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Synthesis and Characterization of Organo-Rare-Earth Metal Monoalkyl Complexes Supported by Carbon σ-Bonded Indolyl Ligands: High Specific Isoprene 1,4-Cis Polymerization Catalysts

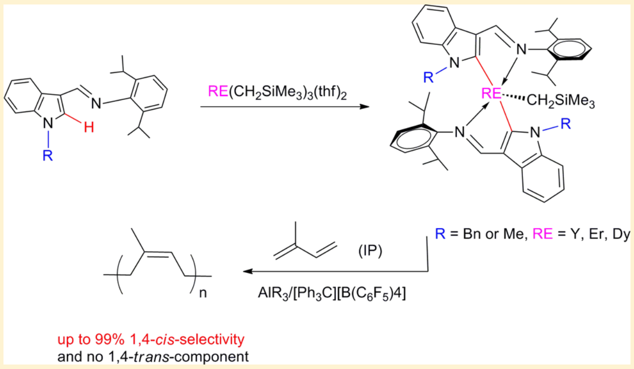
Liping Guo,[†] Xiancui Zhu,[†] Guangchao Zhang,[†] Yun Wei,[†] Lixin Ning,[‡] Shuangliu Zhou,*[,†] Zhijun Feng,[†] Shaowu Wang,*[,†,§] Xiaolong Mu,[†] Jun Chen,[†] and Yuzhe Jiang[†]

[†]Laboratory of Functional Molecular Solids, Ministry of Education, Anhui Laboratory of Molecule-Based Materials, College of Chemistry and Materials Science and [‡]College of Physics and Electronic Information, Anhui Normal University, Wuhu, Anhui 241000, China

[§]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, People's Republic of China

Supporting Information

ABSTRACT: A series of *N*-protected 3-imino-functionalized indolyl ligands 1-R-3-(R′N═CH)C_8H_5N [R = Bn, R′ = 2,6-$^iPr_2C_6H_3$ (**HL^1**); R = CH_3, R′ = 2,6-$^iPr_2C_6H_3$ (**HL^2**); R = Bn, R′ = ^tBu (**HL^3**)] and 1-CH_3-2-(2,6-$^iPr_2C_6H_3N$═CH)-C_8H_5N (**HL^4**) was prepared via reactions of *N*-protected indolyl aldehydes with corresponding amines. The C−H σ-bond metathesis followed by alkane elimination reactions between $RE(CH_2SiMe_3)_3(thf)_2$ and **HL^1**−**HL^3** afforded the carbon σ-bonded indolyl-ligated rare-earth metal monoalkyl complexes. Reactions of $RE(CH_2SiMe_3)_3(thf)_2$ with 2 equiv of **HL^1** or **HL^2** gave the carbon σ-bonded indolyl-ligated rare-earth metal monoalkyl complexes $L^1_2RECH_2SiMe_3$ (RE = Y(**1**), Er(**2**), Dy(**3**)) and $L^2_2RECH_2SiMe_3$ (RE = Y(**5**), Er(**6**), Dy(**7**), Yb(**8**)), while reaction of $Yb(CH_2SiMe_3)_3(thf)_2$ with 2 equiv of **HL^1** afforded the ytterbium dialkyl complex $L^1Yb(CH_2SiMe_3)_2(thf)_2$ (**4**). Reactions of $RE(CH_2SiMe_3)_3(thf)_2$ with **HL^3** gave the tris(heteroaryl) rare-earth metal complexes L^3_3RE (RE = Y(**9**), Er(**10**)). In the presence of cocatalysts, the rare-earth metal monoalkyl complexes initiated isoprene polymerization with a high activity (90% conversion of 1000 equiv of isoprene in 25 min) producing polymers with high regio- and stereoselectivity (1,4-cis polymers up to 99%).



up to 99% 1,4-*cis*-selectivity
and no 1,4-*trans*-component

INTRODUCTION

Cyclometalation via C−H bond activation is an attractive area of organometallic chemistry, which provides a mild route for constructing a new M−C bond.[1] This process has been incorporated into the development of a new methodology in catalytic synthetic chemistry and envisioned great progress in this field.[2] In contrast with the well-known oxidative addition of a C−H bond catalyzed by late-transition metals, using rare-earth metals as catalysts in catalytic synthetic chemistry via C−H activation is still an ongoing project.[3] Aromatic heterocyclic compounds such as furan,[4a] thiophene,[4b,c] and pyridine[4d,e] can be cyclometalated or functionalized using rare-earth metal complexes. It was found that reactions of 3-*tert*-butylimino-functionalized indole 3-(^tBu-N═CH)C_8H_5NH with rare-earth metal amides $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$ (RE = Yb, Y) produced unusual indolyl-1,2-dianion-ligated rare-earth metal complexes via sp^2 C−H bond activation.[5a] Indole and its derivatives, for their electron-rich property, have been widely used in organometallic chemistry with findings of multi-hapticities modes, e.g., η^1, η^3, η^5, η^6, and high active catalysts for small molecules transformations.[5] Very recently, we developed novel μ-η^2:η^1:η^1-bonding indolyl-supported dinuclear rare-earth metal alkyl complexes (monoalkyl/per metal), which displayed a high catalytic activity with a high 1,4-cis selectivity (1,4-cis content up to 99%) for isoprene polymerization.[5d] In contrast to the extensive use of 1*H*-indolyl ligands, the *N*-protected indolyls act as spectator ligands and their coordinative modes with early-transition metal complexes have not been reported.

