Side-Arm Assisted Anilido-Imine Based Rare-Earth Metal Complexes for Isoprene Stereoselective Polymerization

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Abstract: Anilido-imine ligands o-C₃H₄(NHAr₁)(CH=NAr₂), in which Ar₁ is 2,6-diisopropylbenzyl group and Ar₂ contains fluorine (HL₁) or methoxy (HL₂) group on ortho-position of phenyl substituent, were synthesized for constructing rare-earth metals based complexes of 1a–1c (HL₁ based Sc, Lu, Y) and 2a–2c (HL₂ based Sc, Lu, Y). Based on their NMR spectra and X-ray single-crystal structures, the side-arm group of -F and -OMe is identified to chelate to the corresponding central metal. The twisted angles between two planes formed by chelated heteroatoms (N, N, F for HL₁ and N, N, O for HL₂) are observed, in which the largest dihedral angle (53.3°) for HL₁-Y and the smallest dihedral angle (44.32°) for HL₂-Sc are detected. After being activated by Al′Bu3 and [PhₓC][B(C₆F₅)ₓ], these catalysts showed great activity for isoprene polymerization. Bearing the same ligand HL₁, smaller scandium based complex 1a and middle size of lutetium based 1b provided lower cis-1,4-selectivity (57.3% and 64.2%), larger yttrium complex 1c displayed high cis-1,4-selectivity (84%). Chelating by crowded HL₂, small size of scandium complex 2a provided impressive trans-1,4-selectivity (93.0%), middle lutetium based 2b displayed non-selectivity and larger yttrium complex 2c showed clear cis-1,4-selectivity (83.3%). Moreover, 2a/Al′Bu3 system showed the quasi-living chain transfer capability.

Keywords: rare-earth metal catalyst; polyisoprene; stereoselectivity

1. Introduction

According to the different regio- and stereo-selective polymerization method, polyisoprene is commonly divided into cis-1,4-polyisoprene, trans-1,4-polyisoprene and 3,4-polyisoprene. Among them, cis-1,4-polyisoprene has similar chemical composition, stereoselectivity and mechanical properties to natural rubber. It is widely used in tires, conveyor belts, adhesives, sports equipment, etc. In recent years, due to the shortage of natural resources and the aggravation of environmental pollution, it has become a trend to produce high performance tires with low rolling resistance, high wet skid resistance and low fuel consumption [1]. It is reported that the high-performance rubber can be obtained by mixing a small amount of trans-1,4-polyisoprene with cis-1,4-polyisoprene or natural rubber [2]. In addition, trans-1,4-selective polyisoprene has unique applications in medical materials and shape memory materials, etc. For example, trans-1,4-polyisoprene is an ideal material for making medical splints, orthopedic components and prosthetics.

So far, a large number of rare-earth metal catalysts for the cis-1,4-selective and 3,4-selective polyisoprene have been reported [3–12], such as arylidinium (NCN)-ligated rare-earth metal dichlorides (cis-1,4-selectivity up to 98.8%) [13]; bis(carbene)phenyl (CCC) rare-earth metal dibromides (cis-1,4-selectivity up to 99.6%) [14]; bis(phosphino)-carbazolide (PNP)-chelated rare-earth metal complexes (cis-1,4-selectivity up to 99%) [15,16], etc. For 3,4-selective polyisoprene, there are amidino N-heterocyclic carbene ligated lutetium complex (3,4-selectivity 98.7%) [17], iminophosphoramide (NPN) ligated rare-earth metal bis(alkyl)
Comparatively, there are only a few reports on the trans-1,4-selective catalysts [2,20–23]. For the trans-1,4 polymerization of isoprene, the half-sandwich rare-earth metal complexes (CpQ)Ln(AlMe₂)₂ (CpQ = 2,3,4,5-tetramethyl-1-(8-quinolyl)cyclopentadienyl; Ln = Y, La) (trans-1,4-stereoselectivity >93%) [24], (Flut-Bu)La(AlMe₂)₂ (trans-1,4-stereoselectivity >85%) reported by Anwander and the chiral mononuclear dialkyl pincer complexes [(S,S)-BOPA]Ln(CH₂SiMe₃)₂ (BOPA = (S,S)-bis(oxazolinylphenyl)lamido; Ln = Sc, Lu) discovered by Xiaofang Li (trans-1,4-stereoselectivity > 99%) are efficient catalysts [25,26]. Interestingly, efficient modulating the stereoselective polymerization of isoprene has also been achieved by changing the size of metal center and/or rational adjusting the steric/electronic effect of chelating ligand or co-catalyst. For example, Shojiro Kaita et.al reported high cis-1,4/trans-1,4 selective polymerization of butadiene controlled by synergetic influence of metal size and type of AlR₃ [27].

