Highly 3,4-Selective Living Polymerization of Isoprene with Rare Earth Metal Fluorenyl N-Heterocyclic Carbene Precursors

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Received November 11, 2007; Revised Manuscript Received January 9, 2008

ABSTRACT: Fluorenyl modified N-heterocyclic carbene ligated rare earth metal bis(alkyl) complexes, (Flu-NHC)Ln$(CH_2SiMe_3)_2$ (Flu-NHC = $(C_{13}H_8CH_2CH_2(NCHCCHN)C_6H_2Me_3$-2,4,6); Ln = Sc (**1a**); Ln = Y (**1b**); Ln = Ho (**1c**); Ln = Lu (**1d**)), were synthesized and fully characterized by NMR and X-ray diffraction analyses. Complexes **1b**−**d** with the activation of Al^iBu_3 and $[Ph_3C][B(C_6F_5)_4]$ exhibited high activity, medium syndio- but remarkably high 3,4-regio-selectivity, and the unprecedented livingness for the polymerization of isoprene. Such distinguished catalytic performances could be maintained under various monomer-to-initiator ratios (500−5000) and broad polymerization temperatures (25−80 °C). The resultant polymers are crystalline, having syndiotactically enriched (racemic enchainment triad *rr* = 50%, pentad *rrrr* = 30%) 3,4-regulated (99%) microstructure and high glass-transition temperatures (40−49 °C). In contrast, complex **1a** was almost inert, while complexes bearing indenyl modified N-heterocyclic carbene moiety, (Ind-NHC)Ln$(CH_2SiMe_3)_2$ (Ind-NHC = $C_9H_6CH_2CH_2(NCHCCHN)C_6H_2Me_3$-2,4,6; Ln = Sc (**2a**); Ln = Y (**2b**); Ln = Ho (**2c**); Ln = Lu (**2d**)), also showed low activity or selectivity. These differences in catalytic performance could be attributed mainly to the electronics and spacial sterics of the metal center of these precursors.

Introduction

Investigation of efficient catalyst systems providing regio- and stereoselectivity and living mode for the polymerization of isoprene to afford polymers with designated molecular weight and microstructure has been a fascinating and challenging subject for decades. Ziegler−Natta catalyst systems,[1,2] f- and d-block element metallocenes,[3−5] non-Cp (Cp: cyclopentadienyl and its derivatives) ligated lanthanide alkylaluminates,[6] and PNP- or NNN-type rare earth metal complexes[7] have been extensively investigated for *cis*-1,4-selective. The resultant polymer mimics natural rubber. In the meantime, the interest in *trans*-1,4-regulated polyisoprene has emerged in rubber and tire industries;[8] thus, catalyst systems of Ln(allyl)$_2$Cl$(MgCl_2)_2$/AlR_3,[9] Cp*Nd$(BH_4)_2(THF)_2$/Mg$(n\text{Bu})_2$,[10] $TiCl_4$−AlR_3, and VCl_3−AlR_3[11] have been invented to provide *trans*-1,4-selectivity. In contrast, 3,4-selective catalyst systems are few and remain less explored, although 3,4-regulated polyisoprene is an important component of high-performance rubbers such as those with wet-skid resistance or low-rolling resistance tread.[12] To date, efficient 3,4-selective systems are the patented organolithium and ferric acetylacetate[13] and the transition-metal domain complexes such as $AlEt_3$−$Ti(OR)_4$,[14a] $(dmpe)_2CrCl_2$-MAO (dmpe: 1,2-bis(dimethylphosphino)ethane)[14b] and ferric complexes chelated by nitrogen ligands.[15] Medium-to-high 3,4-regularity or strain-crystalline polyisoprene could be obtained by lowering the polymerization temperature. Rare earth metal complexes that have exerted distinguished performances in *cis*- and *trans*-1,4 control polymerization usually show non-3,4-selectivity until a breakthrough achieved very recently by Hou's group, who employs bimetallic lanthanide cations to give isotactic 3,4-polyisoprene.[16] However, few cases of the above-mentioned systems provide 3,4-selectivity over 90%; none induces living polymerization. Therefore, further exploration of new catalyst systems based on rare earth metals and other elements to provide more controllable 3,4-selective polymerization with respect to molecular weight and molecular weight distribution and microstructure is obviously challengeable and attractive.

Thermally stable N-heterocyclic carbene (NHC) compounds have garnered upsurge in interest in the past decade and become versatile ligands to stabilize and activate metal centers in quite different key catalytic steps. The NHC−Ru complexes, for instance, have found wide applications in olefin metathesis[17] and olefin metathesis polymerization.[18] The NHC−Ni and Pd hydrocarbyls, however, undergo the reductive elimination reactions leading to imidazolium salts, which limits the application of such complexes to polymerization reactions.[19] Thus, examples in the addition polymerization of vinyl monomers remain scarce.[20] We released recently the synthesis of the first rare earth metal bis(alkyl) complexes stabilized by indenyl-modified N-heterocyclic carbene,[21] a new type of constrained-geometry-configuration (CGC) ligand. Such CGC-type NHC ligand is hemiliable and covalently bonds to the metal center, tuning coordination sphere and rigidity and chirality of the complex that may have potential in the area of homogeneous catalysts.[22] Herein we report fluorenyl-modified N-heterocyclic carbene supported rare earth metal bis(alkyl) complexes, which, activated by aluminum alkyls and borate, initiate the unprecedented living polymerization of isoprene with high activity, high 3,4-selectivity, and medium syndioselectivity. The influences of the electronics and sterics of rare earth metal precursors and polymerization conditions on the catalytic performances will also be presented.

