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Article

Living 3,4-Polymerization of Isoprene by Cationic Rare Earth Metal Alkyl Complexes Bearing Iminoamido Ligands

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Treatment of rare earth metal trialkyl complexes $Ln(CH_2SiMe_3)_3(THF)_2$ (Ln = Sc, Lu, and Y) with 1 equiv of α-diimine ligands $2,6\text{-}R_2C_6H_3N{=}CH{-}CH{=}NC_6H_3R_2\text{-}2,6$ (R = ^{i}Pr, Me) affords straightforwardly monoanionic iminoamido rare earth metal dialkyl complexes $[2,6\text{-}R_2C_6H_3N{-}CH_2{-}C(CH_2SiMe_3){=}NC_6H_3R_2\text{-}2,6]Ln(CH_2SiMe_3)_2(THF)$ (**1**: Ln = Sc, R = ^{i}Pr; **2**: Ln = Lu, R = ^{i}Pr; **3**: Ln = Y, R = ^{i}Pr; **4**: Ln = Sc, R = Me; **5**: Ln = Lu, R = Me; **6**: Ln = Y, R = Me) in 65−85% isolated yields. X-ray analyses show these complexes have decreasing steric hindrance in the coordination spheres of the metal centers in the order **1** > **2** > **3** > **4** > **5** > **6**. A mechanism involving intramolecular alkyl and hydrogen migration is supported on the basis of DFT calculations to account for ligand alkylation. Activated by $[Ph_3C][B(C_6F_5)_4]$, all of these iminoamido rare earth metal dialkyl complexes are active for living polymerization of isoprene, with activity and selectivity being significantly dependent on the steric hindrance around the metal center to yield homopolyisoprene materials with different microstructures and compositions. The sterically crowded complexes **1**−**3** give a mixture of 3,4- and *trans*-1,4-polyisoprenes (3,4-selectivities: 48−82%, *trans*-1,4-selectivities: 50−17%), whereas the less sterically demanding complexes **4**−**6** show high 3,4-selectivities (3,4-selectivities: 90−100%). In the presence of 2 equiv of Al^iBu_3, the complexes **1**−**6**/activator systems exhibit higher activities and 3,4-selectivities in the living polymerization of isoprene. A similar structure−reactivity relationship in polymerization catalysis can be also observed in these ternary systems. A possible mechanism of the isoprene polymerization processes is proposed on the basis of the DFT calculations.

Introduction

Cationic alkyl rare earth (group 3 and lanthanide) metal complexes are of current interest as potentially novel olefin polymerization catalysts.[1−19] A number of cationic alkyl rare earth metal complexes supported by various ancillary ligands such as cyclopentadienyls,[2] deprotonated aza-crowns,[3] benzamidinates,[4] β-diketiminates,[5] anilido-imines,[6] triazacyclononanes,[7] amide-functionalized triazacyclononanes,[8] phosphides,[9] tris(oxazolyl)ethane,[10] crown ethers,[11] bis(phosphinophenyl)-amido,[12] indenyl- or fluorenyl-functionalized N-heterocyclic carbene,[13] iminophosphonamido,[14] thiophene-NPN,[15] indolide-imine,[16] pyrrolide,[17] arylamido,[18] and aminopyridinate[19] have been synthesized and have had their reactivities studied. Despite these recent extensive efforts, however, a cationic alkyl rare earth metal complex based on an iminoamido ligand is rare, and little is known about the catalytic potential of these complexes for olefin polymerization.[20]

α-Diimine ligands, which allow an extensive adjustment in both the geometric and donor−acceptor properties by varying the substituents in the ligand frame and thereby a control over properties of the prepared catalysts, represent one of the most widely utilized groups of nitrogen donor chelating ligands in coordination chemistry.[21] In some cases, the neutral α-diimine ligands can transform into monoanionic iminoamido ligands via ligand alkylation by reacting with alkyls and hydrides of main-group metals Al, Mg, and Zn and transition metals Zr, Hf, and Ni.[22] For example, reactions of the substituted α-diimine compounds with $AlEt_2Cl$ afford a mixture of products via an ethyl transfer from aluminum to either the imine nitrogen atom (N-alkylation) or the imine carbon atom (C-alkylation) with formation of an enamine aluminum compound **A** or an iminoamido aluminum compound **B**, respectively (Scheme 1).[22g,h] Treatment of the nonsubstituted α-diimine ligand with $AlEt_2Cl$ affords an iminoamido product **C** possibly resulting from the C-alkylation followed by a 1,2-hydrogen shift (Scheme 1).[22g,h] Recently, the rediscovery and nice extension of Keim's work

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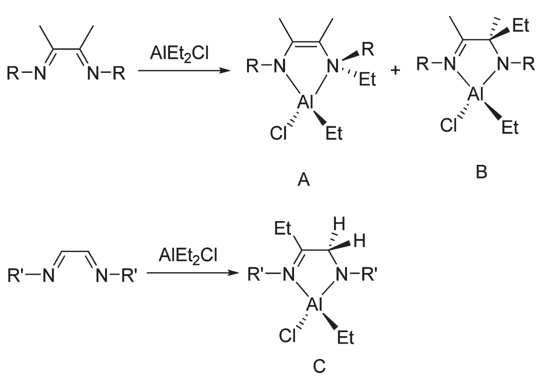
Scheme 1. Intramolecular Alkyl Transfer and Hydrogen Shift in α-Diimine Aluminum Complexes



of α-diimine nickel and palladium complexes as highly active catalysts for ethylene polymerization by Brookhart and coworkers has renewed research on the late transition metal catalysts.[23] Of special importance is that the steric properties of these α-diimine ligands allow controlling the molecular weights and microstructures of the resultant polymers. This gives a great impetus to the syntheses of a variety of such ligands and their organometallic complexes with different

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transition metals.[24] However, the incorporation of α-diimine ligands into rare earth (group 3 and lanthanide) metal complexes has never been reported.[25] More recently, the synthesis of the dialkyl scandium and yttrium complexes based on α-diimine ligands and their performance in the intramolecular hydroamination/cyclization of aminoalkenes have been reported by Mashima et al. when this paper was in progress.[26] However, their catalytic activities in olefin polymerization reactions are not known yet.

Cationic alkyl rare earth metal complexes usually exhibit distinguished catalytic proformances in the precisely controlled polymerization of 1,3-conjugated dienes such as isoprene (IP).[27−29] Most of these catalysts serve as efficient catalysts for the production of *cis*-1,4-[2g,y,j,x,5c,11d,12,16,17,27] or *trans*-1,4-polyisoprenes.[15,28] In contrast, 3,4-polyisoprene, far less studied, has attracted renewed interest recently because of its peculiar mechanical properties such as wet-skid-resistant and low-rolling-resistant tread.[2m,13,14,18a,19c,29] However, few cases of the catalytic systems show both high 3,4-selectivity ($>90\%$) and living mode.[13b] Herein, we report the one-pot synthesis and structural characterization of a new class of cationic alkyl rare earth metal complexes bearing iminoamido ligands based on α-diimine ligands. X-ray structures show that these complexes have decreasing steric hindrance around the metal centers in the order **1** > **2** > **3** > **4** > **5** > **6**. A mechanism involving intramolecular alkyl and hydrogen migration is supported on the basis of DFT calculations to account for the observed ligand alkylation. Activated by an equivalent of [Ph$_3$C][B(C$_6$F$_5$)$_4$], these complexes are active for living 3,4-polymerization of isoprene, with activity and selectivity being significantly dependent on the steric hindrance around the metal center to yield homopolyisoprene materials with different microstructures and compositions. In the presence of 2 equiv of Al^{i}Bu$_3$, these cationic catalytic systems show higher activities and 3,4-selectivities for the living polymerization of isoprene. A similar structure−reactivity relationship in polymerization catalysis can also be observed in these ternary systems. A possible mechanism of the isoprene polymerization processes is proposed on the basis of DFT calculations.