Previously we reported β-iminophosphonamine ligated complexes can realize the switchable stereoselectivity of polyisoprene from 3,4-selectivity of 94% to trans-1,4-selectivity of 95% by changing the metal size from Lu³⁺ (84.8 pm) to La³⁺ (106.1 pm) [2]. In addition to the type of metal and co-catalyst, the strategy of using the flexible side arm on ligand to adjust the electronic/steric properties of complex and thus finely change the capability of catalysts has also attracted much attention. As introduced by Yong Tang et.al, the additional “side-arm” groups near the catalytic center to regulate the electronic properties and spatial shape of the metal center, thus affecting the coordination of the monomer, and achieving the purpose of regulating the activity and catalytic properties of the catalyst [28,29]. However, there are few of report that fine modulate the stereoselectivity of catalyst by “side-arm strategy”.

Herein, we devised an aniline-imine ligated rare-earth metal complexes and introduced flexible heteroatom groups near the metal center to further control the polymerization process of isoprene. The skeleton of aniline-imine ligands might well be interpreted as a hybridization of classic salicylaldiminate and β-diketiminate ligands, which are widely applied to construct catalysts for olefin polymerization [30,31]. Through combining the “side-arm strategy” and suitable metal size influence, we have successfully realized the switchable stereoselectivity of polyisoprene from cis-1,4 to trans-1,4 selectivity. Furthermore, the efficient chain transfer polymerization for high trans-1,4 polymerization system was fine developed.

2. Results and Discussion

2.1. Synthesis and Characterization of Rare-Earth-Metal Complexes

The deprotonation of anilido-imine ligands with 1 equiv of rare-earth metal tris(alkyl)s afforded a series of rare-earth metal–bis(alkyl) complexes in high yields (Scheme 1). All the complexes are soluble in polar solvent like toluene and THF, but insoluble in unpolar hexane. The solid-state structures of complexes 1a, 1c, 2a and 2c were confirmed by X-ray diffraction measurements (Figures 1–4). And the crystallographic data were summarized in Table S1 (see Supplementary Materials). Except for the coordinated bidentate ligands, the fluorine group and methoxy substituent on the phenyl group also coordinate to the corresponding central metal. The Y–N (amido) distances [2.313(5) Å for 1c, 2.310(2) Å for 2c] are shorter than the Y–N (imine) distances [2.451(5) Å for 1c, 2.476(2) Å for 2c], respectively. Except for 2a, additional one THF molecule was involved in their crystal structures, which implies that 2a owns the most crowded coordinating environment. A twisted angle between two planes formed by chelated heteroatoms (N, N, F for HL₁ and N, N, O for HL₂) were observed. Interestingly, the highest cis-1,4-selectivity of 1c owns the largest dihedral angle (53.3°) among them, and the highest trans-1,4-selectivity of 2a shows the smallest dihedral angle (44.32°), which are depicted below in detail. For complex 2a, O, N₁ and N₂ all coordinate with the central metal scandium forming a chelating complex. The O–Sc bond length is 2.2387(13), Sc–N₁ bond length is 2.1415(15),...
Sc–N2 bond length is 2.2540(15), which are close to the bond lengths between scandium and coordinated nitrogen atoms in the chelating catalyst [(S,S)-BOPA]Sc(CH2SiMe3)2 (BOPA = (S,S)-bis(oxazolinylphenyl)amido) reported by Xiaofang Li. Therefore, their catalytic behaviors are similar, and they both show high trans-1,4 selectivity for isoprene polymerization [26].

Scheme 1. Synthesis of complexes 1a–1c and 2a–2c.