Results and Discussion

Preparation of Complexes 1a−d and 2c. The fluorenyl-modified imidazolium bromide $[C_{13}H_9CH_2CH_2(NCHCHN(C_6H_2Me_3\text{-}2,4,6)CH)Br]$ ((FluH−NHC−H)Br)[23] was treated with $LiCH_2SiMe_3$ to afford ethylene bridged fluorenyl N-heterocyclic carbene (FluH−NHC). FluH−NHC reacted with rare earth metal tris(alkyl)s $(Ln(CH_2SiMe_3)_3(THF)_2)$ (THF = tetrahydrofuran)

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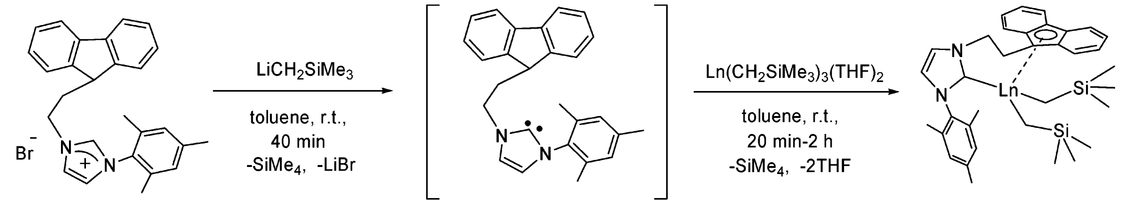
10.1021/ma702505n CCC: \$40.75

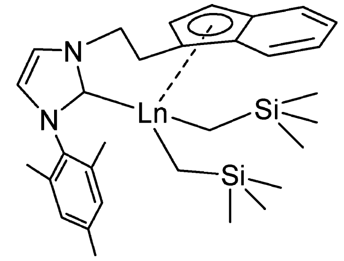
Scheme 1. Synthesis of Fluorenyl N-Heterocyclic Carbene (Flu-NHC) Ligated Rare Earth Metal Bis(alkyl) Complexes 1a−1d



(FluH-NHC-H)Br

$(Flu\text{-}NHC)Ln(CH_2SiMe_3)_2$
1a: Ln = Sc; **1b**: Ln = Y
1c: Ln = Ho; **1d**: Ln = Lu
THF: tetrahydrofuran

Chart 1. Molecular Structure of Indenyl N-Heterocyclic Carbene (Ind-NHC) Ligated Rare Earth Metal Bis(alkyl) Complexes 2a−2d



$(Ind\text{-}NHC)Ln(CH_2SiMe_3)_2$
2a: Ln = Sc; **2b:** Ln = Y
2c: Ln = Ho; **2d:** Ln = Lu

to give the CGC-type rare earth metal bis(alkyl) complexes $(Flu{-}NHC)Ln(CH_2SiMe_3)_2$ (Ln = Sc (**1a**); Ln = Y (**1b**); Ln = Ho (**1c**); Ln = Lu (**1d**)) via alkane elimination (Scheme 1). X-ray diffraction and NMR spectrum analyses revealed that complexes **1a**−**d** are analogous monomers without coordinating THF molecule, adopting tetrahedron geometry around metal center with the cent of the five-membered ring as the apex. The two alkyl ligands locate in *cis*-positions with one *endo* and the other *exo* against the carbene ring, paralleling to the N-aryl ring (Figure 1 for **1d**; Figure S1 for **1a**; Figure S2 for **1c**). The CGC ligand coordinates to the metal ion in a η^5/κ^1 mode via the five-membered ring and the ylidene carbon, leading to rigidity and chirality of the complexes. Thus, the ^1H NMR spectra of complexes **1a**, **1b**, and **1d** (**1c** is paramagnetic) display AB spin systems at the upfield region (δ −1.1 to −2.1 ppm) assigned to the diastereotopic methylene protons of the metal alkyl species (Figures S3, S5, and S7). The resonances at the very low field region in ^{13}C NMR spectra around δ 180−200 ppm are arising from the $Ln{-}C_{ylidene}$, suggesting that the coordination of the carbene moiety to the central metal ion is robust and maintains in solution (Figures S4, S6, and S8). The bond angles of C(28)−Sc−C(29) (103.68(15)°) in **1a** and C(28)−Ho−C(29) (104.40(12)°) in **1c** and C(28)−Lu−C(29) (103.93(12)°) in **1d** are comparable, falling in the normal range observed in other lanthanide bis(alkyl) complexes.[24] Following the literature procedure,[21] sequential protonolysis reactions of $[C_9H_7CH_2CH_2(NCHCHN(C_6H_2Me_3\text{-}2,4,6)CH)Br]$ ((IndH−NHC−H)Br) with $LiCH_2SiMe_3$ and $Ho(CH_2SiMe_3)_3(THF)_2$ gave the corresponding indenyl N-heterocyclic carbene-stabilized holmium bis(alkyl) complex **2c** (Chart 1). The coordination geometry of **2c** shown in Figure 2 is similar to the Flu-NHC stabilized Ho analogue **1c** (Figure S2) albeit with less shielded metal center, which influences significantly its catalytic performances (vide infra).

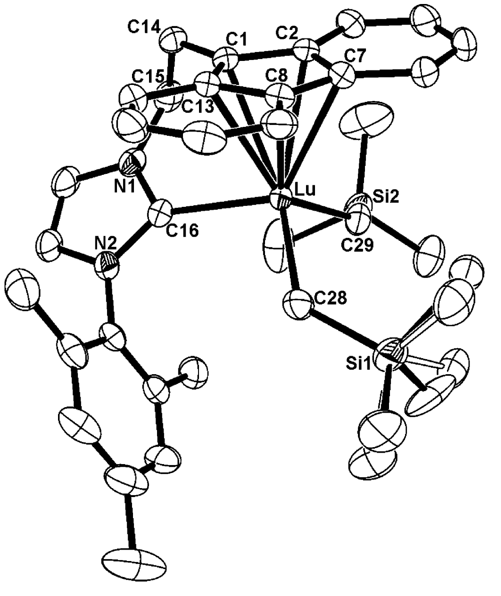


Figure 1. X-ray structure of **1d** with 40% probability of thermal ellipsoids. Hydrogen atoms and solvent molecule are omitted for clarity. Selected bond distances (Å) and angles (deg): $Lu{-}C_{Cp}$ = 2.654 (av), $Lu{-}C_{Cent}$ = 2.357, Lu−C(1) 2.638(3), Lu−C(2) 2.652(3), Lu−C(7) 2.630(3), Lu−C(8) 2.670(3), Lu−C(13) 2.680(3), Lu−C(16) 2.431(3), Lu−C(28) 2.325(3), Lu−C(29) 2.304(3); C(28)−Lu−C(29) 103.93(12), C(28)−Lu−C(16) 105.65(11), C(29)−Lu−C(16) 103.77(11), Lu−C(16)−N(2) 133.8(2).