Organo-rare-earth metal monoalkyl complexes of the type $L_2RE(R)$ (L = supporting ligands, RE = rare-earth metal, R = alkyl), unlike group 4 and late-transition metal analogues, could serve as active catalysts for ethylene or active polar monomers (for example, alkyl acrylates and lactones) polymerization in the absence of a cocatalyst.[6] Such complexes exhibited no or very low observed activity toward the polymerization of conjugated 1,3-dienes probably due to easy formation of stable η^3-allyl

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complexes.[7] Thus, suitable ligation systems for rare-earth metal monoalkyl complexes which could make such a stable η^3-allyl species active in subsequent propagation steps need to be developed. Therefore, a range of organo-rare-earth metal dialkyl complexes of the type LRE(R)$_2$ (L = supporting ligands, RE = rare-earth metal, R = alkyl) have been developed with the discovery of higher olefin polymerization catalysts in the presence of cocatalysts.[8] Moreover, organo-rare-earth metal alkyl complexes of the type L$_2$RE(R), or LRE(R)$_2$ (R = alkyl), after being activated by borate, would produce different active species [(L$_2$RE)$^+$ or (LRE(R)$^+$], which would behave different for the polymerization process in the initiation step; thus, the ligand's effect on controllable stereoregularly polymerization of higher olefins or 1,3-conjugated dienes would also be different. Although some organo-rare-earth monoalkyl complexes have been designed and tested for isoprene polymerization, very few noncyclopentadienyl ligands-supported rare-earth metal monoalkyl complexes with a cooperation of borate and aluminum reagents were found to display controllable stereoselectively 1,4-cis polymerization of isoprene,[9a,b] and the ternary system Cp*$_2$Gd[(μ-Me)AlMe$_2$(μ-Me)]$_2$GdCp*$_2$/AlR'$_3$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] (R' = ^{i}Bu), in which Cp*$_2$Gd[(μ-Me)AlMe$_2$(μ-Me)]$_2$GdCp*$_2$ species can be generated by reaction of the monomethyl [Cp*$_2$Gd(μ-Me)]$_2$ with AlMe$_3$, was found to display a high cis-1,4 selectivity (97.3%) for the polymerization of butadiene.[9c,d] Thus, development of highly active rare-earth metal monoalkyl complexes with new ligation systems for isoprene stereoregularly 1,4-cis polymerization is still highly required because the high cis-1,4-regioselectivity polymerization of isoprene is a prerequisite for obtaining polymers with excellent properties comparable to the natural rubber.

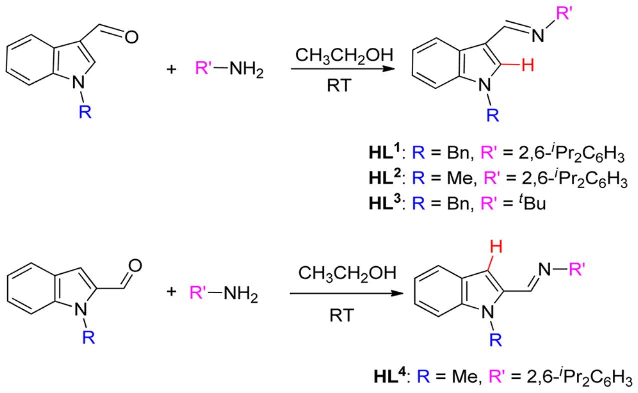
Herein, we report the synthesis and characterization of a series of rare-earth metal monoalkyl complexes incorporating new carbon σ-bonded indolyl ligands through C−H activation, which displayed a high activity for isoprene polymerization with high regio- and stereoselectivity upon activation with AlR$_3$ and [Ph$_3$C][B(C$_6$F$_5$)$_4$].

RESULTS AND DISCUSSION

Synthesis and Characterization of Rare-Earth Metal Monoalkyl Complexes Bearing *N*-Protected 3-Imino-Functionalized Indolyl Ligands. The ligands 1-R-3-(2,6-^{i}Pr$_2$C$_6$H$_3$N═CH)C$_8$H$_5$N [R = Bn (**HL^1**), Me (**HL^2**)], 1-Bn-3-(^{t}BuN═CH)C$_8$H$_5$N (**HL^3**), and 1-Me-2-(2,6-^{i}Pr$_2$C$_6$H$_3$N═CH)C$_8$H$_5$N (**HL^4**) can be obtained by reactions of the appropriate aldehydes with amines in 50−80% yields (Scheme 1). All proligands were well characterized by spectroscopic methods and HR-MS analyses.

Reactions of **HL^1** or **HL^2** with RE(CH$_2$SiMe$_3$)$_3$(thf)$_2$ in a molar ratio of 2:1 afforded the carbon σ-bonded indolyl-supported rare-earth metal monoalkyl complexes L$_2$RECH$_2$SiMe$_3$ [L = **L^1**, RE = Y (**1**), Er (**2**), Dy (**3**); L = **L^2**, RE = Y (**5**), Er (**6**), Dy (**7**), Yb (**8**)] through sp^2 C−H activation (Scheme 2). The ytterbium dialkyl complex **4** was obtained by reaction of **HL^1** with Yb(CH$_2$SiMe$_3$)$_3$(thf)$_2$, which might be attributed to the smaller ionic radius of Yb^{3+}, and it cannot hold two bulky ligands.[10] Attempts to prepare the carbon σ-bonded indolyl-supported rare-earth metal monoalkyl complexes of the type **L^3**$_2$RECH$_2$SiMe$_3$ failed. Instead, the tris(indolyl) rare-earth metal complexes **L^3**$_3$RE [RE = Y (**9**), Er (**10**)] were obtained (Scheme 2), probably due to the steric difference between **HL^1** and **HL^3**. The precursor **HL^4**, which has the imino group at the 2 position of the indolyl ring, cannot react with RE(CH$_2$SiMe$_3$)$_3$(thf)$_2$ to produce the carbon σ-bonded indolyl rare-earth metal complex. These results showed that the position of the imino group and substituent groups on the nitrogen atom of imine has a pronounced influence on the reactions. All carbon σ-bonded indolyl rare-earth metal complexes were fully characterized by spectroscopic methods and elemental analyses. The structures of complexes **1**−**8** were determined by single-crystal X-ray diffraction. The disappearance of the protons at the 2-indolyl position (at about δ 6.89 in C$_6$D$_6$ for free ligands) in ^{1}H NMR spectra of the diamagnetic yttrium complexes **1**, **5**, and **9** proved sp^2 C−H activation. In addition, the signals centered at 206 ppm in ^{13}C NMR spectra are assigned to the resonances of the carbon atoms at the 2 position of the indolyl ligands coupled to the yttrium nucleus with $J_{\text{Y−C}}$ = 50.0 Hz for complex **1** and $J_{\text{Y−C}}$ = 45.0 Hz for complexes **5** and **9**. The ^{1}H NMR spectra of complexes **1** and **5** in C$_6$D$_6$ at 25 °C showed two distinct singlets of the *C*H(CH$_3$)$_2$ group on the phenyl groups. The protons of the four methyl groups are diastereotopic and display four distinct singlets, revealing a large rotation barrier of the N−C$_{\text{Ar}}$ bonds. Meanwhile, the signals of the protons of the methylene of the benzyl group in complexes **1** and **9** exhibited AB spins at 4.25/4.55 ppm for **1** and 4.78/4.90 ppm for **9** (compared to the resonances of the protons of the methylene of the benzyl group at 4.71 ppm for the proligands) with $J_{\text{H−H}}$ = 15.0 Hz, indicating the rotation of the methylene hydrogen atoms was restricted to some extent.