Results and Discussion

Synthesis and Structural Characterization of Monoanionic Iminoamido Rare Earth Metal Dialkyl Complexes. Recently, the synthesis of the dialkyl scandium and yttrium complexes based on α-diimine ligands and the structural characterization of a iminoamido scandium dialkyl complex by X-ray ananlysis have been reported by Mashima et al.[26] To develop more efficient, selective catalysts for the polymerization of isoprene and to gain more insight into the structure−activity

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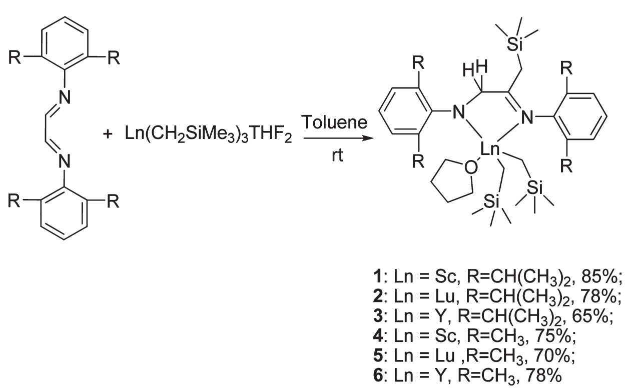
Scheme 2. Synthesis of Monoanionic Iminoamido Rare Earth Metal Dialkyl Complexes Based on α-Diimine Ligands



relation of the catalysts, we then synthesized and structurally characterized a series of monoanionic iminoamido rare earth metal dialkyl complexes. The reaction between rare earth metal trialkyl complexes $Ln(CH_2SiMe_3)_3(THF)_2$ (Ln = Sc, Lu, and Y) and 1 equiv of α-diimine ligands 2,6-$R_2C_6H_3N{=}CH{-}CH{=}NC_6H_3R_2$-2,6 (R = ^{i}Pr, Me) in toluene at room temperature gave straightforwardly monoanionic iminoamido rare earth metal dialkyl complexes **1**−**6** [2,6-$R_2C_6H_3N{-}CH_2{-}C(CH_2SiMe_3){=}NC_6H_3R_2$-2,6]$Ln(CH_2SiMe_3)_2$(THF) (**1**: Ln = Sc, R = ^{i}Pr, 85%; **2**: Ln = Lu, R = ^{i}Pr, 78%; **3**: Ln = Y, R = ^{i}Pr, 65%; **4**: Ln = Sc, R = Me, 70%; **5**: Ln = Lu, R = Me, 65%; **6**: Ln = Y, R = Me, 78%) in high yields (Scheme 2). All of these complexes **1**−**6** are soluble in common organic solvents, such as THF, toluene, and hexane, and gave well-resolved NMR spectra in C_6D_6. ^{1}H NMR spectra indicated a loss of symmetry in the chelating ligands, implying that the target tris(trimethylsilylmethyl) products containing neutral α-diimine ligands could not be obtained, whereas one singlet for the imino-methylene group at 1.80 ppm integrating for two protons and another singlet for the amino-methylene groups at 4.50 ppm integrating for two protons were observed. Characteristic high-field resonances for the metal alkyl group Ln-$CH_2Si(CH_3)_3$ appeared around −0.58 ppm (s, 4H, CH_2) and 0.22 ppm (s, 18H, $Si(CH_3)_3$), suggesting that only two trimethylsilylmethyl groups coordinated with the metal center. Moreover, only one singlet for the methylene protons of the Ln-alkyl groups indicated that the metal alkyl species in complexes **1**−**6** are fluxional in the solution state, which can freely rotate. One THF molecule, which showed signals at 1.0 and 3.5 ppm, was also found in the ^{1}H NMR spectra. In the ^{13}C NMR spectra of complexes **1**−**6**, a downfield shift resonance assignable to the imine carbon of $N{-}CH_2{-}CR'{=}N$ appeared around 190.2 ppm. Similar observations were also obtained by Mashima et al.[26]

Crystals of complexes **3**−**6** suitable for an X-ray crystal structure determination were grown from a concentrated hexane solution at −30 °C. X-ray analyses revealed that complexes **4**−**6** are isostructural and isomorphous. Their selected bond lengths and angles are summarized in Table 1, and the ORTEP drawings of **3**−**6** are shown in Figure 1. Each of complex **3**−**6** adopts a distorted trigonal-bipyramidal geometry, in which the rare earth metal center is bonded with one monoanionic iminoamido unit [2,6-$R_2C_6H_3N{-}CH_2{-}C(CH_2SiMe_3){=}NC_6H_3R_2$-2,6], two trimethylsilylmethyl alkyls (in *cis* position), and one THF. The Ln−N bond with the formally negatively charged amido nitrogen N1 is significantly shorter at 2.066(2)−2.222(2) Å than the neutral imino nitrogen Ln−N2 at 2.350(2)−2.515(4) Å. The bond distances of N2−C10 (1.288(4)−1.300(7) Å), which lie in the normal range of a C=N double bond, are shorter than those of N1−C9 (1.447(7)−1.453(4) Å) in the normal range of a single bond. Because of the ionic radius of the metal center in the trend Sc (0.89 Å) < Lu (1.00 Å) < Y (1.04 Å), the bond distances of the chelating Ln−N1, Ln−N2, Ln−O, Ln−C1, and Ln−C5 bonds increase in the order **4** < **5** < **3**, **6**. The bond distances of the Ln−N1 (2.481(6) Å), Ln−N2 (2.336(6) Å), and Ln−O (2.382(3) Å) bonds in **4** are comparable with those found in a similar scandium complex reported by Mashima et al. recently.[26]

Table 1. Selected Bond Lengths [Å] and Angles [deg] for Complexes 3−6

	3	**4**	**5**	**6**
	Ln = Y	Ln = Sc	Ln = Lu	Ln = Y
Ln−N1	2.213(5)	2.066(2)	2.182(3)	2.222(2)
Ln−N2	2.515(4)	2.350(2)	2.428(3)	2.483(2)
Ln−O	2.357(4)	2.217 (2)	2.304(2)	2.352(2)
Ln−C1	2.419(5)	2.247(2)	2.365(4)	2.421(3)
Ln−C5	2.429(6)	2.256(2)	2.366(3)	2.415(3)
N1−C9	1.447(7)	1.450(3)	1.453(4)	1.449(3)
N2−C10	1.300(7)	1.291(3)	1.288(4)	1.292(3)
C9−C10	1.497(8)	1.486(3)	1.485(5)	1.485(4)
∠N1−Ln−O	90.4(2)	90.1 (1)	89.3(1)	89.8 (1)
∠N1−Ln−C1	123.2(2)	122.0 (1)	122.5(1)	122. 6(1)
∠O−Ln−C1	93.6 (2)	92.0 (1)	92.4(1)	92.1(1)
∠N1−Ln−C5	122.8(2)	124.1(1)	122.7(1)	122.0 (1)
∠O−Ln−C5	86.8(2)	90.9 (1)	91.0(1)	91.4(1)
∠C1−Ln−C5	114.1(2)	113.7 (1)	114.8(1)	115.3 (1)
∠N1−Ln−N2	70.3(2)	74.0 (1)	71.2 (1)	69.8(1)
∠O−Ln−N2	160.3 (1)	161.9 (1)	158.1(1)	156.8 (1)
∠C1−Ln−N2	100.0(2)	103.6 (1)	106. 5(1)	107.9 (1)
∠C5−Ln−N2	100.4(2)	91.0(1)	91.2 (1)	90.4 (1)
∠N1−C9−C10	114.5(4)	113.8(2)	114.6(3)	114.6(2)
∠N2−C10−C9	118.9(5)	117.2 (2)	117.6(3)	117.9(2)
∠C9−N1−Ln	119.9(3)	120.1(1)	120.2(2)	121.2(2)
∠C10−N2−Ln	113.5(3)	114.7(1)	116.3(2)	116.3(2)
Ln−N1C9C10N2	0.454(10)	0.096(4)	0.101(6)	0.099(5)
C15−N1C9C10N2	−0.629(9)	−0.212(4)	−0.216(6)	−0.226(4)
C27−N1C9C10N2	−0.229(9)			
C23−N1C9C10N2		−0.188(4)	−0.188(6)	−0.180(5)
N1LnN2−N1C9C10N2	13.8(3)	3.26(2)	3.1(3)	3.0(2)
(C15−C20)−N1C9C10N2	88.6(2)	89.5(1)	88.0 (2)	86.7(1)
(C27−C32)−N1C9C10N2	82.0(2)			
(C23−C28)−N1C9C10N2		78.4(1)	77.1(1)	76.1 (1)

The angles between N1−Ln−N2 of complexes **3**−**6** are very narrow, about 69.8(1)−74.0(1), maybe due to the bite of the chelating iminoamido ligand.[22f] The N1−C9−C10−N2 (NCCN) portion of the iminoamido ligand is almost planar. The rare earth metal center has a slightly folded geometry with the NCCN plane. The yttrium center in the 2,6-diisopropylphenyl-substituted complex **3** is lying 0.454(10) Å out of the plane of NCCN. In contrast, the distances of the metal centers to the NCCN planes in the 2,6-dimethylphenyl-substituted complexes **4**−**6** are much shorter, only about 0.10 Å. The dihedral angle of the best planes of N1−Ln−N2 and NCCN of complex **3** is 13.8(3)°, which is larger than those of the best planes of N1−Ln−N1 and NCCN of complexes **4**−**6** (av 3.1°), consistent with a planar five-membered metallacyclic ring. The distances of the phenyl carbon atoms C15 and C27 to the NCCN plane of the 2,6-diisopropylphenyl-substituted complex **3** (0.629(9) and 0.229(9) Å, respectively, located in a different direction from the metal center) are longer than those of the corresponding phenyl carbon atoms C15 and C23 to the NCCN planes in complexes **4**−**6** (av 0.218 and 0.185 Å, respectively). Moreover, the different steric hindrance of the 2,6-disubstitutes (^{i}Pr > Me) on the iminoamido ligand and the different ionic radius of the