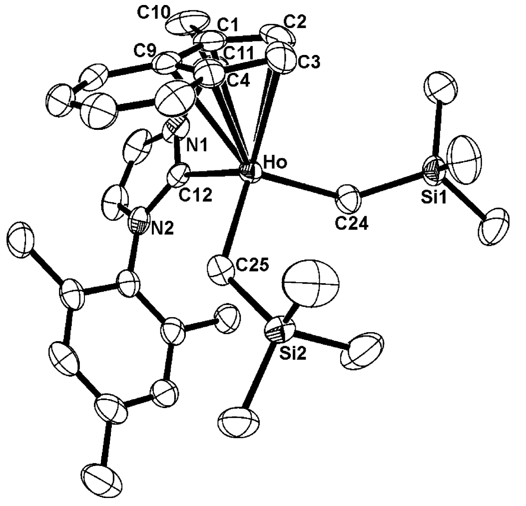


Figure 2. X-ray structure of **2c** with 40% probability of thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ho−C(1) 2.712(3), Ho−C(2) 2.668(3), Ho−C(3) 2.629(3), Ho−C(4) 2.683(3), Ho−C(9) 2.709(2), Ho−C(12) 2.490(2), Ho−C(24) 2.361(2), Ho−C(25) 2.364(2), $Ho{-}C_{cent}$ 2.393(2), $Ho{-}C_{Cp}$(av.) 2.680; $C_{cent}{-}Ho{-}C12$ 100.1, $C_{cent}{-}Ho{-}C24$ 121.5, $C_{cent}{-}Ho{-}25$ 120.7, C(24)−Ho−C(25) 107.33(9), C(24)−(Ho)−C(12) 95.21(8), C(25)−Ho−C(12) 107.27(8), Ho−C(12)−N(2) 131.25(16).

Table 1. Polymerization of Isoprene by Using Rare Earth Metal Precursors 1a−d and 2a−d under Various Conditions[a]

entry	Ln	[IP]/[Ln]	temp (°C)	time (h)	yield (%)	3,4-[b]	M_n[c] × 10^{-4}	M_w/ M_n[c]	T_g[d] (°C)	eff[e] (%)
1	**1a**	500	25	6	trace	nd[h]	nd	nd	nd	nd
2	**1b**	500	25	4	100	98.2	4.72	1.06	41	72.2
3	**1c**	500	25	3	100	98.3	3.94	1.07	43	86.4
4	**1d**	500	25	6	100	99.0	4.08	1.05	45	83.5
5	**1d**	1000	25	12	100	98.6	8.61	1.11	45	79.1
6	**1d**	2000	25	24	100	96.6	16.7	1.12	48	81.6
7	**1d**	3000	25	36	100	96.7	25.1	1.22	48	81.4
8	**1d**	4000	25	48	100	96.5	32.9	1.27	48	82.8
9	**1d**	5000	25	72	93	95.2	39.4	1.29	47	80.4
10	**1d**	500	40	5	100	97.4	3.90	1.22	49	87.3
11	**1d**	500	50	4	100	97.3	3.73	1.27	48	91.3
12	**1d**	500	60	3	100	95.4	3.85	1.19	47	88.5
13	**1d**	500	70	3	100	95.4	4.02	1.19	46	84.7
14	**1d**	500	80	2	100	94.5	3.91	1.22	46	87.1
15	**1d**[f]	500	25	12	100	98.1	3.86	1.38	40	88.2
16	**1d**[g]	500	25	2	100	98.2	4.26	1.10	45	80.0
17	**2a**	500	25	6	trace	nd	nd	nd	nd	nd
18	**2b**	500	25	6	50	89.4	2.03	1.36	23	83.9
19	**2c**	500	25	6	93	76.1	3.81	1.40	3	83.1
20	**2d**	500	25	6	15	91.0	nd	nd	nd	nd

[a] Ln: rare earth metal precursors; IP: isoprene; M_n: number-average molecular weight; M_w: weight-average molecular weight; M_w/M_n: molecular weight distribution; T_g: glass transition temperature; eff: catalyst efficiency. Conditions: toluene (3.0 mL); Ln (10 μmol); $[Ph_3C][B(C_6F_5)_4]$ (10 μmol); Al^iBu_3 (100 μmol). [b] Measured by means of ^{1}H NMR and ^{13}C NMR spectroscopy in $CDCl_3$. [c] Determined by means of gel permeation chromatography (GPC) against polystyrene standards. [d] Determined by differential scanning calorimetry (DSC). [e] Catalyst efficiency = M_n(calculated)/M_n(measured). [f] Hexane as solvent. [g] Chlorobenzene as solvent. [h] nd: not determined.

Polymerization of Isoprene. Complex **1** or **2** was activated with $[Ph_3C][B(C_6F_5)_4]$ to generate cationic units that showed low activity for the polymerization of isoprene. This might be ascribed to the impurities in the polymerization solution or the unstable nature of these cationic units that decomposed into nonactive species. Meanwhile, complexes **1** or **2** combined with Al^iBu_3 led to neutral inert catalytic systems. In contrast, the ternary system composed of complex **1** or **2** and $[Ph_3C][B(C_6F_5)_4]$ and Al^iBu_3 exhibited varied catalytic activity and selectivity. The polymerization results are summarized in Table 1. Addition of 500 equiv of isoprene to the toluene solution of **1a**/$[Ph_3C][B(C_6F_5)_4]$/Al^iBu_3 did not induce obvious polymerization at room temperature within 6 h (entry 1). Under the same conditions, switching to lutetium complex **1d**, the resultant ternary system could initiate the polymerization of isoprene (IP) with complete conversion. While for the yttrium counterpart **1b**, much higher activity was observed that a complete conversion was achieved in 4 h. The holmium complex **1c** was the highest active precursor that the polymerization was finished in less than 3 h. Strikingly, this ternary system provided high 3,4-selectivity for the polymerization of isoprene varying from 98.2% for the yttrium complex **1b** to 98.3% for the holmium counterpart **1c** and 99% for the lutetium analogue **1d**. The highest selectivity found for **1d** could be attributed to the smallest ionic radius of Lu^{3+} (Y^{3+}: 0.900 Å; Ho^{3+}: 0.901 Å; Lu^{3+}: 0.861 Å[25]), leading to the more crowded environment of the lutetium metal center, which was favored by the 4,3-insertion of isoprene monomer during the polymerization (entries 2−4). In addition, the catalyst system exhibited some stereoregularity. In the ^{1}H NMR spectrum of the obtained polyisoprene (PIP) (Figure 3), two singlets at δ 4.57 ppm and δ 4.70 ppm could be assigned to the olefinic protons (H_e and H_d) from stereoregular 3,4-microstructure (syndiotactic or isotactic 3,4-PIP[16]) as those from atactic 3,4-enchainments displayed multiple signals in this region. This was proved further by the ^{13}C NMR spectrum (Figure 4). The signals between δ 147 ppm and δ 148 ppm were arising from the atactic sequences while the isotactic triad *mm* showed at δ 148.3 ppm. The resonances at δ 146.3 ppm and δ 146.5 ppm could be assigned to the syndiotactic triad *rr* and pentad *rrrr*, respectively.[26] Thus, PIP obtained by using this catalyst system had syndiotactically enriched (*rr* = 50%, *rrrr* = 30%) 3,4-regulated microstructure. Such microstructure endowed the product crystallinity evidenced by wide-angle X-ray diffraction analysis (Figures S11 and S12)[27] and high T_g (glass-transition temperature) varying from 41 to 49 °C, the highest value found for PIP, as far as we are aware.