![Figure 1. X-ray molecular structure of complex 1a with 35% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (degree): Sc1–F1 = 2.493(3), Sc1–N1 = 2.156(4), Sc1–N2 = 2.331(4), Sc1–O1 = 2.210(3), Sc1–C1 = 2.227(4), Sc1–C2 = 2.234(4), Si1–C1–Sc1 = 129.3(2), Si2–C2–Sc1 = 135.2(2).](image)

The 1H NMR spectrum of complex 1a (Figure S3) was indicative of the formation of bis(alkyl) species and the resonance at 0.25 ppm is attributed to the methylene protons of scandium alkyl species. Compared with many other rare earth metal alkyl species, the bis(alkyl) species and the resonance at 0.25 ppm is attributed to the methylene protons of scandium alkyl species. Compared with many other rare earth metal alkyl species, the bis(alkyl) species and the resonance at 0.25 ppm is attributed to the methylene protons of scandium alkyl species.

2.2. Polymerization of Isoprene

Isoprene polymerization was investigated in detail and the representative data are summarized in Table 1. The isoprene polymerization was initiated immediately as the complex was activated by [Ph3C][B(C6F5)4] and aluminum alkyls. The monomer was completely consumed within 0.5 h at room temperature (Table 1, entries 1–9).
Figure 2. X-ray molecular structure of complex 1c with 35% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (degree): Y1–F1 = 2.639(4), Y1–N1 = 2.451(5), Y1–N2 = 2.313(5), Y1–O1 = 2.361(5), Y1–C1 = 2.381(7), Y1–C2 = 2.365(8), Si1–C1–Y1 = 135.2(4), Si2–C2–Y1 = 135.8(5).

Figure 3. X-ray molecular structure of complex 2a with 35% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (degree): Sc1–O1 = 2.2387(13), Sc1–N1 = 2.1415(15), Sc1–N2 = 2.2540(15), Sc1–C1 = 2.217(2), Sc1–C2 = 2.221(2), Si1–C1–Sc1 = 129.79(11), Si2–C2–Sc1 = 121.75(10).

Bearing the ligand L1, the scandium complex 1a had medium cis-1,4-selectivity (57.3%), while yttrium complex 1c and 2c provided predominant cis-1,4-selectivity (84.0%, 83.3%) (Table 1, entries 1, 3, 7). This may be due to the fact that the larger yttrium provided a more open space, which is beneficial to the η⁴-cis-coordinating mode of monomer. Bearing the same metal center, the complex 2b had medium trans-1,4-selectivity (58.3%), while the complex 1b had medium cis-1,4-selectivity (64.2%) (Table 1, entries 2, 6). This may be attributed to the small steric hindrance of fluorine group facilitating η⁴-coordination. On the other hand, the electronic absorption of fluorine group increased the Lewis acidity of Lu³⁺ ion, which could increase the chance of η⁴-coordination [18]. Surprisingly, scandium
complex 2a displayed high trans-1,4-selectivity (93.0%), and exhibited a promising catalytic activity even at a low temperature (−30 °C, 98% yield in 4 h) with an increased trans-1,4-selectivity (97.0%) (Table 1, entries 4–5). Compared with 1a, the side arm of ligand L2 adopted methoxy group with larger steric hindrance, making the ligand have a bulky space shielding on the metal center. The more planar structure of complex 2a together with bulky space may only allow η2-trans-coordination mode of isoprene, on the other hand, the consecutive insertion of trans-monomer into the allyl-metal bond of active species with syn-prenyl moiety and anti-syn isomerization prior to monomer insertion lead to trans-1,4 unit [32–37].

![Figure 4. X-ray molecular structure of complex 2c with 35% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (degree): Y1–O1 = 2.4025(19), Y1–2O2 = 2.5277(19), Y1–N1 = 2.476(2), Y1–N2 = 2.310(2), Y1–C1 = 2.389(4), Y1–C2 = 2.417(4), Si1–C1 = 1.79/93.0/5.3 2.05 1.54 69.7/36.7, Si2–C2–Y1 = 132.38(18).](image)

Table 1. Polymerization of isoprene by using catalytic precursors under various conditions.