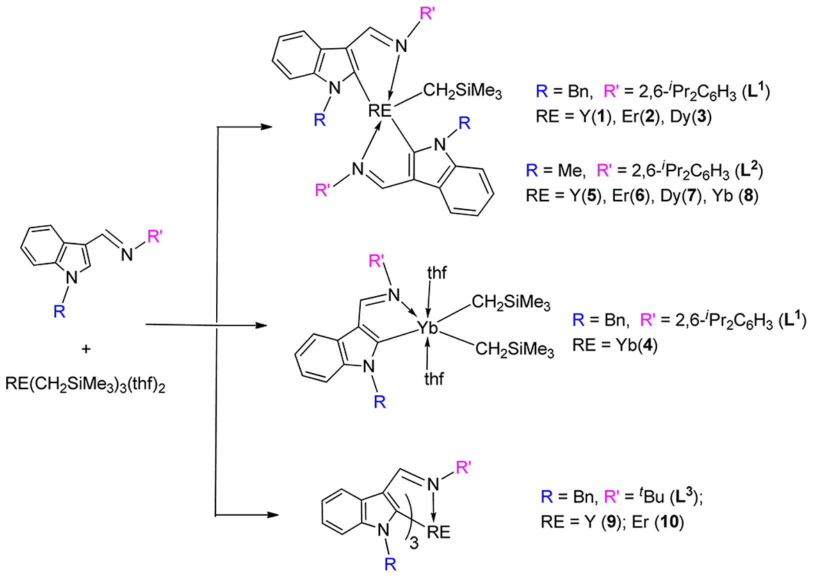
Scheme 1. Preparation of the Proligands HL^1−HL^4



X-ray diffraction revealed that the central metal of complexes **1**−**3** and **5**−**8** adopts a five-coordinate distorted trigonal bipyramidal geometry with the central metal ions bonded to the carbon atom of the trimethylsilylmethyl group and the carbon atoms of indolyl moiety and the nitrogen atoms of imino groups. The representative structures of complexes **1** and **5** are shown in Figures 1 and 2. The coordination geometry of the central metal in complex **4** (Figure 3) adopts a six-coordinate octahedral geometry. Selected bond lengths and bond angles are listed in Table 2.

From Table 2 it is found that the bond lengths between the yttrium atom and the sp^2 carbon atoms of the indolyl ligands are slightly different in complexes **1** and **5** [2.483(2) Å for **1**, 2.472(4) Å for **5**], probably due to the steric difference between the methyl and the benzyl groups connected to the indolyl nitrogen atoms. These distances are longer than the bond length of Y−C(sp^2) [2.435(5) Å] in yttrium anilidophosphinimino complex formed via intermolecular C−H activation.[11] The Y−CH$_2$SiMe$_3$ distance of 2.354(5) Å in **1** is slightly longer than that of 2.339(4) Å found in **5**, as a result of the more bulky

Scheme 2. Synthesis of Cyclometalated Rare-Earth Metal Complexes 1−10



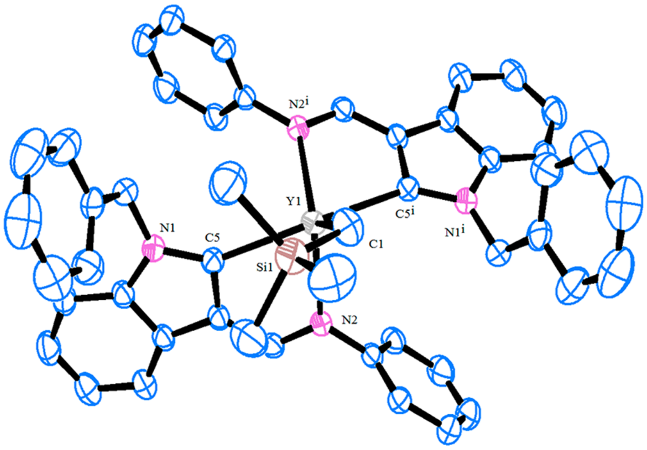


Figure 1. ORTEP diagram of complex **1** with thermal ellipsoids at the 30% probability level. All hydrogen atoms and isopropyl groups are omitted for clarity.

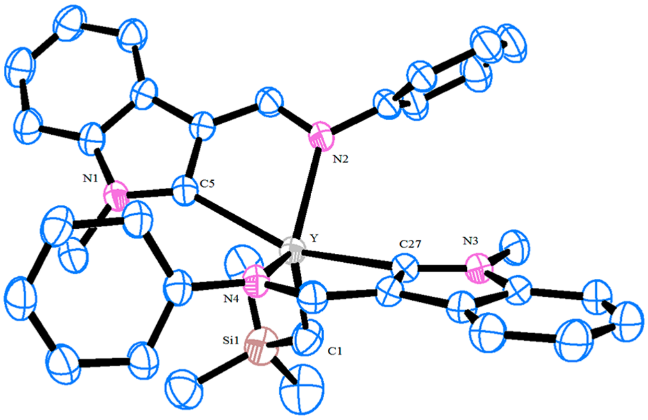


Figure 2. ORTEP diagram of complex **5** with thermal ellipsoids at the 30% probability level. All hydrogen atoms and isopropyl groups are omitted for clarity.