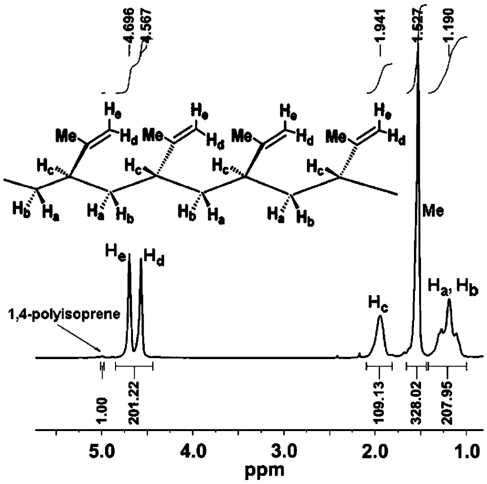


Figure 3. ^{1}H NMR ($CDCl_3$) spectrum of 99% 3,4-regulated polyisoprene (Table 1, entry 4).

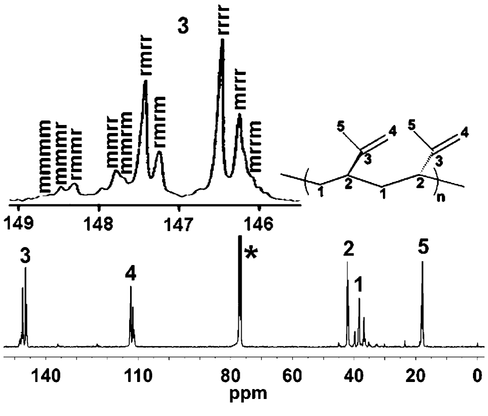


Figure 4. ^{13}C NMR (* $CDCl_3$) spectrum of 99% 3,4-regulated polyisoprene (Table 1, entry 4).

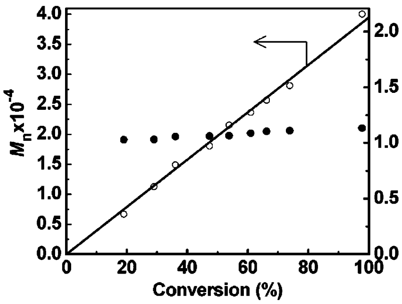


Figure 5. Polymerization of isoprene (IP) with complex **1d**/[(Ph$_3$C)(B(C$_6$F$_5$)$_4$)]/Al^{i}Bu$_3$ (**1d**: (Flu-NHC)Lu(CH$_2$SiMe$_3$)$_2$; Flu-NHC: fluorenyl N-heterocyclic carbine) as precursor: molecular weight vs conversion. Conditions: [IP]/[Lu] = 500, [Lu]$_0$ = 3.33 μmol/mL, [(Ph$_3$C)(B(C$_6$F$_5$)$_4$)]/[Lu] = 1, [Al^{i}Bu$_3$]/[Lu] = 10, toluene, 25 °C.

Therefore, complexes **1b**−**d** represented the first rare earth metal precursors providing syndiotactically enriched 3,4-selectivity for the polymerization of isoprene.

Dynamic study demonstrated that the conversion increased with polymerization time, which had linear correlation with the number-average molecular weight (M_n) of the obtained polymer; meanwhile, the molecular weight distribution (M_w/M_n) remained almost unchanged (1.05−1.10) (Figure 5). This result was indicative for a single-site nature of this ternary catalyst system that induced, for the first time, the remarkable living 3,4-polymerization of isoprene. To evaluate the catalytic efficiency, polymerization was performed under a wide range of monomer-to-catalyst ratios varying from 500 to 5000. The molecular weights of the obtained PIP increased with the ratios, close to the theoretic values. Thus, an as high as 82.8% efficiency was achieved although a slight drop in 3,4-regularity was observed when the ratio was over 2000 (entries 4−9).