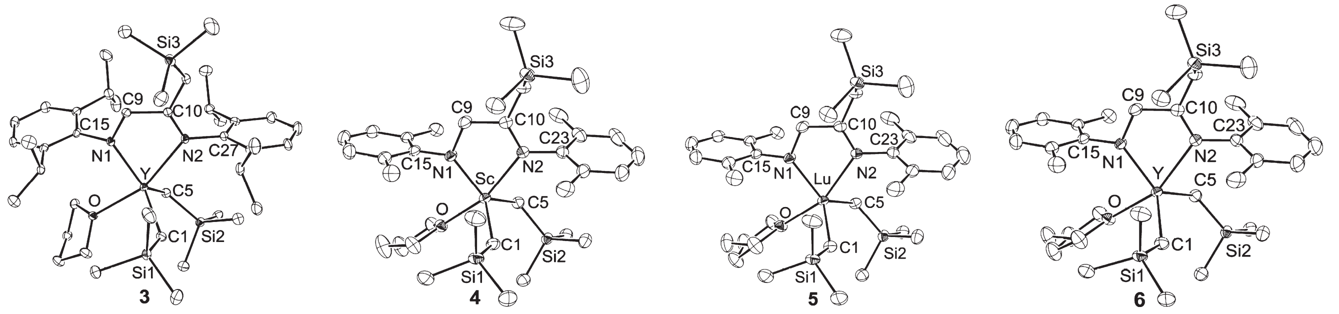
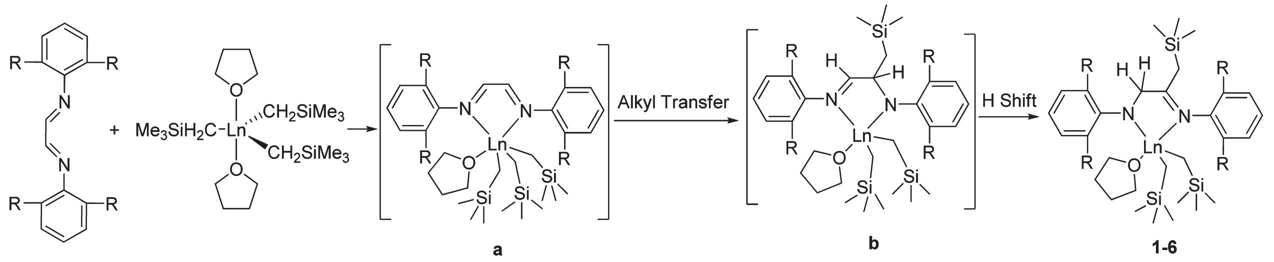
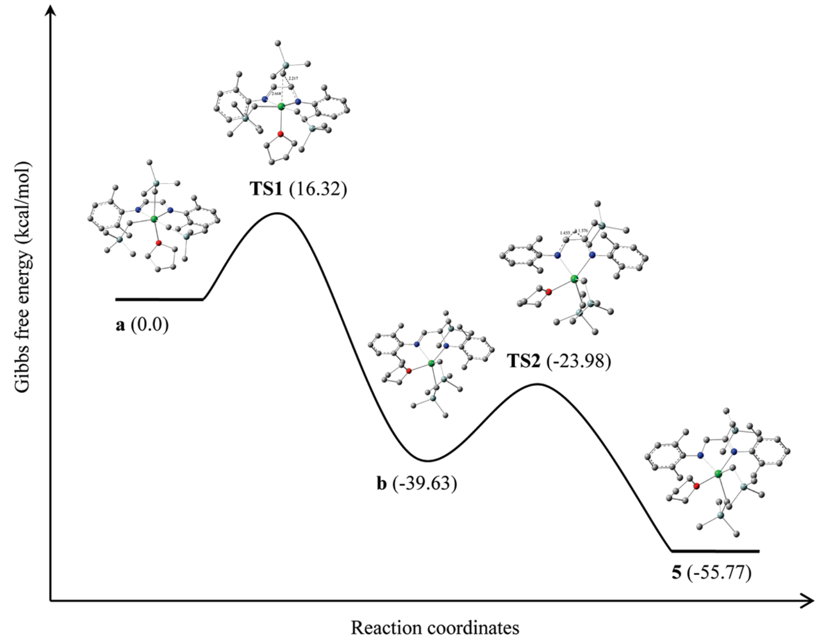


Figure 1. ORTEP drawings of complexes **3**−**6** with 30% thermal ellipsoids. The hydrogen atoms in **3**−**6** are omitted for clarity.

Scheme 3. Possible Mechanism Involving Intramolecular Alkyl and Hydrogen Migration for Formation of Complexes 1−6



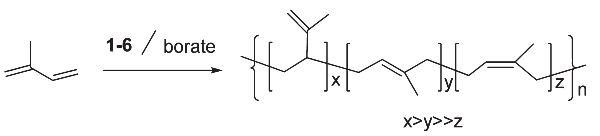
Scheme 4. DFT Calculations for Possible Mechanism of Ligand Alkylation Reaction



metal center result in the different rotation angles of the 2,6-disubstituted phenyl rings to NCCN plane. In contrast to derivatives containing sterically unhindered phenyl substituents in which one phenyl group is virtually coplanar with the AlNCCN ring, the two aromatic rings of the iminoamido ligand are planar (C15−C20 and C23(C27)−C28(C32)), the former plane is almost perpendicular to the NCCN plane (av 88.2°), while the latter forms a rotated angle decreasing in the order 82.0(2)° > 78.4(1)° > 77.1(1)° > 76.1(1)°. As a result, these complexes have decreasing steric hindrance around the metal centers in the order **1** > **2** > **3** > **4** > **5** > **6**.

Reaction Mechanism. The observation described above demonstrated that the reaction between the α-diimine ligands and the rare earth metal trialkyl complexes gave the mono-anionic iminoamido rare earth metal dialkyl complexes **1**−**6** in high yields. In view of ligand alkylation via alkyl transfer in combination with a hydrogen shift having been proposed previously by Vrieze et al.,[22a] a mechanism involving intramolecular alkyl transfer to an imine carbon atom followed by hydrogen migration was performed based on DFT calculations to account for the observed isomerization of the α-diimine rare earth metal trialkyl complex **a** (Schemes 3 and 4). The calculations were done in the same conditions as in the experiments; namely, the toluene solvation effects were included for the $-CH_2SiMe_3$ transfer and hydrogen migration. The 2,6-dimethylphenyl-substituted iminoamido lutetium complex **5** was used as a model. The calculated structures and the relative Gibbs free energies are summarized in Scheme 4. It is clear that the isomerization of complex **a** involves two steps; in the first one, a $-CH_2SiMe_3$ group transfers from the lutetium to a carbon atom through a

Table 2. Isoprene Polymerization by Complexes 1−6/Borate Binary Systems[a]



entry	cat.	*t*/h	yield (%)	microstructures[b]			M_n[c]/10^3	M_w/M_n[c]	T_g[d]/°C
				cis-1,4-	*trans*-1,4-	3,4-			
1	**1(Sc)**	3	15	2	50	48	28	1.04	−36
2	**2(Lu)**	3	40	2	28	70	45	1.12	−10
3	**3(Y)**	3	100	1	17	82	96	1.36	10
4	**4(Sc)**	1.5	60	0	10	90	62	1.18	25
5	**5(Lu)**	1.5	100	0	2	98	110	1.22	37
6	**6(Y)**	1.5	100	0	1	99	100	1.17	39
7	**5(Lu)**	0.25	20	0	1	99	62	1.27	38
8	**5(Lu)**	0.5	48	0	1	99	82	1.27	40
9	**5(Lu)**	1	91	0	1	99	110	1.22	39
10[e]	**5(Lu)**	24	10	0	0	100	20	1.12	40
11[f]	**5(Lu)**	1.5	100	0	1	99	107	1.20	40

[a] Conditions: 25 μmol of Ln complex, 25 μmol of $[Ph_3C][B(C_6F_5)_4]$, 10 mL of toluene, 25 °C. [b] Determined by ^1H, ^{13}C NMR spectra. [c] Determined by GPC in THF at 40 °C against polystyrene standard. [d] Measured by DSC. [e] Reaction temperature is 0 °C. [f] $[PhNMe_2H][B(C_6F_5)_4]$ served as activator.