benzyl group. Similar results can also be found in complexes **2** and **6** and **3** and **7** (Table 1). The bond lengths of Yb−C(sp^3)

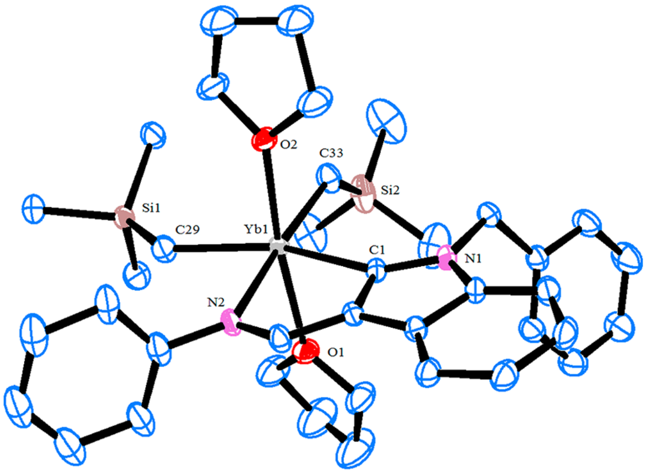


Figure 3. ORTEP diagram of complex **4** with thermal ellipsoids at the 30% probability level. All hydrogen atoms and isopropyl groups are omitted for clarity. Selected bond lengths (Angstroms) and angles (degrees): Yb(1)−C(1) 2.522(4), Yb(1)−N(2) 2.570(3), Yb(1)−C(29) 2.389(4), Yb(1)−C(33) 2.369(4), Yb(1)−O(1) 2.310(4), Yb(1)−O(2) 2.342(3), C(1)−Yb(1)−N(2) 69.57(10).

Table 1. Selected Bond Lengths (Angstroms) and Angles (degrees) of Complexes 1−3 and 5−8

	1	2	3	
RE−C(1)	2.354(5)	2.324(6)	2.360(5)	
RE−C(5)	2.483(2)	2.468(3)	2.489(3)	
RE−N(2)	2.4049(18)	2.388(2)	2.4209(19)	
C(5)−RE−N(2)	71.99(7)	72.33(8)	71.89(7)	
	5	**6**	**7**	**8**
RE−C(1)	2.339(4)	2.319(5)	2.339(5)	2.306(4)
RE−C(5)	2.473(4)	2.466(4)	2.472(4)	2.422(3)
RE−C(27)	2.471(4)	2.457(3)	2.484(4)	2.431(3)
RE−N(2)	2.397(3)	2.382(3)	2.407(3)	2.363(3)
RE−N(4)	2.387(2)	2.373(3)	2.412(3)	2.368(3)
C(5)−RE−N(2)	72.63(12)	72.94(11)	72.30(12)	73.20(10)
C(27)−RE−N(4)	72.53(12)	72.85(11)	72.49(12)	73.57(10)

Table 2. Polymerization of Isoprene (IP)[a]

entry	precatalyst (solvent)	cocatalyst (equiv)	time (min)	conv (%)	structure[b]		M_n[c] ($\times10^{-4}$)	PDI[c]	eff[f] (%)	T_g[g] (°C)
					cis-1,4	3,4				
1	**1**($C_6H_5CH_3$)	Al^{i}Bu$_3$(5)	25	99	87	13	26.03	1.7	0.13	−57
2	**1**(CH_2Cl_2)	Al^{i}Bu$_3$(5)	25	99	98	2	7.85	1.8	0.43	−60
3	**1**(C_6H_5Cl)	Al^{i}Bu$_3$(5)	25	97	99	1	32.2	1.9	0.10	−59
4	**1**(C_6H_5Cl)	AlEt$_3$(5)	35	93	98.2	1.8	44.9	1.6	0.07	−58
5	**1**(C_6H_5Cl)	AlMe$_3$(5)	45	90	91.2	8.8	41.6	1.7	0.07	−57
6	**1**(C_6H_5Cl)	Al^{i}Bu$_3$(10)	35	95	99	1	16.3	2.2	0.20	−56
7	**2**(C_6H_5Cl)	Al^{i}Bu$_3$(5)	25	100	98.1	1.9	34.0	1.9	0.10	−60
8	**3**(C_6H_5Cl)	Al^{i}Bu$_3$(5)	15	100	98.5	1.5	31.2	1.9	0.11	−56
9	**5**(C_6H_5Cl)	Al^{i}Bu$_3$(5)	60	89	98.7	1.3	37.9	1.9	0.08	−57
10	**6**(C_6H_5Cl)	Al^{i}Bu$_3$(5)	50	91	98.2	1.8	34.5	1.9	0.09	−58
11	**7**(C_6H_5Cl)	Al^{i}Bu$_3$(5)	20	100	98	2	27.7	1.9	0.12	−56
12	**8**(C_6H_5Cl)	Al^{i}Bu$_3$(5)								
13[d]	**3**(C_6H_5Cl)	Al^{i}Bu$_3$(5)	25	90	98.5	1.5	59.2	2.1	0.10	−58
14[e]	**3**(C_6H_5Cl)	Al^{i}Bu$_3$(5)	30	58	98	2	70.8	2.2	0.11	−57

[a] General conditions: [RE] = 10 μmol, [RE]:[Ph_3C][$B(C_6F_5)_4$]:[IP] = 1:1:500, temperature = 30 °C, Vol(IP)/Vol(solvents) = 1:10. [b] Determined by ^{1}H and ^{13}C NMR. [c] Determined by means of GPC against polystyrene standards in THF at 30 °C. [d] [RE]:[IP] = 1:1000. [e] [RE]:[IP] = 1:2000. [f] Catalyst efficiency = M_n(calcd)/M_n(measd). [g] Measured by DSC.

in **4** are similar [2.389(4) and 2.369(4) Å], and these distances are longer than those found in the six-coordinate ytterbium alkyl complexes supported by [$Me_2Si(C_5Me_4)PR$]$^{2-}$ ligands [R = Ph, 2.318(9) Å; R = Cy, 2.298(4) Å].[12]

Catalytic Activity toward Isoprene Polymerization. As evidenced, very few organo-rare-earth metal complexes bearing one alkyl group exhibited activity on controllable polymerization of 1,3-conjugated dienes. With the above new carbon σ-bonded indolyl-ligated rare-earth metal alkyl complexes in hand, their catalytic activities toward isoprene polymerization were investigated.