Further investigation was focused on the catalytic behaviors at elevated temperatures. When the other polymerization conditions were kept constant, with the increase of the temperature, the catalytic activity increased that a complete conversion need 2 h at 80 °C compared to 6 h at room temperature. Meanwhile, the molecular weight and the molecular weight distribution of the isolated PIP did not vary obviously. Remarkably, the catalytic system maintained its high 3,4-selectivity at elevated temperatures, which dropped slightly to 94.5% when performing the polymerization at 80 °C compared to 99% at room temperature (entries 4, 10−14). These results suggested that the active species of this catalyst system was thermal stable to avoid chain transfer side reactions, and the livingness of the polymerization was remained at elevated temperatures. This was in striking contrast to the previous results that 1,4- and 3,4-selectivity were extremely sensitive to the polymerization temperature[4,5c] and should be highly welcomed by industry. Replacing the reaction medium toluene with polar chlorobenzene or nonpolar aliphatic hexane brought about minor influence on the catalytic activity and the selectivity in contrast to the cationic systems favoring polar solvent (entries 15 and 16).[16]

Compared to the polymerization conditions, the types of ligand and central metal ion played crucial roles in the control of the catalytic activity and the selectivity. Both the scandium complexes **1a** (vide supra) and **2a** were completely inert (entry 17). This was in disagreement with the half-metallocene rare earth metal precatalysts Cp′Ln(CH$_2$SiMe$_3$)$_2$(THF)$_2$ (Cp′: C$_5$Me$_4$SiMe$_3$)[28] for olefin polymerization and our recently reported nonmetallocene rare earth metal complexes [(NPN)Ln(CH$_2$SiMe$_3$)$_2$(THF)] (NPN: N(Ph)PPh$_2$=NC$_6$H$_2$Me$_3$-2,4,6) for the polymerization of isoprene,[29] where Sc^{3+} is the mostly favored central metal ion. While using less steric indenyl-modified N-heterocyclic carbene (NHC) stabilized precursors **2b** and **2d**, low yields were obtained and the 3,4-selectivity also decreased below 91% (entries 18 and 20). The catalytic activity of the holmium complex **2c** was close to that of its analogous **1c**, however, affording very low regioregular product (entry 19). These results demonstrated that the spacially bulky fluorenyl-modified NHC ligand endowed much higher regioselectivity to the corresponding complexes than the less steric indenyl modified NHC, as the metal center was much more shielded, which favored a η^2-coordination of isoprene leading to 4,3-insertion product. While the concert effects of the electron-donating fluorenyl or indenyl moieties and the electron-donating NHC ligand made the Lewis-basic rare earth metal complexes more active than the Lewis-acidic scandium counterparts. Although the initiation active species was not identified, it could be assigned to cationic lanthanide−alkyl aluminate according to the literature.[30] The mechanism investigation is in process.

Conclusion

We has demonstrated that a ternary catalyst system composed of rare earth metal bis(alkyl) complexes bearing fluorenyl or indenyl modified N-heterocyclic carbene ancillary ligands, aluminum alkyls, and organoborate is syndiotactically enriched highly 3,4-selective for the polymerization of isoprene. The polymerization was performed in an unprecedented living fashion at various monomer-to-catalyst ratios under a broad range of temperatures. The resultant polyisoprene is crystalline, having 3,4-regularity up to 99% with 50% triad racemic enchainments. The catalytic activity and the specific selectivity are strongly dependent on the steric bulkiness of the ancillary moiety and the type of the central metal ion. The polymerization temperature and medium, on the other hand, show less influence on the selectivity, in contrast to the patented and literature results. This represented the first rare-earth-metal-based precursors initiating syndiotactically enriched 3,4-selective polymerization of isoprene. In addition, it is the rare example that a catalytic system saturates regio- and stereoselectivity and livingness for the polymerization of a conjugated diene simultaneously.

Experimental Section

General Considerations. All manipulations were performed under a dry and oxygen-free argon atmosphere using standard high-vacuum Schlenk techniques or in a glovebox. All solvents were purified from the MBRAUN SPS system. Fluorene (98%), Al^{i}Bu$_3$ (1.0 M in hexane), and LiCH$_2$SiMe$_3$ solution (1.0 M in pentane) were purchased from Aldrich. Bromoethylidene, mesitylamine, glyoxal, and paraformaldehyde were purchased from the National Medicine Co. (China) and were used without further purification. [Ph$_3$C][B(C$_6$F$_5$)$_4$] was prepared according to the literature.[31] Isoprene (99%, Acros) was dried over CaH$_2$ while stirring for 48 h and distilled before use. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV400 (FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C). NMR assignments were confirmed by the ^{1}H−^{1}H COSY (correlation spectroscopy), ^{1}H−^{13}C HMQC (^{1}H-detected heteronuclear multiple quantum coherence), and ^{1}H−^{13}C HMBC (^{1}H-detected heteronuclear multiple-bond correlation) experiments when necessary. IR spectra were recorded on a VERTEX 70 FT-IR. Elemental analyses were performed at National Analytical Research Centre of Changchun Institute of Applied Chemistry (CIAC). The number-average molecular weights (M_n) and molecular weight distributions (M_w/M_n) of the polymer samples were measured by means of gel permeation chromatography (GPC) on a TOSOH HLC-8220 GPC apparatus (Column: Super HZM-Hx3) at 40 °C using THF as eluent (the flowing rate is 0.35 mL/min) against polystyrene standards. Differential scanning calorimetry (DSC) analyses were carried out on a Q 100 DSC from TA Instruments under a nitrogen atmosphere. The instrument was calibrated for temperature and enthalpy using pure indium (mp = 156.6 °C) and sapphire before experiment. Measurements during the first heating from 25 to 180 °C and then the first cooling from 180 to −50 °C as well as the second heating from −50 to 180 °C at 40 °C/min were performed. Wide-angle X-ray diffraction (WAXD) measurements were performed using a Rigaku D/Max 2500V PC X-ray diffractometer (Cu Kα, $\lambda = 1.5406$ Å). The diffraction patterns were collected during continuous scan at a speed of 4°/min between the angles of 5 and 50°. Crystallographic data were collected at −86.5 °C on a Bruker SMART APEX diffractometer with a CCD area detector (Mo Kα, $\lambda = 0.710\,73$ Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The structures were solved by using the SHELXTL program.