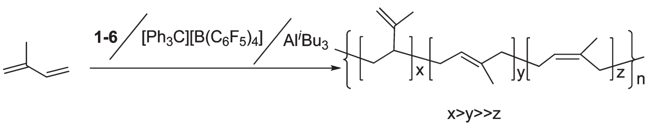
transition state (TS1) with a barrier height of 16.32 kcal·mol^{-1}, forming an intermediate (**b**) with a free energy of −39.63 kcal·mol^{-1} relative to the reactant; in the second step, a hydrogen atom shifts from the carbon atom connected with the tranferred $-CH_2SiMe_3$ group to the nearby carbon atom through a transition state (TS2) with a barrier height of 15.65 kcal·mol^{-1}, yielding the final product **5**, which will pack into crystals as determined in experiments, with a free energy of −55.77 kcal·mol^{-1} relative to the reactant. These results indicate that the reaction process from the reactant to the product **5** is exothermic and can proceed automatically due to the low reaction barrier heights. The driving force for the alkyl shift, which is restricted to tertiary alkyl groups, is maybe due to the release of steric strain in the five-membered NCCN rare earth metal chelate ring.

Polymerization of Isoprene (IP) by Complexes 1−6/Borate Binary Systems. The cationic iminoamido rare earth metal alkyl species in situ generated by the reaction of complexes **1**−**6** and 1 equiv of activator such as $[Ph_3C][B(C_6F_5)_4]$ or $[PhMe_2NH][B(C_6F_5)_4]$ were active for the living polymerization of isoprene, with activity and selectivity being significantly dependent on the steric hindrance around the metal center to yield homopolyisoprene materials with different microstructures and compositions. Some representative results are summarized in Table 2. The neutral iminoamido rare earth metal dialkyl complexes **1**−**6** showed no activities in the absence of an activator. The trityl perfluorophenyl borate $[Ph_3C][B(C_6F_5)_4]$ alone acted as a cationic polymerization initiator, yielding amorphous polyisoprene with a mixture of 3,4- and 1,4-*cis*/*trans* microstructures,[2m] while the ammonium borate $[PhNHMe_2][B(C_6F_5)_4]$ was inactive for IP polymerization under the same conditions. In contrast, the combination of **1**−**6** and $[Ph_3C][B(C_6F_5)_4]$ exhibited good activity and regioselectivity for the polymerization of IP at room temperature (Table 2, entries 1−6). Moreover, significant influences of the steric hindrance of the metal centers on the polymerization activities and selectivities were observed in these binary systems. With the decreasing steric hindrance of the metal center in the order **1** > **2** > **3** > **4** > **5** > **6**, the 3,4-regioselectivity gradually increased from 48% to 99% (Table 2, entries 3−8). Among them, the sterically crowded complexes **1**−**3** gave a mixture of 3,4- and *trans*-1,4 polyisoprenes (3,4-selectivities: 48−82%; *trans*-1,4-selectivities: 50−17%), whereas the less sterically demanding complexes **4**−**6** showed high 3,4-selectivities (3,4-selectivities: 90−99%). For the complex **5**/$[Ph_3C][B(C_6F_5)_4]$ system, with the increasing polymerization time, the molecular weight of the resulting polymer increased linearly with the conversion of IP, while the molecular weight distribution stayed less than 1.5, indicating that the IP polymerization behavior by these binary systems has living properties (Table 2, entries 5, 7−9; see Supporting Information). When the isoprene polymerization by the **5**/$[Ph_3C][B(C_6F_5)_4]$ system was carried out at the lower temperature, further higher regioselectivity (3,4-selectivity: 100%) was observed, as shown by the ^1H and ^{13}C NMR analyses (see Supporting Information) (Table 2, entries 5, 10). If the anilinium borate $[PhNHMe_2][B(C_6F_5)_4]$ was used as activator, similar activity and selectivity were obtained (Table 2, entry 11).

The 3,4-polyisoprenes all showed good solubilities in THF and $CHCl_3$. The ^1H NMR spectra of the polyisoprenes obtained by the complexes **1**−**3**/borate systems in $CDCl_3$ indicated a mixture of 3,4- and 1,4-microstructures (3,4-PIP:1,4-PIP = 1:1−1:4), and the ^{13}C NMR spectra showed diagnostic signals for both a *trans* configuration (δ 16.2, 26.9, 39.9, 124.4, and 135.1 ppm) and a 3,4-configuration (δ 18.8, 37.6, 111.4, and 147.9 ppm). The ^1H NMR spectra of the polyisoprenes obtained by the complexes **4**−**6**/borate systems in $CDCl_3$ indicated a predominant 3,4-microstructure (above 90%), and the ^{13}C NMR spectra showed main resonances assigned to 3,4-isoprene units. The GPC curves of the resulting copolymers were all unimodal with moderate polydispersities (M_w/M_n = 1.04−1.36), consistent with the predominance of a homogeneous single-site catalytic species. The glass transition temperature (T_g) of the polymers showed an almost linear correlation with the 3,4-isoprene content.

Polymerization of Isoprene (IP) by the Complexes 1−6/Borate/Al^{i}Bu$_3$ Ternary Systems. To thoroughly investigate the structure−reactivity relationship of these cationic iminoamido rare earth metal catalysts-promoted isoprene polymerization, 2 equiv of Al^{i}Bu$_3$ was added to the complexes **1**−**6/**activator binary system in the isoprene polymerization under the same conditions. Representative results are summarized in Table 3. In contrast with the complexes **1**−**6/**activator binary systems, the presence of 2 equiv of Al^{i}Bu$_3$ dramatically increased catalytic activities and regioselectivities under the same conditions (Table 3, entries 1−6). Only **8**−**15** min was needed for all of the complexes **1**−**6**/$[Ph_3C][B(C_6F_5)_4]$/Al^{i}Bu$_3$ ternary systems to convert quantitatively 600 equiv of isoprene into polyisoprenes at room temperature (Table 3, entries 1−6), which was much faster than those of the complexes **1**−**6**/activator binary systems. Significant influences of the steric hindrance of the metal centers on the polymerization activities and selectivities were also observed in these ternary systems. As the steric hindrance of the metal center decreased in **1** > **2** > **3** > **4** > **5** > **6**, the content of the 3,4-isoprene unit in the resulting polyisoprene gradually increased from 54% to 99% (Table 3, entries 1−6), which was slightly higer than that of the corresponding complexes **1**−**6**/activator binary systems. Similar to the complex **5**/borate binary system, the **5**/$[Ph_3C][B(C_6F_5)_4]$/Al^{i}Bu$_3$ ternary system also showed higher 3,4-selectivities at lower temperatures (3,4-selectivities: 100%) (Table 3, entries 10−11). Moreover, the small amount of aluminum compounds had less effect on

Table 3. Isoprene Polymerization by Complexes 1−6/Borate/Al^{i}Bu$_3$ Ternary Systems[a]



entry	cat.	time/min	yield (%)	microstructures[b] *cis*-1,4-	*trans*-1,4-	3,4-	M_n[c]/10^3	M_w/M_n[c]	T_g[d]/°C
1	**1(Sc)**	15	100	6	40	54	59	1.26	−30
2	**2(Lu)**	10	100	1	22	77	69	1.27	−3
3	**3(Y)**	8	100	2	10	88	75	1.14	10
4	**4(Sc)**	8	100	1	8	91	59	1.18	29
5	**5(Lu)**	8	100	0	1	99	72	1.30	36
6	**6(Y)**	8	100	0	1	99	78	1.16	36
7	**5(Lu)**	1	23	0	1	99	38	1.15	36
8	**5(Lu)**	3	55	0	1	99	53	1.19	37
9	**5(Lu)**	5	95	0	1	99	70	1.27	35
10[e]	**5(Lu)**	12[f]	71	0	0	100	102	1.25	43
11[e]	**5(Lu)**	42[f]	9	0	0	100	65	1.35	43

[a] Conditions: 25 μmol of Ln complex, 25 μmol of $[Ph_3C][B(C_6F_5)_4]$, 50 μmol of Al^{i}Bu$_3$, 10 mL of toluene, 25 °C. [b] Determined by ^1H, ^{13}C NMR spectra. [c] Determined by GPC in THF at 40 °C against polystyrene standard. [d] Measured by DSC. [e] Reaction temperature is 0 °C and −20 °C, respectively. [f] The unit for reaction time is hour.