None of the above carbon σ-bonded indolyl rare-earth metal monoalkyl complexes alone could initiate the polymerization of isoprene. The binary systems of complexes/AlR_3 and complexes/[Ph_3C][$B(C_6F_5)_4$] also did not initiate the polymerization. The ternary system of complexes/AlR_3/[Ph_3C][$B(C_6F_5)_4$] could initiate the polymerization. ^{1}H NMR monitoring the reaction of complex **1** with 1 equiv of [Ph_3C][$B(C_6F_5)_4$] in $C_6D_5CD_3$ showed that the carbonium borate primarily abstracted the CH_2SiMe_3 group, resulting in the formation of cationic rare-earth metal species [$\mathbf{L}^1{}_2$Y]$^+$ supported by two carbon σ-bonded indolyl ligands. Furthermore, DFT calculation of the reaction of complex **5** with 1 equiv of [Ph_3C][$B(C_6F_5)_4$] showed that abstraction of the CH_2SiMe_3 group to form the cationic species [$\mathbf{L}^2{}_2$Y]$^+$ is energetically more favorable (by 0.083 atomic unit or 2.277 eV) than abstraction of the ligand $\mathbf{L}^2$ to form the cationic species [$\mathbf{L}^2$YCH$_2$SiMe$_3$]$^+$. All results indicated favorable abstraction of the CH_2SiMe_3 group to form the cationic species [$\mathbf{L}_2$Y]$^+$, which initiates polymerization (see Supporting Information for ^{1}H NMR monitoring spectra and the detailed DFT calculation).

A previous report showed that the solvent has a significant impact on the group 3 metal cationic species, which in turn influence the activity and selectivity of the olefin polymerization.[13b] In this account, rare-earth metal complex **1** for isoprene polymerization was tested in different solvents. When the polymerization was carried out in toluene (IP/RE = 500), almost quantitative polyisoprene was obtained in 25 min (Table 2, entry 1). The resulting polymer possessed a high molecular weight and narrow moderate molecular weight distribution (M_n = 260 300, PDI = 1.7). The NMR spectra showed the polymer has 87% cis-1,4 content and no trans-1,4 content. The selectivities of the cis-1,4 component were significantly enhanced to 98% and 99% when the less coordinated solvents CH_2Cl_2 and C_6H_5Cl[13] were used in the polymerization, respectively, and the activities of the catalytic system have almost no change (Table 2, entries 2 and 3). However, polymers with a relatively low molecular weight were obtained in CH_2Cl_2. The solvent effects on the selectivity could be attributed to the π coordination of toluene to the rare-earth metal cation partly blocking the formation of the *anti*-η^3-π-allylic intermediate which was produced from the η^1-σ-allyl intermediate via rotation of the C−C single bond.[14] The cis-1,4 selectivity was also affected by the steric effect of the aluminum alkyls with observation of Al^{i}Bu$_3$ (99%) > AlEt$_3$ (98.2%) > AlMe$_3$ (91.2%) (Table 2, entries 3−5). The same observation was also found in the polymerization of 1,3-butadiene with the Cp*$_2$Ln[(μ-Me)AlMe$_2$(μ-Me)]$_2$LnCp*$_2$/AlR_3/[Ph_3C][$B(C_6F_5)_4$] catalytic system.[15] It is found that the [Al^{i}Bu$_3$]/[RE] ratio strongly affects the molecular weight of the polymers. Increasing the [Al^{i}Bu$_3$]/[RE] ratio from 5 to 10 significantly reduced the molecular weight of the polymers and broadened the molecular weight distribution (Table 2, entries 3 and 6), indicating that the aluminum alkyl played the role of cocatalyst acting as a chain transfer agent to initiate polymerization during polymerization. These results are consistent with those of ^{1}H NMR monitoring the reaction of complex **1** with [Ph_3C][$B(C_6F_5)_4$] and the result of DFT calculation of the reaction of complex **5** with [Ph_3C][$B(C_6F_5)_4$] with abstraction of the CH_2SiMe_3 group. The metal centers also have a great influence on the activity of the ternary catalyst systems (Table 2, entries 3 and 7−12). The Er analogue **2** showed a similar activity to that of yttrium complex **1** with 98.1% cis-1,4 selectivity, while the Dy analogue **3**, which has a larger ionic radius than Er and Y, can finish the polymerization within 15 min under the same conditions (Table 2, entry 8). Complexes **5**−**7**, bearing a less bulky ligand, exhibited lower activity than that of complexes **1**−**3** (Table 2, entries 9−11), indicating lthe ligand's effects on the catalytic activity. However, the catalytic activity of the complexes increases with increasing ionic radii of the central metal ions; again complex **7** exhibited higher catalytic activity and has the trend Dy > Er ≈ Y. Unfortunately, ytterbium

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analogue **8** showed no activity for isoprene polymerization under the same conditions. The result is consistent with previous literature reports, which is probably attributed to the Yb^{3+}/Yb^{2+} redox activity.[16] Furthermore, the higher activity of the catalyst system **3**/Al^iBu_3/$[Ph_3C][B(C_6F_5)_4]$ could initiate isoprene polymerization with different monomer to initiator ratios. On increasing the monomer to complex ratio from 500 to 1000, the molecular weight of the resulting polymers increased from 3.12×10^5 to 5.92×10^5 with almost unchanged regio- and stereoselectivity (Table 2, entries 8 and 13); on further increasing the monomer to initiator ratio, the molecular weight of polymer can be further increased (Table 2, entries 8, 13, and 14).