| Entry | Cat | Al’Bu3/Cat | T (°C) | Time (h) | Conv. (%) | Microstructure (%) | $M_n$ (10^4) | PDI | $T_g/T_m$ (°C) |
|-------|-----|------------|--------|----------|-----------|--------------------|------------|-----|----------------|
| 1 | 1a | 10 | 25 | 0.5 | >99 | cis, 1,4/trans, 1,4/3,4 | 4.03 | 1.62 | −55.9/− |
| 2 | 1b | 10 | 25 | 0.5 | >99 | cis, 1,4/trans, 1,4/3,4 | 5.83 | 1.64 | −60.3/− |
| 3 | 1c | 10 | 25 | 0.5 | >99 | cis, 1,4/trans, 1,4/3,4 | 6.24 | 1.12 | −59.9/− |
| 4 | 2a | 10 | 25 | 0.5 | >99 | cis, 1,4/trans, 1,4/3,4 | 2.05 | 1.54 | −69.7/36.7 |
| 5 | 2a | 10 | −30 | 4 | 98 | trans, 1,4/cis, 1,4/3,4 | 2.03 | 1.34 | −68.3/37.8 |
| 6 | 2b | 10 | 25 | 0.5 | >99 | cis, 1,4/trans, 1,4/3,4 | 5.76 | 1.29 | −66.5/− |
| 7 | 2c | 10 | 25 | 0.5 | >99 | cis, 1,4/trans, 1,4/3,4 | 6.05 | 1.16 | −64.8/− |
| 8 | 2a | 2 | 25 | 0.5 | >99 | cis, 1,4/trans, 1,4/3,4 | 4.58 | 1.51 | −69.6/36.5 |
| 9 | 2a | 5 | 25 | 0.5 | >99 | cis, 1,4/trans, 1,4/3,4 | 3.08 | 1.61 | −69.3/37.6 |
| 10 | 2a | 20 | 25 | 0.5 | >99 | cis, 1,4/trans, 1,4/3,4 | 1.34 | 1.56 | −69/36.4 |
| 11 | 2a | 40 | 25 | 2 | >99 | cis, 1,4/trans, 1,4/3,4 | 0.85 | 1.53 | −69.5/36.8 |

* General polymerization conditions: rare earth complex 10 μmol, [IP]/[Cat]/[Ph3C][B(C6F5)4] = 1000/1/1 (mol/mol), toluene 4 mL.

Determined by gel permeation chromatography (GPC) in THF at 40 °C against polystyrene standard. D Determined by differential scanning calorimetry (DSC).

It is well known that Al’Bu3 is not only used as a cocatalyst for the activation of catalyst precursors, but also as a chain transfer agent to regulate the molecular weight. In general, the molecular weight distribution increases with the amount of Al’Bu3 due to the deactivation of active sites by excessive Al’Bu3 [38–40]. In contrast, using the 2a/Al’Bu3/[Ph3C][B(C6F5)4] system, the molecular weight of PIP decreased inversely with the increase of [Al]/[2a] ratio, meanwhile the molecular weight distribution were almost the same, showing the quasi-living chain transfer mode. For example, with the increase of [Al]/[2a] ratios from 2:1 to 40:1, the molecular weight of polyisoprene decreased from...
4.58 × 10^4 to 0.85 × 10^4 g/mol, together with a slightly lower selectivity was observed (Table 1, entries 4, 8–11).

3. Materials and Methods

3.1. General Information

All manipulations were performed under nitrogen atmosphere using standard high-vacuum Schlenk techniques or in a glovebox (Braun, Germany). All solvents were purified with a SPS system (Braun, Germany). The NMR data of the organometallic samples were obtained on a Bruker AV500 spectrometer (Switzerland) in chloroform-d or benzene-d6 at room temperature. The molecular weight and molecular weight distribution of the polyisoprene were measured with a HLC-8420 GPC (Tosoh corporation, Shunan, Yamaguchi, Japan) at 40 °C using THF as eluent (the flow rate was 0.35 mL/min) against polystyrene standards. Differential scanning calorimetry analyses were carried out on a Q 100 DSC (METTLER TOLEDO, Switzerland) from TA instrument under a nitrogen atmosphere. Any thermal history difference in the polymers was eliminated by first heating the specimen to above 80 °C, then cooling to ~80 °C at 10 °C/min, and finally recording the second DSC scan from ~80 to 80 °C at 10 °C/min. Isoprene was dried over CaH2 with stirring for 48 h and distilled under vacuum before use. [Ph3C][B(C6F5)4] was synthesized following the literature [41].