Synthesis of Complex (Flu-NHC)Sc($\mathbf{CH_2SiMe_3}$)$_2$ (1a). (FluH−NHC−H)Br (0.168 g, 0.366 mmol) and $\mathrm{LiCH_2SiMe_3}$ (0.035 g, 0.366 mmol) and 10 mL of toluene were added to a flask. After reacting for 20 min under vigorous stirring, the reaction mixture was added to a toluene solution (10 mL) of $\mathrm{Sc(CH_2SiMe_3)_3(THF)_2}$ (0.165 g, 0.366 mmol). The mixture remained stirring for another 2 h until turned to clear solution. Concentration, filtration, and cooling at −30 °C afforded yellow single crystals of complex **1a** (0.143 g, 65.3%). ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$, 25 °C): δ −1.55, −1.17 (AB, $^2J_{\mathrm{H-H}} = 10.8$ Hz, 4H, $\mathrm{Sc{-}C}H_2\mathrm{SiMe_3}$), 0.17 (s, 18H, $\mathrm{Sc{-}CH_2Si}Me_3$), 1.88 (s, 6H, $\mathrm{C_6H_2}Me_3$), 2.16 (s, 3H, $\mathrm{C_6H_2}Me_3$), 3.02 (t, $^3J_{\mathrm{H-H}} = 5.2$ Hz, 2H, $\mathrm{C}H_2\mathrm{CH_2}$), 3.91 (t, $^3J_{\mathrm{H-H}} = 5.2$ Hz, 2H, $\mathrm{C}H_2\mathrm{CH_2}$), 5.89 (d, $^3J_{\mathrm{H-H}} = 1.2$ Hz, 1H, $\mathrm{NC}H$), 6.12 (d, $^3J_{\mathrm{H-H}} = 1.2$ Hz, 1H, $\mathrm{NC}H$), 6.69 (s, 2H, $\mathrm{C_6}H_2\mathrm{Me_3}$), 7.26 (t, $^3J = 7.3$ Hz, 2H, fluorene), 7.32 (d, $^3J = 8.3$ Hz, 2H, fluorene), 7.38 (d, $^3J = 7.3$ Hz, 2H, fluorene), 8.41 (d, $^3J_{\mathrm{H-H}} = 8.3$ Hz, 1H, fluorene); ^{13}C NMR (100 MHz, $\mathrm{C_6D_6}$, 25 °C): δ 4.60 (s, 6C, $\mathrm{Sc{-}CH_2Si}Me_3$), 18.79 (s, 2C, $\mathrm{C_6H_2}Me_3$), 21.31 (s, 1C, $\mathrm{C_6H_2}Me_3$), 27.36 (s, 1C, $C\mathrm{H_2CH_2}$), 50.26 (s, 2C, $\mathrm{Sc{-}}C\mathrm{H_2SiMe_3}$), 52.51 (s, 1C, $\mathrm{CH_2}C\mathrm{H_2}$), 93.49 (s, 1C, *ipso*-fluorene), 119.62 (s, 6C, *ipso*-fluorene), 120.68 (s, 1C, $\mathrm{N}C\mathrm{H}$), 121.31 (s, 1C, $\mathrm{N}C\mathrm{H}$), 125.25 (s, 2C, fluorene), 126.13 (s, 2C, fluorene), 129.71 (s, 2C, $C_6\mathrm{H_2Me_3}$), 132.15 (s, 2C, *ipso*-fluorene), 135.61 (s, 2C, *ipso*-$C_6\mathrm{H_2Me_3}$), 136.64 (s, 1C, *ipso*-$C_6\mathrm{H_2Me_3}$), 139.74 (s, 1C, *ipso*-$C_6\mathrm{H_2Me_3}$), 187.64 ppm (s, 1C, $\mathrm{Sc{-}C_{ylidene}}$); IR (KBr pellets): ν 3126 (w, ν(=C−H)), 3036 (m, ν(=C−H)), 2954 (s, $\nu(\mathrm{CH_3})$), 2891 (m, $\nu(\mathrm{CH_3})$), 1680 (w, imidazole, ν(C=C)), 1609 (w, Ar, ν(C=C)), 1486 (m, $\delta(\mathrm{CH_2})$), 1449 (m, $\delta(\mathrm{CH_3})$), 1378 (w, $\delta(\mathrm{CH_3})$), 1249 (s, $\delta(\mathrm{SiCH_3})$), 862 (s, γ(=C−H)), 741(s, γ(=C−H)) cm^{-1}. Anal. Calcd for $\mathrm{C_{35}H_{47}ScN_2Si_2}$ (%): C, 70.43; H, 7.94; N, 4.69. Found: C, 69.13; H, 7.68; N, 4.57.

Synthesis of Complex (Flu-NHC)Y($\mathbf{CH_2SiMe_3}$)$_2$ (1b). Following the procedure described for the formation of **1a**, the reaction of (FluH−NHC−H)Br (0.168 g, 0.366 mmol) with $\mathrm{LiCH_2SiMe_3}$ (0.035 g, 0.366 mmol, 10 mL of toluene) and $\mathrm{Y(CH_2SiMe_3)_3(THF)_2}$ (0.181 g, 0.366 mmol) afforded **1b** (0.145 g, 61.7%). ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$, 25 °C): δ −1.90, −1.59 (AB, $^2J_{\mathrm{H-H}} = 10.8$ Hz, 4H, $\mathrm{Y{-}C}H_2\mathrm{SiMe_3}$), 0.22 (s, 18H, $\mathrm{Y{-}CH_2Si}Me_3$), 1.85 (s, 6H, $\mathrm{C_6H_2}Me_3$), 2.17 (s, 3H, $\mathrm{C_6H_2}Me_3$), 3.05 (t, $^3J_{\mathrm{H-H}} = 4.8$ Hz, 2H, $\mathrm{C}H_2\mathrm{CH_2}$), 3.90 (t, $^3J_{\mathrm{H-H}} = 4.8$ Hz, 2H, $\mathrm{C}H_2\mathrm{CH_2}$), 5.89 (s, 1H, $\mathrm{NC}H$), 6.12 (s, 1H, $\mathrm{NC}H$), 6.70 (s, 2H, $\mathrm{C_6}H_2\mathrm{Me_3}$), 7.26 (t, $^3J = 7.4$ Hz, 2H, fluorene), 7.30 (d, $^3J = 8.4$ Hz, 2H, fluorene), 7.40 (d, $^3J = 7.4$ Hz, 2H, fluorene), 8.39 (d, $^3J_{\mathrm{H-H}} = 8.4$ Hz, 1H, fluorene); ^{13}C NMR (100 MHz, $\mathrm{C_6D_6}$, 25 °C): δ 4.92 (s, 6C, $\mathrm{Y{-}CH_2Si}Me_3$), 18.60 (s, 2C, $\mathrm{C_6H_2}Me_3$), 21.32 (s, 1C, $\mathrm{C_6H_2}Me_3$), 27.66 (s, 1C, $C\mathrm{H_2CH_2}$), 42.81 (d, $J_{\mathrm{Y-C}} = 40.1$ Hz 2C, $\mathrm{Y{-}}C\mathrm{H_2SiMe_3}$), 52.82 (s, 1C, $\mathrm{CH_2}C\mathrm{H_2}$), 92.16 (s, 1C, *ipso*-fluorene), 118.29 (s, 2C, fluorene), 118.50 (s, 2C, *ipso*-fluorene), 119.54 (s, 2C, fluorene), 121.05 (s, 1C, $\mathrm{N}C\mathrm{H}$), 121.64 (s, 1C, $\mathrm{N}C\mathrm{H}$), 124.28 (s, 2C, fluorene), 126.33 (s, 2C, fluorene), 129.99 (s, 2C, $C_6\mathrm{H_2Me_3}$), 132.71 (s, 2C, *ipso*-fluorene), 135.39 (s, 2C, *ipso*-$C_6\mathrm{H_2Me_3}$), 135.99 (s, 1C, *ipso*-$C_6\mathrm{H_2Me_3}$), 140.04 (s, 1C, *ipso*-$C_6\mathrm{H_2Me_3}$), 190.77 ppm (d, $J_{\mathrm{Y-C}} = 45.8$ Hz, 1C, $\mathrm{Y{-}C_{ylidene}}$). IR (KBr pellets): ν 3133 (w, ν(=C−H)), 3037 (m, ν(=C−H)), 2952 (s, $\nu(\mathrm{CH_3})$), 2890 (m, $\nu(\mathrm{CH_3})$), 1678 (w, imidazole, ν(C=C)), 1608 (w, Ar, ν(C=C)), 1486 (m, $\delta(\mathrm{CH_2})$), 1449 (m, $\delta(\mathrm{CH_3})$), 1378 (w, $\delta(\mathrm{CH_3})$), 1248 (s, $\delta(\mathrm{SiCH_3})$), 861 (s, γ(=C−H)), 739 (s, γ(=C−H)) cm^{-1}. Anal. Calcd for $\mathrm{C_{35}H_{47}YN_2Si_2}$ (%): C, 65.60; H, 7.39; N, 4.37. Found: C, 65.33; H, 7.13; N, 4.19.