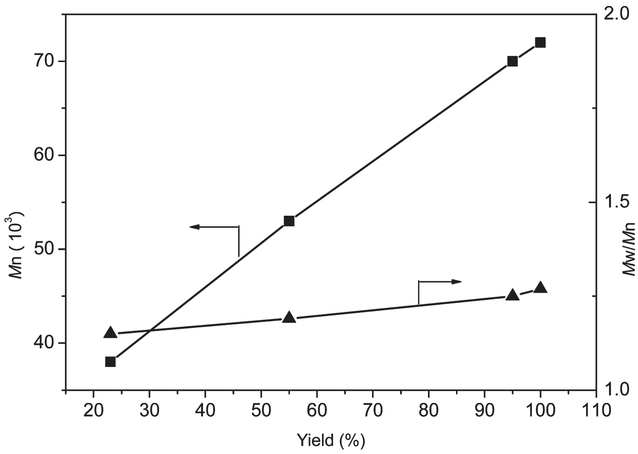


Figure 2. Plot of yield versus molecular weight and molecular weight distribution of the PIPs obtained by the complex **5**/$[Ph_3C][B(C_6F_5)_4]$/Al^{i}Bu$_3$ system in Table 3 (entries 5, 7−9).

the living nature of the complexes **1**−**6**/activator binary systems in the isoprene polymerization (Table 3, entries 1−9). For the complex **5**/borate/Al^{i}Bu$_3$ ternary system, with the increasing isoprene conversion from 23% to 100%, the molecular weight of the resulting polymer increased linearly, while the molecular weight distribution stayed less than 1.5, indicating that the IP polymerization behavior by these ternary systems is still living (Table 3, entries 5, 7−9, Figures 2 and 3). The GPC curves of these polymers were all unimodal with narrow molecular weight distributions (M_w/M_n = 1.18−1.35), consistent with the predominance of a single homogeneous catalytic species. These results showed that the chain transfer reaction did not occur in the presence of the small amount of Al^{i}Bu$_3$ compounds (2 equiv) in these ternary systems.

Polymerization Mechanism. To gain more insight into the influence of the steric hindrance around the rare earth metal center on the isoprene polymerization processes, the DFT calculations on the polymerization mechanism by cationic species **5** $[2,6\text{-}Me_2C_6H_3N{-}CH_2{-}C(CH_2SiMe_3){=}NC_6H_3Me_2\text{-}2,6]Lu(CH_2SiMe_3)(THF)_n][B(C_6F_5)_4]$ were carried out. It has been demonstrated that the selective polymerization of isoprene on the lanthanide center is dominated by the relative stability of the different coordination isomers of isoprene with the catalyst system (η^4-*cis*-1,4, η^4-*trans*-1,4, η^2-*cis*-3,4, η^2-*trans*-3,4, η^2-*cis*-1,2, η^2-*trans*-1,2). In the present study, we found only two coordination isomers, i.e., the *cis*-3,4,-mode and the *trans*-3,4-mode, and the latter is 2.73 kcal·mol^{-1} more stable than the former. It was revealed that the coordination of isoprene to the metal center in an η^2-*trans*-3,4 fashion is the most favored fashion among six possible isoprene coordination modes. As described elaborately in an earlier paper,[2w] the *trans*-3,4-mode coordination complex will selectively form the 3,4-insertion product.

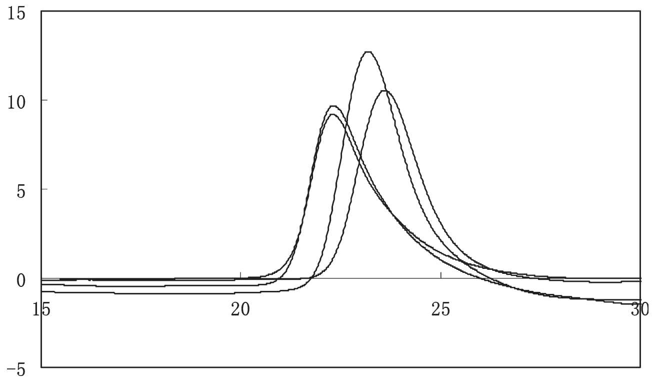
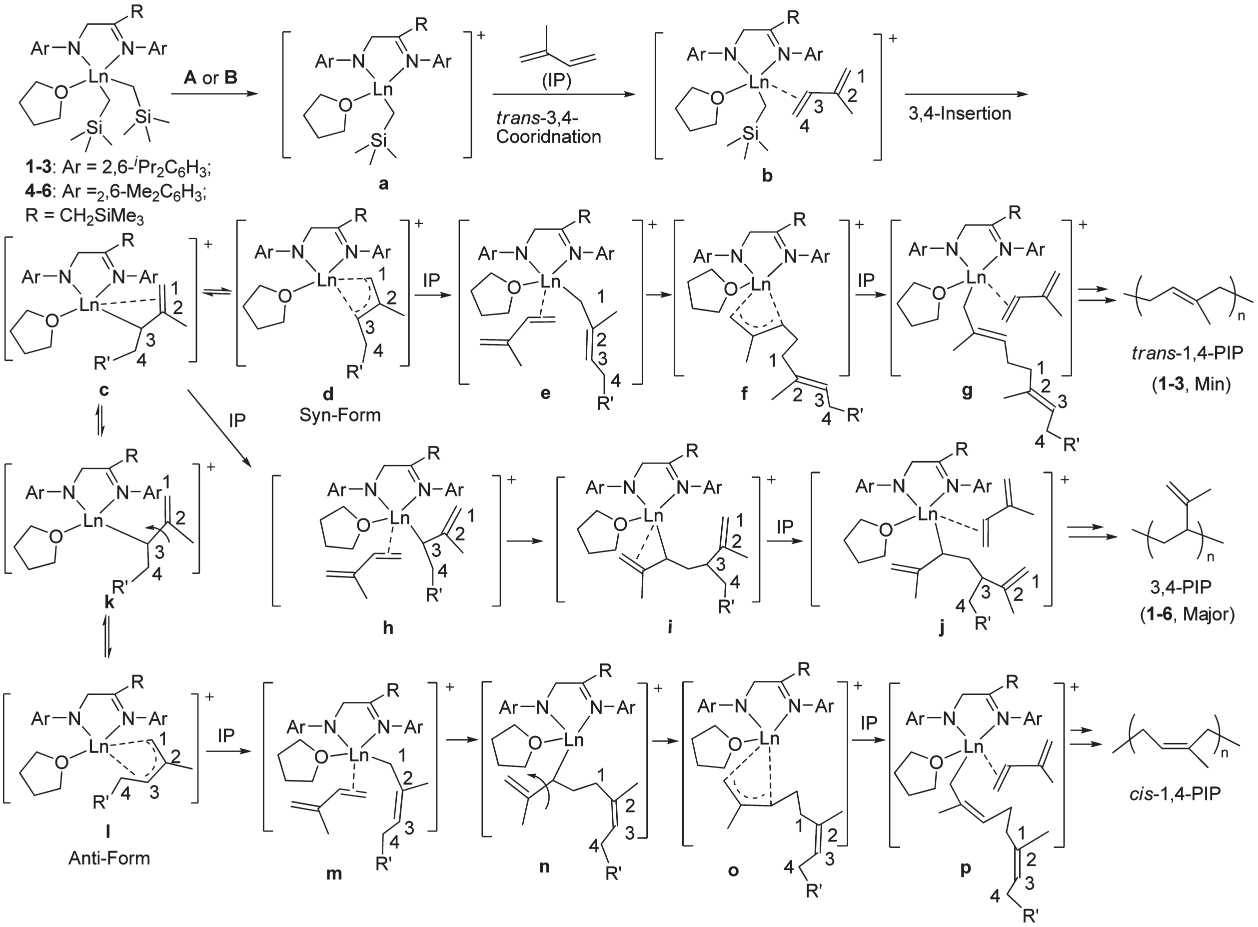


Figure 3. GPC curves of the PIPs obtained by the complex **5**/$[Ph_3C][B(C_6F_5)_4]$/Al^{i}Bu$_3$ system in Table 3 (entries 5, 7−9).

Therefore, the η^2-*trans*-3,4-coordination (e.g., **b** in Scheme 5) might be prevailing in the chain initiation process of the present catalyst systems. The subsequent 3,4-isoprene insertion into the Sc−alkyl bond could lead to the formation of an η^3-σ-allyl intermediate (**c**) as a secondary growing chain. There could be three competitive pathways to carry out the chain propagation process from **c** (Scheme 5). One is the coordination (in a *trans*-3,4-mode) and subsequent insertion of another molecule of isoprene at the metal center of **c** to give **h**; others are the isomerization of **c** to give the *syn*-η^3-π-allylic intermediate (**d**) or that to the *anti*-η^3-π-allylic intermediate (**l**) via rotation of the C3−C2 single bond of the η^1-σ-allyl intermediate (**k**). These competitive pathways would result in

Scheme 5. Possible Scenarios of Isoprene Polymerization Catalyzed by Cationic Iminoamido Rare Earth Metal Alkyl Species



different microstructures (3,4-, *trans*-1,4-, and *cis*-1,4-) in the polymer chains. For the less sterically demanding catalysts **4**−**6**, which bear 2,6-dimethylphenyl-substituted iminoamido ligands, the more electropositive metal center and the sufficient coordinative space around the metal center would relatively favor the coordination of the next isoprene monomer to the metal center. That is to say that isoprene coordination is faster than the isomerization of the σ-allyl intermediate **c** to the π-η^3-allylic intermediates **d** and **l**. Therefore, the coordination of an incoming isoprene monomer to the σ-allyl intermediate **c** to give **h** led to formation of the 3,4-polyisoprene sequences as a major part in the resulting polymers (cf. **h**−**j**, Scheme 5; see also Table 2). Regarding a possible chain termination reaction, the steric hindrance of the 2,6-dimethylphenyl-substituted iminoamido ligands and the THF ligand in these catalysts would prevent β-hydrogen elimination from a species like **i**. Therefore, a chain transfer reaction would be difficult, thus accounting for the living feature of these catalysts for the polymerization of isoprene.