■ CONCLUSIONS

New *N*-protected carbon σ-bonded indolyl ligands were developed for the rare-earth metal chemistry. Reactions of *N*-protected 3-imino-indolyl proligands with $RE(CH_2SiMe_3)_3(thf)_2$ produced the novel carbon σ-bonded indolyl-ligated organo-rare-earth metal monoalkyl complexes via the σ-bond metathesis reaction of the sp^2 C−H bond with the $RE-CH_2SiMe_3$ bond. Study of the catalytic activity of these complexes indicated that these monoalkyl complexes are distinguished precatalysts for the polymerization of isoprene upon activation with Al^iBu_3 and $[Ph_3C][B(C_6F_5)_4]$ with a high activity (90% conversion of 1000 equiv of monomer in 25 min in the presence of 0.1 mol %), producing polymers with an excellent regio- and stereoselectivity (1,4-cis selectivity up to 99%, and no 1,4-trans content) at room temperature. It is found that complexes having a more bulky ligand and the central metal having larger ionic radii displayed higher catalytic activity. It is also found that more bulky aluminum reagents are favorable for the regio- and stereoselective polymerization of isoprene. This work implies that electron-rich carbon σ-bonded indolyl ligands may have prevalence as supporting ligands for organometallic complexes as catalysis in the regio- and stereoselective polymerization of isoprene. Further work in this field is now in progress.

■ EXPERIMENTAL SECTION

General Procedures. All syntheses and manipulations of air- and moisture-sensitive materials were carried out under an atmosphere of argon using standard Schlenk techniques or in an argon-filled glovebox. THF, toluene, and hexane were refluxed and distilled over sodium benzophenone ketyl under argon prior to use unless otherwise noted. Dichloromethane and chlorobenzene were distilled over CaH_2 under argon prior to use. Benzyl chloride was dried by stirring with P_2O_5 for 48 h and distilled under reduced pressure before use. $[Ph_3C][B(C_6F_5)_4]$ was purchased from STREM. $AlMe_3$, $AlEt_3$, and Al^iBu_3 were purchased from Sigma-Aldrich and used as received. Isoprene was purchased from TCI, dried with CaH_2, and distilled before use. 1-Benzyl-3-indolealdehyde, 1-methyl-3-indolealdehyde, and 1-methyl-2-indolealdehyde were prepared following the literature procedures.[17] Elemental analysis data were obtained on a Perkin-Elmer model 2400 Series II elemental analyzer. ^1H NMR and ^{13}C NMR spectra for analyses of compounds were recorded on a Bruker AV-300 (300 MHz for ^1H; 75.0 MHz for ^{13}C) or AV-500 NMR spectrometer (500 MHz for ^1H; 125 MHz for ^{13}C) in C_6D_6 for rare-earth metal complexes and in $CDCl_3$ for polyisoprene. Quantitative ^{13}C NMR were realized using the zgig sequence, and the relaxation time d1 was set to 5 s. Chemical shifts (δ) were reported in ppm. *J* values are reported in Hertz. HR-MS measurements were conducted with an Agilent model 6220 ESI-TOF mass spectrometer. IR spectra were recorded on a Shimadzu model FTIR-8400s spectrometer (KBr pellet). Gel permeation chromatography (GPC) analyses of the polymer samples were carried out at 30 °C using THF as an eluent on a Waters-2414 instrument and calibrated using monodispersed polystyrene standards at a flow rate of 1.0 mL min^{-1}. DSC measurements were performed on DSCQ 2000; the baseline was equilibrated at −90 °C followed by heating to 100 °C at a rate of 10 °C/min.

*Preparation of 1-Bn-3-(2,6-$^iPr_2C_6H_3N{=}CH)C_8H_5N$ (**HL^1**).* 1-Benzyl-3-indolealdehyde (2.35 g, 10.0 mmoL) was dissolved in ethanol (30 mL); then 2,6-diisopropylaniline (1.77 g, 10.0 mmoL) and a catalytic amount of *p*-toluenesulfonic acid were added to the solution. The mixture was stirred at room temperature for 12 h. The precipitate was filtered and washed with ice-cold methanol to give the white product (2.64 g, 67% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 1.15 (d, *J* = 6.6 Hz, 12H, $CHMe_2$), 3.08 (m, 2H, $CHMe_2$), 5.34 (s, 2H, $CH_2C_6H_5$), 7.05−7.33 (m, 11H), 7.50 (s, 1H, 2-indole), 8.29 (s, 1H), 8.51 (d, *J* = 3.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.6, 27.9, 50.6, 110.0, 115.3, 121.7, 122.7, 122.8, 123.4, 123.4, 126.3, 127.1, 128.0, 129.0, 133.3, 136.3, 137.5, 138.1, 150.6, 155.6. HR-MS calcd for $C_{28}H_{30}N_2$ 395.2487, found 395.2486.

*Preparation of 1-Me-3-(2,6-$^iPr_2C_6H_3N{=}CH)C_8H_5N$ (**HL^2**).* 1-Me-3-indolealdehyde (1.59 g, 10.0 mmoL) was dissolved in ethanol (30 mL); then 2,6-diisopropylaniline (1.77 g, 10.0 mmoL) and a catalytic amount of *p*-toluenesulfonic acid were added to the solution. The mixture was stirred at room temperature for 12 h. The precipitate was filtered and washed with ice-cold methanol to give the white product (1.72 g, 54% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 1.20 (d, *J* = 6.9 Hz, 12H), 3.15 (m, 2H), 3.88 (s, 3H, N−CH_3), 7.07−7.42 (m, 6H), 7.50 (s, 1H), 8.34 (s, 1H), 8.51 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.5, 27.9, 33.2, 109.5, 114.7, 121.5, 122.5, 122.8, 123.3, 123.4, 133.9, 137.9, 138.1, 155.5. HR-MS calcd for $C_{22}H_{26}N_2$ 319.2174, found 319.2175.