Synthesis of Complex (Flu-NHC)Ho($\mathbf{CH_2SiMe_3}$)$_2$ (1c). Following the procedure described above, (FluH−NHC−H)Br (0.168 g, 0.366 mmol) reacted with $\mathrm{LiCH_2SiMe_3}$ (0.035 g, 0.366 mmol) and $\mathrm{Ho(CH_2SiMe_3)_3(THF)_2}$ (0.209 g, 0.366 mmol) gave **1c** (0.164 g, 62.4%). IR (KBr pellets): ν 3126 (w, ν(=C−H)), 3036 (m, ν(=C−H)), 2952 (s, $\nu(\mathrm{CH_3})$), 2889 (m, $\nu(\mathrm{CH_3})$), 1678 (w, imidazole, ν(C=C)), 1609 (w, Ar, ν(C=C)), 1486 (m, $\delta(\mathrm{CH_2})$), 1449 (m, $\delta(\mathrm{CH_3})$), 1378 (w, $\delta(\mathrm{CH_3})$), 1248 (s, $\delta(\mathrm{SiCH_3})$), 862 (s, γ(=C−H)), 739 (s, γ(=C−H)) cm^{-1}. Anal. Calcd for $\mathrm{C_{35}H_{47}HoN_2Si_2}$ (%): C, 58.64; H, 6.61; N, 3.91. Found: C, 58.53; H, 6.56; N, 3.75.

Synthesis of Complex (Flu-NHC)Lu($\mathbf{CH_2SiMe_3}$)$_2$ (1d). Following the procedure described above, treatment of (FluH−NHC−H)Br (0.168 g, 0.366 mmol) with $\mathrm{LiCH_2SiMe_3}$ (0.035 g, 0.366 mmol) and $\mathrm{Lu(CH_2SiMe_3)_3(THF)_2}$ (0.213 g, 0.366 mmol, 10 mL of toluene) generated **1d** in a 67.7% yield (0.180 g). ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$, 25 °C): δ −2.18, −1.90 (AB, $^2J_{\mathrm{H-H}} = 10.8$ Hz, 4H, $\mathrm{Lu{-}C}H_2\mathrm{SiMe_3}$), 0.22 (s, 18H, $\mathrm{Lu{-}CH_2Si}Me_3$), 1.85 (s, 6H, $\mathrm{C_6H_2}Me_3$), 2.18 (s, 3H, $\mathrm{C_6H_2}Me_3$), 3.05 (t, $^3J_{\mathrm{H-H}} = 4.8$ Hz, 2H, $\mathrm{C}H_2\mathrm{CH_2}$), 3.91 (t, $^3J_{\mathrm{H-H}} = 4.8$ Hz, 2H, $\mathrm{C}H_2\mathrm{CH_2}$), 5.90 (d, $^3J_{\mathrm{H-H}} = 1.2$ Hz, 1H, $\mathrm{NC}H$), 6.12 (d, $^3J_{\mathrm{H-H}} = 1.2$ Hz, 1H, $\mathrm{NC}H$), 6.70 (s, 2H, $\mathrm{C_6}H_2\mathrm{Me_3}$), 7.27 (t, $^3J = 6.8$ Hz, 2H, fluorene), 7.32 (d, $^3J = 8.4$ Hz, 2H, fluorene), 7.40 (d, $^3J = 6.8$ Hz, 2H, fluorene), 8.39 (d, $^3J_{\mathrm{H-H}} = 8.4$ Hz, 1H, fluorene). ^{13}C NMR (100 MHz, $\mathrm{C_6D_6}$, 25 °C): δ 5.12 (s, 6C, $\mathrm{Lu{-}CH_2Si}Me_3$), 18.65 (s, 2C, $\mathrm{C_6H_2}Me_3$), 21.32 (s, 1C, $\mathrm{C_6H_2}Me_3$), 27.47 (s, 1C, $C\mathrm{H_2CH_2}$), 48.05 (s, 2C, $\mathrm{Lu{-}}C\mathrm{H_2SiMe_3}$), 53.04 (s, 1C, $\mathrm{CH_2}C\mathrm{H_2}$), 91.17 (s, 1C, *ipso*-fluorene), 118.19 (s, 2C, *ipso*-fluorene), 118.43 (s, 2C, fluorene), 119.04 (s, 2C, fluorene), 121.29 (s, 1C, $\mathrm{N}C\mathrm{H}$), 121.75 (s, 1C, $\mathrm{N}C\mathrm{H}$), 124.66 (s, 2C, fluorene), 126.39 (s, 2C, fluorene), 129.90 (s, 2C, $C_6\mathrm{H_2Me_3}$), 132.75 (s, 2C, *ipso*-fluorene), 135.44 (s, 2C, *ipso*-$C_6\mathrm{H_2Me_3}$), 136.09 (s, 1C, *ipso*-$C_6\mathrm{H_2Me_3}$), 140.00 (s, 1C, *ipso*-$C_6\mathrm{H_2Me_3}$), 199.18 ppm (s, 1C, $\mathrm{Lu{-}C_{ylidene}}$). IR (KBr pellets): ν 3126 (w, ν(=C−H)), 3034 (m, ν(=C−H)), 2951 (s, $\nu(\mathrm{CH_3})$), 2890 (m, $\nu(\mathrm{CH_3})$), 1678 (w, imidazole, ν(C=C)), 1610 (w, Ar, ν(C=C)), 1487 (m, $\delta(\mathrm{CH_2})$), 1449 (m, $\delta(\mathrm{CH_3})$), 1378 (w, $\delta(\mathrm{CH_3})$), 1248 (s, $\delta(\mathrm{SiCH_3})$), 864 (s, γ(=C−H)), 751 (s, γ(=C−H)) cm^{-1}. Anal. Calcd for $\mathrm{C_{35}H_{47}LuN_2Si_2}$ (%): C, 57.83; H, 6.52; N, 3.85. Found: C, 57.03; H, 6.46; N, 3.73.