3.2. Synthesis

3.2.1. Synthesis of o-C6H4NH(C6H4-F-o)(CH=NC6H3-i-Pr2-2,6) (L1)

Anilido-imine ligands L1–L2 were prepared according to the literature procedures [30,31]. Taking the preparation method of ligand L1 as an example: o-fluorobenzaldehyde (6.2 g, 50 mmol), 2,6-diisopropylaniline (8.9 g, 50 mmol) and MgSO4 were mixed in hexane and stirred for 1 h. The mixture was filtered, and the solvent was removed to obtain the yellow solid o-C6H4F(CHNC6H3-i-Pr2-2,6), which was recrystallized in hexane to obtain pure product. A solution of n-BuLi (6 mL, 14.7 mmol) in hexane was added into hexane solution of o-fluoroaniline (1.4 mL, 14 mmol) at ~78 °C, and the white lithium salt LiNHAr precipitated immediately; then the mixture was warmed to room temperature and stirred for 2 h, then it was added into a solution of o-C6H4F(CHNC6H3-i-Pr2-2,6) (4 g, 14 mmol) in THF at 25 °C. After stirring 5 h, the reaction was terminated by adding water, extracted with hexane and the solvent was removed to obtain the yellow solid crude product. The pure product was obtained by recrystallization in hexane (3, 60%). 1H NMR (500 MHz, CDCl3, 7.26 ppm, 25 °C): δ 1.19 (d, 12H, CH(CH3)2), 3.07 (m, 2H, CH(CH3)2), 6.88 (t, 1H, Ph-H), 7.03–7.4 (m, 9H, Ph-H), 7.56 (m, t, 1H, Ph-H), 8.33 (s, 1H, CH = NAr), 11.12 (s, 1H, NH). Analitical Calculated (Anal. Calcd) for C, 80.79; H, 7.82; N, 7.48. Found: C, 80.18; H, 7.27; N, 7.48. Found: C, 80.45; H, 7.01; N, 7.73.

3.2.2. Synthesis of o-C6H4NH(C6H4-OMe-o)(CH=NC6H3-i-Pr2-2,6) (L2)

The preparation method of ligand L2 is similar to that of ligand L1. 1H NMR (500 MHz, CDCl3, 7.26 ppm, 25 °C): δ 1.19 (d, 12H, CH(CH3)2), 3.10 (m, 2H, CH(CH3)2), 3.77 (s, 3H, OCH3), 6.82 (t, 1H, Ph-H), 6.92–6.98 (m, 2H, Ph-H), 7.04 (t, 1H, Ph-H), 7.12–7.31 (m, 4H, Ph-H), 7.37 (d, 1H, Ph-H), 7.44 (d, 1H, Ph-H), 7.56 (d, 1H, Ph-H), 8.3 (s, 1H, CH = NAr), 10.95 (s, 1H, NH). Anal. Calcd for C28H30N2O (%): C, 80.79; H, 7.82; N, 7.25. Found: C, 80.55; H, 8.08; N, 7.51.

3.2.3. Synthesis of L1Sc(2H2SiMe3)2(THF) (1a)

The hexane solution (4.0 mL) of Sc(2H2SiMe3)2(THF)2 (0.22 g, 0.5 mmol) was added dropwise to the ligand L1 solution (0.187 g, 0.5 mmol in 4 mL hexane) at 0 °C. The mixture was stirred for 1 h and then cooling to ~30 °C for 1 day afforded crystalline solids, which dried in vacuo to give orange solids of 1a (0.23 g, 69%). Single crystals suitable for X-ray analysis were obtained from hexane at ~30 °C. 1H NMR (500 MHz, C6D6, 7.16 ppm, 25 °C): δ 0.11 (s, 18H, CH2SiMe3), 0.25 (s, 4H, CH2SiMe3), 0.99 (d, 6H, CH(CH3)2), 1.24 (m, 4H,
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THF), 1.29 (d, 6H, CH(CH₃)₂), 3.31 (br s, 2H, CH(CH₃)₂), 3.59 (m, 4H, THF), 6.43–7.39 (m, 11H, Ph-H), 8.00 (s, 1H, CH = NAr). ¹³C NMR (125 MHz, C₆D₆, 128 ppm, 25 °C): 3.22, 25.6, 29.0, 45.9, 68.5, 114.9, 118.7, 119.5, 120.5, 121.8, 124.4, 126.5, 135.2, 136.2, 138.4, 141.5, 146.6, 151.8, 157.3, 159.1, 170.4. Anal. Calcd for C₄₀H₇₄FN₂O₃Si₂ (%): C, 67.75; H, 9.10; N, 3.95. Found: C, 67.53; H, 8.90; N, 4.20.