For the more sterically demanding complexes **1**−**3**, bearing the 2,6-diisopropylphenyl-substituted iminoamido ligands, the less electropositive metal center and more steric hindrance around the metal center hampered the next isoprene coordination to such an extent that the isomerization reaction of the σ-allyl intermediate **c** to the less sterically crowding *syn*-π-η^3-allylic intermediates **d** became relatively favored. In contrast, the isomerization reaction of the σ-allyl intermediate **c** to the sterically overcrowding *anti*-π-η^3-allylic intermediates **l** via rotation of the C3−C2 single bond of the η^1-σ-allyl intermediate (**k**) became impossible because of the steric hindrance around metal center. As a result, both the next isoprene coordination and the isomerization of the σ-allyl intermediate **c** to the *syn*-η^3-π-allyl species **d** should occur at the same time. The former process gave the 3,4-polyisoprene sequences, while the latter process afforded *trans*-1,4-polyisoprene sequences via the coordination of an incoming isoprene monomer to the metal center of **d** (**e**) followed by isoprene insertion (**f**). The steric hindrance of both the 2,6-diisopropylphenyl-substituted iminoamido ligands and the THF ligands could account for the livingness observed in isoprene polymerization, as described above in the case of **4**−**6**. These scenarios are in agreement with the experimental results (see Table 2).

Conclusion

A series of rare earth metal dialkyl complexes bearing monocationic iminoamino ligands (**1**−**6**) can be easily prepared in high yields by reaction of the tris(trimethylsilylmethyl) scandium complexes with neutral α-diimine ligands. Complexes **3**−**6** are fully characterized by ^{1}H and ^{13}C NMR and X-ray analyses. The different steric hindrance of 2,6-disubstitutes (^{i}Pr > Me) on the iminoamido ligand and the ionic radius of the metal center in the trend Sc (0.89 Å) < Lu (1.00 Å) < Y (1.04 Å) result in the different distance of the metal center to the iminoamido plane (NCCN), the different dihedral angle of the best planes of N1−Ln−N2 and the iminoamido NCCN plane, and the different rotation angle of the 2,6-disubstituted phenyl rings to the iminoamido NCCN plane. As a result, these complexes have decreasing steric hindrance around the metal center in the order **1** > **2** > **3** > **4** > **5** > **6**. The DFT calculations determine whether the possible mechanism process involving intramolecular alkyl and hydrogen migration is exothermic and can proceed automatically due to the low reaction barrier heights. Activated by borate such as $[Ph_3C][B(C_6F_5)_4]$, complexes **1**−**6** show high catalytic activities for the living polymerization of isoprene to afford mainly the 3,4-poly(IP)s (3,4-selectivities: 48−99%) with narrow molecular weight distributions. A catalytic structure−reactivity relationship is observed in the isoprene polymerization catalyzed by these cationic iminoamido rare earth metal catalysts. The diisopropylphenyl-substituted iminoamido complexes **1**−**3** give a mixture of 3,4- and *trans*-1,4-polyisoprenes (3,4-selectivities: 48−82%; *trans*-1,4-selectivities: 50−17%), whereas the dimethylphenyl-substituted iminoamido demanding complexes **4**−**6** show high 3,4-selectivities (3,4-selectivities: 90−100%). In the presence of 2 equiv of Al^iBu_3, the complexes **1**−**6**/activator systems exhibit higher activities and 3,4-selectivities in the living polymerization of isoprene. Significant influences of the steric hindrance of the metal centers on the polymerization activities and selectivities are also observed in these ternary systems. A fundamental understanding of the chelating ligand effects, and hence the elucidation of the structure−reactivity relationship in polymerization catalysis, has been obtained based on DFT calculation. Further studies on the details of the polymerization mechanism and the polymerization and copolymerization of other monomers by the cationic monocationic iminoamino and related rare earth catalysts are in progress.

Experimental Section

Materials. All manipulations of air- and moisture-sensitive compounds were performed under a dry argon atmosphere by use of standard Schlenk techniques or a nitrogen-filled Mbraun glovebox. Anhydrous THF, hexane, and toluene were refluxed and distilled from sodium/benzophenone under dry nitrogen, degassed by freeze−pump−thaw cycles, and dried over fresh Na chips in the glovebox. Isoprene was purchased from TCI, dried over CaH_2, vacuum-transferred, and degassed by two freeze−pump−thaw cycles prior to polymerization experiments. $[Ph_3C][B(C_6F_5)_4]$ and $[PhMe_2NH][B(C_6F_5)_4]$ were purchased from Strem and used without purification. $LnCl_3$ was purchased from Strem. $LiCH_2SiMe_3$ (1.0 M solution in pentane) was purchased from Aldrich and used as received. Al^iBu_3 (1.1 M solution in toluene) was purchased from Acros and used as received. α-Diimine ligands $[2,6\text{-}R_2C_6H_3N{=}CH{-}CH{=}NC_6H_3R_2\text{-}2,6]$ (R = ^{i}Pr, Me)[23] and $Ln(CH_2SiMe_3)_3(THF)_2$ were synthesized according to the literature.[2w] The deuterated solvents benzene-d_6 (99.6 atom % D), $CDCl_3$ (99.8 atom % D), and 1,1,2,2-tetrachloroethane-d_2 (99.6 atom % D) were obtained from Cambridge Isotope.

General Methods. Samples of rare earth metal dialkyl complexes for NMR spectroscopic measurements were prepared in the glovebox using J. Young valve NMR tubes. The NMR (^{1}H, ^{13}C) spectra were recorded on an AVANCE 400 spectrometer at 45 °C with $CDCl_3$ or C_6D_6 as a solvent. Elemental analyses were performed on an Elementar Vario MICRO CUBE (Germany). The molecular weights and molecular weight distributions of polyisoprenes were determined by gel permeation chromatography on a Waters 2410 HPLC at 35 °C using THF as an eluent at a flow rate of 1 mL/min against polystyrene standards. The DSC measurements were performed on a Q 2000 (TA Co.) at a rate of 20 °C/min. Any thermal history difference in the polymers was eliminated by first heating the specimen to 200 °C, cooling at 5 °C/min to −80 °C, and then recording the second DSC scan.

Synthesis of $[(2,6\text{-}^iPr_2C_6H_3N{-}CH_2{-}C(CH_2SiMe_3){=}NC_6H_3{}^iPr_2\text{-}2,6)]Sc(CH_2SiMe_3)_2(THF)$ (1). To a colorless toluene solution (5 mL) of $Sc(CH_2SiMe_3)_3(THF)_2$ (1.35 g, 2.50 mmol) was added a solution of $2,6\text{-}^iPr_2C_6H_3N{=}CH{-}CH{=}NC_6H_3{}^iPr_2\text{-}2,6$ (1.13 g, 2.50 mmol) in toluene (5.0 mL) at room temperature. The mixture was stirred at room temperature for 3.5 h. After removal of all volatiles in vacuo, the residue was recrystallized from hexane at −30 °C to give **1** as light yellow crystals (1.60 g, 85% yield). ^{1}H NMR (C_6D_6, 25 °C, δ/ppm): −0.58 (s, 4H, $ScCH_2SiMe_3$), −0.09 (s, 9H, $N{-}CH_2C(CH_2Si(CH_3)_3){=}N$), 0.23 (s, 18H, $ScCH_2Si(CH_3)_3$), 1.11 (br, 4H, THF-β-CH_2), 1.20 (d, 6H, $CH(CH_3)_2$), 1.39 (br, 12H, $CH(CH_3)_2$), 1.60 (d, 6H, $CH(CH_3)_2$), 1.80 (s, 2H, $N{-}CH_2C(CH_2SiMe_3){=}N$)), 3.32 (m, 2H, $CH(CH_3)_2$), 3.51 (br, 4H, THF-α-CH_2), 3.96 (m, 2H, $CH(CH_3)_2$), 4.57 (s, 2H, $N\text{-}CH_2C(CH_2SiMe_3){=}N$), 7.04−7.19 (m, 6H, ArH). ^{13}C NMR (C_6D_6, 25 °C, δ/ppm): 0.1 (s, $CH_2Si(CH_3)_3$), 4.2 (s, $ScCH_2SiCH_3$), 24.1 (s, $CH_2Si(CH_3)_3$), 24.6 (s, THF), 25.1, 27.0, 27.6, 27.8, 28.0, 28.5 (m, $CH(CH_3)_2$, $CH(CH_3)_2$), 37.6 (s, $ScCH_2Si(CH_3)_3$), 67.8 (s, $NCH_2C{=}N$), 71.3 (s, THF), 123.7, 123.9, 125.1, 127.1, 140.9, 143.4, 145.9, 153.3 (m, ArC), 190.5 (s, C=N). Anal. Calcd for $C_{42}H_{77}N_2OSi_3Sc$: C, 66.79; H, 10.28; N, 3.71. Found: C, 66.30; H, 9.71; N, 3.14.