Synthesis of Complex (Ind-NHC)Ho($\mathbf{CH_2SiMe_3}$)$_2$ (2c). Following the procedure described above, (IndH−NHC−H)Br (IndH = indenyl) (0.150 g, 0.366 mmol) was treated with $\mathrm{LiCH_2SiMe_3}$ (0.035 g, 0.366 mmol) and $\mathrm{Ho(CH_2SiMe_3)_3(THF)_2}$ (0.209 g, 0.366 mmol) to give **2c** (0.154 g, 63.1%). IR (KBr pellets): ν 3159 (w, ν(=C−H)), 3133 (m, ν(=C−H)), 2949 (s, $\nu(\mathrm{CH_3})$), 1677 (w, imidazole, ν(C=C)), 1607 (w, Ar, ν(C=C)), 1486 (m, $\delta(\mathrm{CH_2})$), 1457 (m, $\delta(\mathrm{CH_2})$), 1378 (w, $\delta(\mathrm{CH_3})$), 1248 (s, $\delta(\mathrm{SiCH_3})$), 863 (s, γ(=C−H)), 740 (s, γ(=C−H)) cm^{-1}. Anal. Calcd for $\mathrm{C_{31}H_{45}HoN_2Si_2}$ (%): C, 55.84; H, 6.80; N, 4.20. Found: C, 54.72; H, 6.77; N, 4.08.

Isoprene Polymerization. A typical polymerization procedure (Table 1, entry 4) was described as follow. **1d** (7.3 mg, 0.010 mmol), a toluene solution of $\mathrm{Al^{\mathit{i}}Bu_3}$ (0.10 mmol, 0.4 mL × 0.25 M), and a toluene solution (2.6 mL) of $\mathrm{[Ph_3C][B(C_6F_5)_4]}$ (8.0 mg, 0.010 mmol) were charged into a flask. The reaction apparatus was placed in a bath at 25 °C. Then 0.5 mL of isoprene (0.34 g, 5 mmol) was added to the above system to start the polymerization and remain stirring for 6 h. Then the viscous reaction solution was poured into ethanol (ca. 30 mL) containing a small amount of hydrochloric acid to terminate the polymerization. The PIP product was precipitated, filtered, washed with ethanol, and dried under vacuum at 40 °C to a constant weight (0.34 g, 100%). The isolated PIP has a 99% 3,4-tacticity and a number-average molecular weight of 4.08×10^4 with molecular weight distribution of 1.05. The glass transition temperature is 45 °C. ^{1}H NMR (Figure 3, 400 MHz, $\mathrm{CDCl_3}$, 25 °C): δ 1.11−1.27 (m, 2H, $-\mathrm{CH_2}-$), 1.53 (s, 3H, $\mathrm{CH_3}$), 1.94 (s, 1H, CH), 4.57 (s, 1H, $=\mathrm{CH_2}$), 4.70 (s, 1H, $=\mathrm{CH_2}$). ^{13}C NMR (Figure 4, 100 MHz, $\mathrm{CDCl_3}$, 25 °C): δ 147.82−146.30 (m, 1C, $C\mathrm{(CH_3){=}CH_2}$), 112.63−111.42 (m, 1C, $=\mathrm{CH_2}$), 42.2−41.85

(m, 1C, CH), 39.87−36.75 (m, 1C, −CH$_2$−), 18.29−17.68 (m, 1C, CH$_3$).

Acknowledgment. The authors are grateful for financial support from The National Natural Science Foundation of China for projects 20571072 and 20674081; The Ministry of Science and Technology of China for project 2005CB623802; the “Hundred Talent Scientist Program” of Chinese Academy of Sciences; Prof. N. Hu and Dr. W. Gao for their help in X-ray diffraction analysis; Prof. Z. Mo and Prof. H. Zhang for their discussions on wide-angle X-ray diffraction analysis; and Prof. Y. Mu for his assistance in borate synthesis.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra of complexes **1a** and **1b**; the ^{1}H, ^{13}C, ^{1}H−^{1}H COSY, HMQC, and HMBC spectra for complex **1d**; the crystallographic information files (CIFs) and the table for the summary of the crystallographic data and refinements for complexes **1a**, **1c**, **1d**, and **2c**; and wide-angle X-ray diffraction traces and DSC diagram for the selected polyisoprene samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA702505N