3.2.4. Synthesis of L₁Lu(CH₂SiMe₃)₂(THF) (1b)

The preparation method of complex 1b is similar to that of complex 1a (67%). ¹H NMR (500 MHz, C₆D₆, 7.16 ppm, 25 °C): δ = −0.77 (s, 4H, CH₂SiMe₃), 0.08 (s, 18H, CH₂SiMe₃), 0.92 (d, 6H, CH(CH₃)₂), 1.23 (m, 4H, THF), 1.34 (d, 6H, CH(CH₃)₂), 3.21 (m, 2H, CH(CH₃)₂), 3.85 (m, 4H, THF), 6.36–7.48 (m, 11H, Ph-H), 7.96 (s, 1H, CH = NAr). ¹³C NMR (125 MHz, C₆D₆, 128 ppm, 25 °C): 4.28, 25.0, 25.4, 28.9, 41.2, 70.3, 114.4, 115, 116, 120.5, 124.1, 125.6, 126.1, 127.2, 133.4, 134.8, 140.6, 141.5, 147.9, 149.2, 156.2, 158.1, 168.6. Anal. Calcd for C₄₀H₇₄FN₂O₃Si₂ (%): C, 57.26; H, 7.69; N, 3.34. Found: C, 57.56; H, 7.90; N, 3.08.

3.2.5. Synthesis of L₁Y(CH₂SiMe₃)₂(THF) (1c)

The preparation method of complex 1c is similar to that of complex 1a (65%). Single crystal suitable for X-ray analysis was obtained from hexane at −30 °C. ¹H NMR (500 MHz, C₆D₆, 7.16 ppm, 25 °C): δ −0.51 (s, 4H, CH₂SiMe₃), 0.11 (s, 18H, CH₂SiMe₃), 0.94 (d, 6H, CH(CH₃)₂), 1.22 (m, 4H, THF), 1.36 (d, 6H, CH(CH₃)₂), 3.21 (m, 2H, CH(CH₃)₂), 3.84 (m, 4H, THF), 6.38–7.49 (m, 11H, Ph-H), 7.98 (s, 1H, CH = NAr). ¹³C NMR (125 MHz, C₆D₆, 128 ppm, 25 °C): 4.13, 25.33, 28.95, 35.30, 70.30, 114.22, 115.45, 120.66, 124.15, 125.90, 126.07, 127.13, 133.29, 134.88, 140.45, 141.33, 147.73, 148.53, 156.32, 158.12, 168.18. Anal. Calcd for C₄₀H₇₄FN₂O₃Si₂Y (%): C, 63.80; H, 8.57; N, 3.72. Found: C, 63.59; H, 8.81; N, 3.95.

3.2.6. Synthesis of L₂Sc(CH₂SiMe₃)₂ (2a)

The hexane solution (4 mL) of Sc(CH₂SiMe₃)₃(THF)₂ (0.22 g, 0.5 mmol) was added dropwise to the ligand L₂ solution (0.193 g, 0.5 mmol in 4 mL hexane) at 0 °C. The mixture was stirred for 1 h and then cooling to −30 °C for 1 day afforded crystalline solids, which dried in vacuo to give orange solids of 2a (0.22 g, 73%). ¹H NMR (500 MHz, C₆D₆, 7.16 ppm, 25 °C): δ −0.05 (s, 4H, CH₂SiMe₃), 0.00 (s, 18H, CH₂SiMe₃), 1.01–1.33 (m, 12H, CH(CH₃)₂), 3.37 (m, 2H, CH(CH₃)₂), 3.90 (s, 3H, OCH₃), 6.48–7.45 (m, 11H, Ph-H), 8.07 (s, 1H, CH = NAr). ¹³C NMR (125 MHz, C₆D₆, 128 ppm, 25 °C): 3.25, 26.07, 58.54, 111.28, 117.43, 118.51, 120.89, 121.24, 124.44, 135.15, 136.36, 139.96, 141.81, 147.12, 149.88, 153.11, 170.63. Anal. Calcd for C₃₅H₆₀N₂O₃Si₂ (%): C, 68.37; H, 9.30; N, 4.31. Found: C, 68.72; H, 9.04; N, 4.58.