*Preparation of 1-Bn-3-($^tBuN{=}CH)C_8H_5N$ (**HL^3**).* 1-Benzyl-3-indolealdehyde (5.6 g, 20.0 mmol) was dissolved in ethanol (30 mL); then *tert*-butylamine (1.48 g, 20.0 mmol) and a catalytic amount of *p*-toluenesulfonic acid were added to the solution. The mixture was stirred at room temperature for 12 h. The precipitate was filtered and washed with ice-cold methanol to give the white product (3.48 g, 60% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 1.31 (s, 9H, CMe_3), 5.32 (s, 2H, $CH_2C_6H_5$), 7.12−7.14 (m, 2H), 7.20−7.30 (m, 6H), 7.44 (s, 1H, 2-indole), 8.38−8.41 (m, 1H), 8.51 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 30.2, 50.2, 56.8, 109.9, 115.7, 121.2, 122.4, 123.0, 126.6, 127.0, 127.9, 128.9, 131.3, 136.9, 137.4, 149.4. HR-MS calcd for $C_{20}H_{22}N_2$ 291.1861, found 291.1860.

*Preparation of 1-Me-2-(2,6-$^iPr_2C_6H_3N{=}CH)C_8H_5N$ (**HL^4**).* 1-Me-2-indolealdehyde (1.6 g, 10.0 mmol) was dissolved in ethanol (30 mL); then 2,6-diisopropylaniline (1.77 g, 10.0 mmoL) and a catalytic amount of *p*-toluenesulfonic acid were added to the solution. The mixture was stirred at room temperature for 12 h. The precipitate was filtered and washed with ice-cold methanol to give the yellow product (2.54 g, 80% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 1.19 (d, *J* = 6.0 Hz, 12H), 3.04 (m, *J* = 6.0 Hz, 2H), 4.27 (s, 3H), 6.94 (s, 1H), 7.08−7.18 (m, 5H), 7.33−7.44 (m, 2H), 7.67 (d, *J* = 9.0 Hz, 1H), 8.26 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.5, 28.1, 32.2, 109.9, 111.6, 120.3, 121.9, 123.0, 124.1, 124.7, 126.9, 134.9, 137.6, 140.4, 149.7, 154.7. HR-MS calcd for $C_{22}H_{26}N_2$ 319.2174, found 319.2173.

*Preparation of $L^1{}_2YCH_2SiMe_3$ (**1**).* To a toluene (15.0 mL) solution of **HL^1** (0.334 g, 1.04 mmoL) was added a toluene (5 mL) solution of $Y(CH_2SiMe_3)_3(thf)_2$ (0.26 g, 0.52 mmoL). The mixture was stirred for 4 h at room temperature, and the color of the solution changed from pistachio to yellow in the process. The solvent was evaporated under reduced pressure. The residue was extracted with *n*-hexane (20.0 mL). The extract was concentrated to about 12.0 mL. Yellow crystals were obtained at 0 °C for several days (0.32 g, 64% yield). Mp: 170−172 °C. ^1H NMR (500 MHz, C_6D_6): δ −0.02 (s, 9H, $SiMe_3$), 0.12, 0.22 (ABX, dd, $^2J_{H-H}$ = 10.0 Hz, $^2J_{Y-H}$ = 2.5 Hz, 2H, CH_2SiMe_3), 0.41 (d, *J* = 10.0 Hz, 6H, $CHMe_2$), 1.03 (d, *J* = 10.0 Hz, 6H, $CHMe_2$), 1.23 (d, *J* = 5.0 Hz, 6H, $CHMe_2$), 1.29 (d, *J* = 5.0 Hz, 6H, $CHMe_2$), 2.90 (hepta, *J* = 5.0 Hz, 2H, $CHMe_2$), 3.73 (hepta, *J* = 5.0 Hz, 2H, $CHMe_2$), 4.25, 4.55 (AB, *J* = 15.0 Hz, 4H, $CH_2C_6H_5$), 6.91−7.06 (m, 18H), 7.23−7.28 (m, 4H), 7.43 (d, *J* = 10.0 Hz, 2H), 8.55 (s, 2H, N=CH). ^{13}C

NMR (125 MHz, C_6D_6): δ 206.5 (d, J_{Y-C} = 50.0 Hz, 2-indolyl), 168.8, 146.7, 142.9, 142.6, 140.8, 137.7, 130.2, 128.4, 128.0, 126.9, 126.3, 126.1, 123.9, 123.7, 122.9, 121.7, 121.6, 116.1, 111.5, 53.0 (d, J_{Y-C} = 37.5 Hz, CH_2SiMe_3), 52.7, 31.6, 30.3, 25.6, 25.0, 23.5, 22.7, 21.1, 3.4. IR (KBr pellets, cm^{-1}): ν 3088 (s), 2958 (w), 2862 (w), 1587 (w), 1436 (w), 1205 (s), 1035 (s), 933 (s), 794 (s), 700 (w). Anal. Calcd for $C_{60}H_{69}N_4SiY$: C, 74.82; H, 7.22; N, 5.82. Found: C, 74.56; H, 7.54; N, 5.58.

*Preparation of $L^1_2ErCH_2SiMe_3$ (**2**).* This complex was obtained as yellow crystals in 60% yield by treatment of $Er(CH_2SiMe_3)_3(thf)_2$ (0.306 g, 0.53 mmoL) with **HL**^{1} (0.42 g, 1.06 mmoL) following procedures similar to those used for preparation of **1**. The color of the solution changed from pink to yellow during the reaction. Mp: 188−190 °C. IR (KBr pellets, cm^{-1}): ν 3062 (s), 2958 (w), 2862 (w), 1587 (w), 1465 (w), 1205 (s), 1035 (s), 933 (s), 794 (s), 700 (w). Anal. Calcd for $C_{60}H_{69}N_4SiEr$: C, 69.19; H, 6.68; N, 5.38. Found: C, 69.24; H, 6.91; N, 5.14.

*Preparation of $L^1_2DyCH_2SiMe_3$ (**3**).* This complex was obtained as yellow crystals in 60% yield by treatment of $Dy(CH_2SiMe_3)_3(thf)_2$ (0.44 g, 0.77 mmoL) with **HL**^{1} (0.606 g, 1.54 mmoL) following procedures similar to those used for preparation of **1**. The color of the solution changed from colorless to yellow during the reaction. Mp: 184−185 °C. IR (KBr pellets, cm^{-1}): ν 3062 (s), 2958 (w), 2862 (w), 1587 (w), 1465 (w), 1205 (s), 1035 (s), 933 (s), 794 (s), 700 (w). Anal. Calcd for $C_{60}H_{69}N_4SiDy$: C, 69.51; H, 6.71; N, 5.40. Found: C, 69.52; H, 6.89; N, 5.16.