Synthesis of $[2,6\text{-}^iPr_2C_6H_3N{-}CH_2{-}C(CH_2SiMe_3){=}NC_6H_3{}^iPr_2\text{-}2,6)]$ $Lu(CH_2SiMe_3)_2(THF)$ (2). To a colorless hexane solution (5 mL) of $Lu(CH_2SiMe_3)_3(THF)_2$ (1.16 g, 2.0 mmol) was added a solution of $2,6\text{-}^iPr_2C_6H_3N{=}CH{-}CH{=}NC_6H_3{}^iPr_2\text{-}2,6$ (0.75 g, 2.00 mmol) in toluene (5.0 mL) at room temperature. The pale yellow mixture was stirred for 3.5 h. After removal of all volatiles in vacuo, the residue was recrystallized from hexane at −30 °C to give **2** as light yellow crystals (1.39 g, 78% yield). ^{1}H NMR (C_6D_6, 25 °C, δ/ppm): −0.74 (s, 4H, $LuCH_2SiMe_3$), −0.09 (s, 9H, $N\text{-}CH_2C(CH_2Si(CH_3)_3){=}N$), 0.22 (s, 18H, $LuCH_2Si(CH_3)_3$), 1.08 (m, 4H, THF-β-CH_2), 1.19 (d, 6H, $CH(CH_3)_2$), 1.37 (q, 12H, $CH(CH_3)_2$), 1.62 (d, 6H, $CH(CH_3)_2$), 1.80 (s, 2H, $N\text{-}CH_2C(CH_2SiMe_3){=}N$)), 3.34 (m, 2H, $CH(CH_3)_2$), 3.53 (m, 4H, THF-α-CH_2), 3.97 (m, 2H, $CH(CH_3)_2$), 4.67 (s, 2H, $N\text{-}CH_2C(CH_2SiMe_3){=}N$), 7.10−7.21 (m, 6H, ArH). ^{13}C NMR (C_6D_6, 25 °C, δ/ppm): 0.0 (s, $CH_2Si(CH_3)_3$), 4.6 (s, $LuCH_2SiCH_3$), 24.5 (s, $CH_2Si(CH_3)_3$), 24.7 (s, THF), 25.2, 26.7, 27.5, 27.6, 28.0, 28.6 (m, $CH(CH_3)_2$, $CH(CH_3)_2$), 40.6 (s, $LuCH_2Si(CH_3)_3$), 68.4 (s, $NCH_2C{=}N$), 70.8 (s, THF), 123.5, 123.7, 124.9, 127.2, 140.8, 143.1, 146.3, 154.2 (m, ArC), 191.9 (s, C=N). Anal. Calcd for $C_{42}H_{77}N_2OSi_3Lu$: C, 56.98; H, 8.77; N, 3.16. Found: C, 57.12; H, 9.21; N, 3.58.

Synthesis of $[2,6\text{-}^iPr_2C_6H_3N{-}CH_2{-}C(CH_2SiMe_3){=}NC_6H_3{}^iPr_2\text{-}2,6)]Y(CH_2SiMe_3)_2(THF)$ (3). To a colorless hexane solution (5 mL) of $Y(CH_2SiMe_3)_3(THF)_2$ (1.48 g, 3.00 mmol) was added a solution of $2,6\text{-}^iPr_2C_6H_3N{=}CH{-}CH{=}NC_6H_3{}^iPr_2\text{-}2,6$ (1.12 g, 3.00 mmol) in toluene (5.0 mL) at room temperature. The pale yellow mixture was stirred for 3.5 h. After removal of all volatiles in vacuo, the residue was recrystallized from hexane at −30 °C to give **3** as light yellow crystals (1.07 g, 45% yield). ^{1}H NMR (C_6D_6, 25 °C, δ/ppm): −0.58 (d, 4H, YCH_2SiMe_3), −0.09 (s, 9H, $N\text{-}CH_2C(CH_2Si(CH_3)_3){=}N$), 0.23 (s, 18H, $YCH_2Si(CH_3)_3$), 1.11 (br, 4H, THF-β-CH_2), 1.20 (d, 6H, $CH(CH_3)_2$), 1.39 (q, 12H, $CH(CH_3)_2$), 1.60 (d, 6H, $CH(CH_3)_2$), 1.80 (s, 2H, $N\text{-}CH_2C(CH_2SiMe_3){=}N$)), 3.32 (m, 2H, $CH(CH_3)_2$), 3.51 (m, 4H, THF-α-CH_2), 3.96 (m, 2H, $CH(CH_3)_2$), 4.57 (s, 2H, $N\text{-}CH_2C(CH_2SiMe_3){=}N$), 7.04−7.19 (m, 6H, ArH). ^{13}C NMR (C_6D_6, 25 °C, δ/ppm): 0.0 (s, $CH_2Si(CH_3)_3$), 4.5 (s, YCH_2SiCH_3), 24.7 (s, $CH_2Si(CH_3)_3$), 24.8 (s, THF), 25.2, 26.4, 27.2, 27.4, 28.1, 28.6 (m, $CH(CH_3)_2$, $CH(CH_3)_2$), 33.9 (d, $YCH_2Si(CH_3)_3$), 68.5 (s, $NCH_2C{=}N$), 70.3 (s, THF), 123.5, 123.8, 125.0, 127.0, 140.6, 143.0, 146.6, 152.8 (m, ArC), 191.6 (s, C=N). Anal. Calcd for $C_{42}H_{77}N_2OSi_3Y$: C, 63.12; H, 9.71; N, 3.51. Found: C, 62.88; H, 9.53; N, 3.21.

Synthesis of $[2,6\text{-}Me_2C_6H_3N{-}CH_2{-}C(CH_2SiMe_3){=}NC_6H_3\text{-}Me_2\text{-}2,6)]Sc(CH_2SiMe_3)_2(THF)$ (4). To a colorless hexane solution (5 mL) of $Sc(CH_2SiMe_3)_3(THF)_2$ (1.29 g, 2.85 mmol) was added a solution of $2,6\text{-}^iMe_2C_6H_3N{=}CH{-}CH{=}NC_6H_3{}^iMe_2\text{-}2,6$ (0.75 g, 2.85 mmol) in toluene (5.0 mL) at room temperature. The pale yellow mixture was stirred at room temperature for

1.5 h. After removal of all volatiles in vacuo, the residue was recrystallized from hexane at −30 °C to give **4** as reddish-brown crystals (1.00 g, 55% yield). ^{1}H NMR (C$_6$D$_6$, 25 °C, δ/ppm): −0.23 (s, 4H, ScCH_2SiMe$_3$), −0.20 (s, 9H, N-CH$_2$C(CH$_2$Si(CH_3)$_3$)=N), 0.24 (s, 18H, ScCH$_2$Si(CH_3)$_3$), 1.01 (br, 4H, THF-β-CH_2), 1.58 (s, 2H, N-CH$_2$C(CH_2SiMe$_3$)=N)), 2.42 (s, 6H, CH_3), 2.50 (s, 6H, CH_3), 3.68 (m, 4H, THF-α-CH_2), 4.18 (s, 2H, N-CH_2C(CH$_2$SiMe$_3$)=N), 6.87−7.16 (m, 6H, ArH). ^{13}C NMR (C$_6$D$_6$, 25 °C, δ/ppm): −0.2 (s, CH$_2$Si(CH$_3$)$_3$), 4.3 (s, ScCH$_2$SiCH$_3$), 19.8 (s, CH$_2$Si(CH$_3$)$_3$), 24.5 (s, THF), 20.1, 25.7 (m, CH$_3$), 37.0 (s, ScCH$_2$Si(CH$_3$)$_3$), 64.6 (s, NCH$_2$C=N), 71.1 (s, THF), 122.4, 126.0, 128.6, 129.4, 130.0, 146.0, 155.6 (m, ArC), 190.7 (s, C=N). Anal. Calcd for C$_{34}$H$_{61}$N$_2$OSi$_3$Sc: C, 63.50; H, 9.56; N, 4.36. Found: C, 63.46; H, 9.38; N, 4.02.