3.2.7. Synthesis of L₂Lu(CH₂SiMe₃)₂(THF) (2b)

The preparation method of complex 2b is similar to that of complex 2a (70%). ¹H NMR (500 MHz, C₆D₆, 7.16 ppm, 25 °C): δ −0.59, −0.84 (4H, CH₂SiMe₃), 0.00 (s, 18H, CH₂SiMe₃), 0.96–1.24 (m, 12H, CH(CH₃)₂), 1.37 (m, 4H, THF), 3.22 (m, 2H, CH(CH₃)₂), 3.55 (m, 4H, THF), 3.75 (s, 3H, OCH₃), 6.44–7.45 (m, 11H, Ph-H), 7.94 (s, 1H, CH = NAr). ¹³C NMR (125 MHz, C₆D₆, 128 ppm, 25 °C): 3.88, 25.71, 29.06, 58.01, 67.99, 111.60, 117.28, 120.12, 120.45, 120.62, 121.47, 124.43, 135.06, 136.57, 140.90, 141.64, 145.97, 149.98, 154.17, 171.05. Anal. Calcd for C₄₄H₅₇LuN₂O₂Si₂ (%): C, 57.86; H, 7.93; N, 3.29. Found: C, 57.63; H, 8.14; N, 3.53.

3.2.8. Synthesis of L₂Y(CH₂SiMe₃)₂(THF) (2c)

The preparation method of complex 2c is similar to that of complex 2a (74%). Single crystals suitable for X-ray analysis were obtained from hexane at −30 °C. ¹H NMR (500 MHz, C₆D₆, 7.16 ppm, 25 °C): δ −0.46, −0.68 (4H, CH₂SiMe₃), 0.06 (s, 18H, CH₂SiMe₃), 1.00–1.33 (m, 12H, CH(CH₃)₂), 1.37 (m, 4H, THF), 3.19 (m, 2H, CH(CH₃)₂), 3.61 (m, 4H, THF), 3.78 (s, 3H, OCH₃), 6.52–7.63 (m, 11H, Ph-H), 7.94 (s, 1H, CH = NAr). ¹³C NMR (125 MHz, C₆D₆, 128 ppm, 25 °C): 4.21, 25.38, 29.00, 31.97, 34.57, 34.88, 57.66, 69.37, 110.62,
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116.03, 117.53, 119.03, 123.94, 124.19, 124.50, 127.20, 128.35, 133.77, 135.46, 140.82, 142.63, 147.58, 150.02, 151.29, 168.84. Anal. Calcd for C\textsubscript{41}H\textsubscript{62}N\textsubscript{2}O\textsubscript{5}Si\textsubscript{2}Y (%): C, 64.37; H, 8.83; N, 3.66. Found: C, 64.65; H, 8.59; N, 3.96.

3.3. Polymerization of Isoprene

In a glovebox, a toluene solution (3 mL) of complex 1a (6.6 mg, 10 μmol), 1 equiv. of [Ph\textsubscript{3}C][B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}] and aluminum alkyls to initiate polymerization of isoprene. The choice of central metal size and the introduction of heteroatom coordination groups with different steric hindrance on the side arm of the ligand are the key to adjust the stereoselectivity of polyisoprene. Therefore, by adjusting these two factors, the stereoselectivity of polyisoprene was successfully switched from cis-1,4 (84%) to trans-1,4 (93%). In addition, the quasi-living chain transfer polymerization for high trans-1,4 polyisoprene system was developed.

