometallics* **2007**, *26*, 4652. (d) Zou, J.; Berg, D. J.; Stuart, D.; McDonald, R.; Twamley, B. *Organometallics* **2011**, *30*, 4958.
(21) Motoyama, Y.; Okano, M.; Narusawa, H.; Makihara, N.; Aoki, K.; Nishiyama, H. *Organometallics* **2001**, *20*, 1580.
(22) (a) Stol, M.; Snelders, D. J. M.; de Pater, J. J. M.; van Klink, G. P. M.; Kooijman, H.; Spek, A. L.; van Koten, G. *Organometallics* **2005**, *24*, 743. (b) Stol, M.; Snelders, D. J. M.; Godbole, M. D.; Havenith, R. W. A.; Haddleton, D.; Clarkson, G.; Lutz, M.; Spek, A. L.; van Klink, G. P. M.; van Koten, G. *Organometallics* **2007**, *26*, 3985.
(23) Effective ionic radius of Ln^{3+} for coordination number 8 (CN = 8), see: Dean, J. A. *Lange's handbook of chemistry*, 15th ed.; McGraw-Hill: New York, 1999; Section 4: 4.5.
(24) (a) IR spectrum of [(*S,S*)-Phebox-^{i}Pr]Br showed absorption bands of the imine C═N at 1665 cm^{-1}. (b) ^{13}C NMR spectrum of [(*S,S*)-Phebox-^{i}Pr]Br showed the resonance of the C═N bond at δ 162.6 ppm in $CDCl_3$: see refs 21 and 22.
(25) Wang, D.; Cui, D.; Miao, W.; Li, S.; Huang, B. *Dalton Trans.* **2007**, 4576.
(26) For other homoleptic rare-earth-metal complexes, see: Zimmermann, M.; Anwander, R. *Chem. Rev.* **2010**, *110*, 6194.
(27) A similar phenomenon was reported previously; see ref 16d.
(28) For the chloride effects in isoprene polymerization, see: Evans, W. J.; Giarikos, D. G. *Macromolecules* **2004**, *37*, 5130.
(29) For some examples in Ziegler–Natta system based on rare-earth metals, see: (a) Pross, A.; Marquardt, P.; Reichert, K.-H.; Nentwig, W.; Knauf, T. *Angew. Makromol. Chem.* **1993**, *211*, 89. (b) Oehme, A.; Gebauer, U.; Gehrke, K.; Lechner, M. D. *Angew. Makromol. Chem.* **1996**, *235*, 121. (c) Porri, L.; Ricci, G.; Shubin, N. *Macromol. Symp.* **1998**, *128*, 53. (d) Koboyashi, E.; Hayashi, N.; Aoshima, S.; Furukaya, J. *J. Polym. Sci., Polym. Chem.* **1998**, *36*, 1707. (e) Iovu, H.; Hubca, G.; Racoti, D.; Hurst, J. S. *Eur. Polym. J.* **1999**, *35*, 335. (f) Boisson, C.; Barbotin, F.; Spitz, R. *Macromol. Chem. Phys.* **1999**, *200*, 1163. (g) Quirk, R.; Kells, A.; Yunlu, K. M.; Cuif, J.-P. *Polymer* **2000**, *41*, 5903. (h) Evans, W. J.; Giarikos, D. G.; Ziller, J. W. *Organometallics* **2001**, *20*, 5751. (i) Kwag, G.; Lee, H.; Kim, S. *Macromolecules* **2001**, *34*, 5367.
(30) Due to isoprene volatilizing partly at high temperature, the yield was 86% at 80 °C.
(31) (a) Baugh. L. S.; Canich. J. A. M. *Stereoselective Polymerization with Single-Site Catalysts*; Taylor & Francis: New York, 2008; p 462. (b) Li, X.; Nishiura, M.; Hu, L.; Mori, K.; Hou, Z. *J. Am. Chem. Soc.* **2009**, *131*, 13870.
(32) *SHELXTL*; PC Siemens Analytical X-ray Instruments: Madison, WI, 1993.
(33) Sheldrick, G. M. *SHELXTL Structure Determination Programs*, version 5.0, PC; Siemens Analytical Systems: Madison, WI, 1994.