Synthesis of [2,6-Me$_2$C$_6$H$_3$N−CH$_2$−C(CH$_2$SiMe$_3$)=NC$_6$H$_3$-Me$_2$-2,6)]Lu(CH$_2$SiMe$_3$)$_2$(THF) (5). To a colorless hexane solution (5 mL) of Lu(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (0.43 g, 0.74 mmol) was added a solution of 2,6-^{i}Me$_2$C$_6$H$_3$N=CH−CH=NC$_6$H$_3$^{i}Me$_2$-2,6 (0.20 g, 0.74 mmol) in toluene (5.0 mL) at room temperature. The pale yellow mixture was stirred at room temperature for 0.5 h. After removal of all volatiles in vacuo, the residue was recrystallized from hexane at −30 °C to give **5** as reddish-brown crystals (0.34 g, 60% yield). ^{1}H NMR (C$_6$D$_6$, 25 °C, δ/ppm): −0.61 (s, 4H, LuCH_2SiMe$_3$), −0.06 (s, 9H, N-CH$_2$C(CH$_2$Si(CH_3)$_3$)=N), 0.40 (s, 18H, LuCH$_2$Si(CH_3)$_3$), 1.14 (br, 4H, THF-β-CH_2), 1.68 (s, 2H, N-CH$_2$C(CH_2SiMe$_3$)=N)), 2.53 (s, 6H, CH_3), 2.69 (s, 6H, CH_3), 3.68 (br, 4H, THF-α-CH_2), 4.47 (s, 2H, N-CH_2C(CH$_2$SiMe$_3$)=N), 7.03−7.31 (m, 6H, ArH). ^{13}C NMR (C$_6$D$_6$, 25 °C, δ/ppm): −0.2 (s, CH$_2$Si(CH$_3$)$_3$), 4.8 (s, LuCH$_2$SiCH$_3$), 19.9 (d, CH$_2$Si(CH$_3$)$_3$), 24.6 (s, THF), 20.0, 25.9 (m, CH$_3$), 40.9 (s, LuCH$_2$Si(CH$_3$)$_3$), 64.9 (s, NCH$_2$-C=N), 70.6 (s, THF), 122.0, 126.1, 128.6, 129.4, 129.8, 135.1, 145.5, 156.6 (m, ArC), 192.0 (s, C=N). Anal. Calcd for C$_{34}$H$_{61}$N$_2$OSi$_3$Lu: C, 52.82; H, 7.95; N, 3.62. Found: C, 53.04; H, 8.08; N, 3.99.

Synthesis of [2,6-Me$_2$C$_6$H$_3$N−CH$_2$−C(CH$_2$SiMe$_3$)=NC$_6$H$_3$-Me$_2$-2,6)]Y(CH$_2$SiMe$_3$)$_2$(THF) (6). To a colorless hexane solution (5 mL) of Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (1.45 g, 2.90 mmol) was added a solution of 2,6-^{i}Me$_2$C$_6$H$_3$N=CH−CH=NC$_6$H$_3$^{i}Me$_2$-2,6 (0.78 g, 2.90 mmol) in toluene (5.0 mL) at room temperature. The pale yellow mixture was stirred at room temperature for 0.5 h. After removal of all volatiles in vacuo, the residue was recrystallized from hexane at −30 °C to give **6** as reddish-brown crystals (1.55 g, 78% yield). ^{1}H NMR (C$_6$D$_6$, 25 °C, δ/ppm): −0.60 (d, 4H, YCH_2SiMe$_3$), −0.21 (s, 9H, N-CH$_2$C(CH$_2$Si(CH_3)$_3$)=N), 0.26 (s, 18H, YCH$_2$Si(CH_3)$_3$), 1.03 (m, 4H, THF-β-CH_2), 1.52 (s, 2H, N-CH$_2$C(CH_2SiMe$_3$)=N)), 2.38 (s, 6H, CH_3), 2.51 (s, 6H, CH_3), 3.49 (m, 4H, THF-α-CH_2), 4.26 (s, 2H, N-CH_2C(CH$_2$SiMe$_3$)=N), 6.88−7.16 (m, 6H, ArH). ^{13}C NMR (C$_6$D$_6$, 25 °C, δ/ppm): −0.3 (s, CH$_2$Si(CH$_3$)$_3$), 4.6 (s, YCH$_2$SiCH$_3$), 19.9 (s, CH$_2$Si(CH$_3$)$_3$), 24.7 (s, THF), 20.0 (m, CH$_3$), 25.5 (m, CH$_3$), 33.3, 33.7 (YCH$_2$Si(CH$_3$)$_3$), 65.2 (s, NCH$_2$C=N), 70.2 (s, THF), 121.9, 126.0, 128.7, 129.4, 129.6, 134.9, 145.3, 155.4 (m, ArC), 191.3 (s, C=N). Anal. Calcd for C$_{34}$H$_{61}$N$_2$OSi$_3$Y: C, 59.44; H, 8.95; N, 4.08. Found: C, 59.55; H, 9.29; N, 4.26.

A Typical Procedure for Isoprene (IP) Polymerization by Complex 5/[Ph$_3$C][B(C$_6$F$_5$)$_4$] Binary Systems (Table 2, entry 5). In a glovebox, a toluene solution (5 mL) of [Ph$_3$C][B(C$_6$F$_5$)$_4$] (0.023 g, 25 μmol) was added to a well-stirred toluene solution (5 mL) of complex **5** (0.019 g, 25 μmol) and isoprene (1.022 g, 15 mmol) at 25 °C in a 30 mL flask. The reaction mixture became viscous rapidly. After 3 h, the flask was taken outside and the polymerization was quenched by addition of methanol (50 mL, containing 5% butylhydroxytoluene (BHT) as a stabilizing agent). Then the mixture was poured into methanol (200 mL) to precipitate the polymer product. The precipitated polymer was dried under vacuum at 60 °C to a constant weight (1.020 g, 100% yield). The resulting polymer is soluble in THF and chloroform at room temperature.

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

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

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

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

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

$$\text{Mol } \textit{trans}\text{-1,4-IP\%} = \{I_{\mathrm{C3}}/(I_{\mathrm{C1}}+I_{\mathrm{C2}}+I_{\mathrm{C3}})\}\times 100 \tag{4}$$

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

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

A Typical Procedure for Isoprene (IP) Polymerization by Complex 5/[Ph$_3$C][B(C$_6$F$_5$)$_4$]/Al^{i}Bu$_3$ Ternary Systems (Table 3, entry 5). In a glovebox, a toluene solution (5 mL) of [Ph$_3$C][B(C$_6$F$_5$)$_4$] (0.023 g, 25 μmol) was added to a well-stirred toluene solution (5 mL) of complex **5** (0.019 g, 25 μmol), Al^{i}Bu$_3$ (45 μL, 1.1 M, 50 μmol), and isoprene (1.022 g, 15 mmol) at 25 °C in a 30 mL flask. The reaction mixture rapidly became viscous. After 8 min, the flask was taken outside and the polymerization was quenched by addition of methanol (50 mL, containing 5% butylhydroxytoluene (BHT) as a stabilizing agent). Then the mixture was poured into methanol (200 mL) to precipitate the polymer product. The precipitated polymer was dried under vacuum at 60 °C to a constant weight (1.020 g, 100% yield). The resulting polymer is soluble in THF and chloroform at room temperature.

X-ray Crystallographic Analysis. A crystal was selected and sealed in a thin-walled glass capillary under a microscope in a glovebox. Data collections were performed at −100 °C on a Bruker Smart-Apex CCD diffractometer with a CCD area detector using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The determination of crystal class and unit cell was carried out by the SMART program package.[30] The raw frame data were processed using SAINT[31] and SADABS[32] to yield the reflection data file. The structures were solved by using the SHELXTL-97 program.[33] Refinements were performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The analytical scattering factors for neutral atoms were used throughout the analysis. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. The residual electron densities were of no chemical significance. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-789585 (**3**), -789586 (**5**), and -789587 (**6**). Crystal data

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(32) Sheldrick, G. M. *SADABS*; Bruker AXS, Inc.: Madison, WI, 1998.

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and data collection and processing parameters for the rare earth metal dialkyl complexes **3**−**6** are summarized in the Supporting Information. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Details. The geometry optimizations and energy estimations were carried out with the M06 density functional method[34] with the sdd basis set,[35] which is adopted in the Gaussian 09 program.[36] The toluene solvation effects were included in all the calculations. Since there is no symmetry in these complexes, the C_1 symmetry point group was used throughout all calculations, and no higher molecular symmetry restriction was imposed. All calculations were performed utilizing the Gaussian 09 program.

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

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