3.4. X-ray Crystallographic Studies

Data collections of Single crystals of complexes were performed at −100 °C on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The SMART program package was used to determine the unit-cell parameters. The absorption correction was applied using SADABS. The structures were solved by direct methods and refined on F\textsuperscript{2} by full-matrix least-squares techniques with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were placed at calculated positions and were included in the structure calculation without further refinement of the parameters. All calculations were carried out using the Olex 2 program. Molecular structures were generated using the ORTEP program.

4. Conclusions

In summary, a series of rare-earth metal complexes (Ln = Sc, Lu, Y) bearing anilidio-amine ligand were successfully synthesized and defined, which were activated with [Ph\textsubscript{3}C][B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}] and aluminum alkyls to initiate polymerization of isoprene. The choice of central metal size and the introduction of heteroatom coordination groups with different steric hindrance on the side arm of the ligand are the key to adjust the stereoselectivity of polyisoprene. Therefore, by adjusting these two factors, the stereoselectivity of polyisoprene was successfully switched from cis-1,4 (84%) to trans-1,4 (93%). In addition, the quasi-living chain transfer polymerization for high trans-1,4 polyisoprene system was developed.

Supplementary Materials: The following are available online: Figure S1: \textsuperscript{1}H NMR spectrum (500 MHz, CDCl\textsubscript{3}, 25 °C) of ligand HL\textsubscript{1}, Figure S2: \textsuperscript{1}H NMR spectrum (500 MHz, CDCl\textsubscript{3}, 25 °C) of ligand HL\textsubscript{2}, Figure S3: \textsuperscript{1}H NMR spectrum (500 MHz, C\textsubscript{6}D\textsubscript{6}, 25 °C) of complex 1a, Figure S4: \textsuperscript{13}C NMR spectrum (125 MHz, C\textsubscript{6}D\textsubscript{6}, 25 °C) of complex 1a, Figure S5: \textsuperscript{1}H NMR spectrum (500 MHz, C\textsubscript{6}D\textsubscript{6}, 25 °C) of complex 1b, Figure S6: \textsuperscript{13}C NMR spectrum (125 MHz, C\textsubscript{6}D\textsubscript{6}, 25 °C) of complex 1b, Figure S7: \textsuperscript{1}H NMR spectrum (500 MHz, C\textsubscript{6}D\textsubscript{6}, 25 °C) of complex 1c, Figure S8: \textsuperscript{13}C NMR spectrum (125 MHz, C\textsubscript{6}D\textsubscript{6}, 25 °C) of complex 1c, Figure S9: \textsuperscript{1}H NMR spectrum (500 MHz, C\textsubscript{6}D\textsubscript{6}, 25 °C) of complex 2a, Figure S10: \textsuperscript{13}C NMR spectrum (125 MHz, C\textsubscript{6}D\textsubscript{6}, 25 °C) of complex 2a, Figure S11: \textsuperscript{1}H NMR spectrum (500 MHz, C\textsubscript{6}D\textsubscript{6}, 25 °C) of complex 2b, Figure S12: \textsuperscript{13}C NMR spectrum (125 MHz, C\textsubscript{6}D\textsubscript{6}, 25 °C) of complex 2b, Figure S13: \textsuperscript{1}H NMR spectrum (500 MHz, C\textsubscript{6}D\textsubscript{6}, 25 °C) of complex 2c, Figure S14: \textsuperscript{13}C NMR spectrum (125 MHz, C\textsubscript{6}D\textsubscript{6}, 25 °C) of complex 2c, Figure S15: \textsuperscript{1}H NMR spectrum (500 MHz, CDCl\textsubscript{3}, 25 °C) of cis-1,4 PIP (Table 1, entry 3), Figure S16: \textsuperscript{13}C NMR spectrum (125 MHz, CDCl\textsubscript{3}, 25 °C) of cis-1,4 PIP (Table 1, entry 3), Figure S17: \textsuperscript{1}H NMR spectrum (500 MHz, CDCl\textsubscript{3}, 25 °C) of trans-1,4 PIP (Table 1, entry 4), Figure S18: \textsuperscript{13}C NMR spectrum (125 MHz, CDCl\textsubscript{3}, 25 °C) of trans-1,4 PIP (Table 1, entry 4), Table S1: Crystal data and structure refinement for complexes 1a, 1c, 2a, 2c.

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