*Preparation of $L^1Yb(CH_2SiMe_3)_2(thf)_2$ (**4**).* This complex was obtained as red crystals in 56% yield by treatment of $Yb(CH_2SiMe_3)_3(thf)_2$ (0.3 g, 0.518 mmoL) with **HL**^{1} (0.165 g, 0.518 mmoL) following procedures similar to those used for preparation of **1**. Mp: 176−177 °C. IR (KBr pellets, cm^{-1}): ν 3062 (w), 2958 (w), 2864 (w), 1913 (s), 1587 (w), 1465 (w), 1205 (w), 1078 (w), 854 (w), 700 (w). Anal. Calcd for $C_{44}H_{67}N_2O_2Si_2Yb$: C, 59.70; H, 7.63; N, 3.16. Found: C, 59.17; H, 7.56; N, 3.17.

*Preparation of $L^2_2YCH_2SiMe_3$ (**5**).* This complex was obtained as pistachio crystals in 64% yield by treatment of $Y(CH_2SiMe_3)_3(thf)_2$ (0.287 g, 0.58 mmoL) with **HL**^{2} (0.37 g, 1.16 mmoL) following procedures similar to those used for preparation of **1**, and the color of the solution changed from pistachio to yellow during the reaction. ^1H NMR (300 MHz, C_6D_6): δ 0.31 (s, 9H, $SiMe_3$), 0.51 (AB, $^2J_{H-H}$ = 10.0 Hz, 2H, CH_2SiMe_3), 0.37 (d, J = 6.0 Hz, 6H, $CHMe_2$), 1.05 (d, J = 6.0 Hz, 6H, $CHMe_2$), 1.33 (d, J = 6.0 Hz, 6H, $CHMe_2$), 1.62 (d, J = 9.0 Hz, 6H, $CHMe_2$), 2.91 (hepta, J = 6.0 Hz, 2H, $CHMe_2$), 2.94 (s, 3H, CH_3), 3.85 (hepta, J = 6.0 Hz, 2H, $CHMe_2$), 6.96 (d, J = 9.0 Hz, 2H), 7.05 (d, J = 6.0 Hz, 2H), 7.15−7.22 (m, 8H), 7.36 (m, 4H), 7.52 (d, J = 6.0 Hz, 2H), 8.55 (s, 2H, N═CH). ^{13}C NMR (75 MHz, C_6D_6): δ 206.1 (d, J_{Y-C} = 45.0 Hz, 2-indolyl), 168.4, 146.6, 142.7, 142.2, 141.4, 129.8, 126.2, 123.5, 122.5, 121.5, 116.1, 110.3, 50.3 (d, J_{Y-C} = 45.0 Hz, CH_2SiMe_3), 35.1, 30.2, 28.8, 25.6, 24.8, 23.8, 21.0, 3.7. Mp: 204−205 °C. IR (KBr pellets, cm^{-1}): ν 3055 (w), 2956 (w), 2864 (w), 1913 (s), 1859 (s), 1575 (w), 1473 (w), 1201 (w), 1074 (w), 854 (w), 694 (w). Anal. Calcd for $C_{48}H_{61}N_4SiY$: C, 71.09; H, 7.58; N, 6.91. Found: C, 71.09; H, 7.75; N, 6.69.

*Preparation of $L^2_2ErCH_2SiMe_3$ (**6**).* This complex was obtained as yellow crystals in 56% yield by treatment of $Er(CH_2SiMe_3)_3(thf)_2$ (0.433 g, 0.75 mmoL) with **HL**^{2} (0.477 g, 1.5 mmoL) following procedures similar to those used for preparation **1**. The color of the solution changed from pink to yellow during the reaction. Mp: 201−202 °C. IR (KBr pellets, cm^{-1}): ν 3055 (w), 2956 (w), 2864 (w), 1913 (s), 1859 (s), 1575 (w), 1473 (w), 1201 (w), 1074 (w), 854 (w), 694 (w). Anal. Calcd for $C_{48}H_{61}N_4SiEr$: C, 64.82; H, 6.91; N, 6.30. Found: C, 64.73; H, 7.02; N, 6.36.

*Preparation of $L^2_2DyCH_2SiMe_3$ (**7**).* This complex was obtained as yellow crystals in 54% yield by treatment of $Dy(CH_2SiMe_3)_3(thf)_2$ (0.344 g, 0.6 mmoL) with **HL**^{2} (0.382 g, 1.2 mmoL) following procedures similar to those used for preparation **1**. The color of the solution changed from colorless to yellow during the reaction. Mp: 203−204 °C. IR (KBr pellets, cm^{-1}): ν 3055 (w), 2956 (w), 2864 (w), 1913 (s), 1859 (s), 1575 (w), 1473 (w), 1201 (w), 1074 (w), 854 (w), 694 (w). Anal. Calcd for $C_{48}H_{61}N_4SiDy$: C, 65.17; H, 6.95; N, 6.33. Found: C, 64.83; H, 6.96; N, 6.41.

*Preparation of $L^2_2YbCH_2SiMe_3$ (**8**).* This complex was obtained as yellow crystals in 72% yield by treatment of $Yb(CH_2SiMe_3)_3(thf)_2$ (0.376 g, 0.65 mmoL) with **HL**^{2} (0.414 g, 1.3 mmoL) following procedures similar to those used for preparation **1**. Mp: 216−217 °C. IR (KBr pellets, cm^{-1}): ν 3055 (w), 2956 (w), 2864 (w), 1913 (s), 1859 (s), 1575 (w), 1473 (w), 1201 (w), 1074 (w), 854 (w), 694 (w). Anal. Calcd for $C_{48}H_{61}N_4SiYb$: C, 64.40; H, 6.87; N, 6.26. Found: C, 64.42; H, 6.86; N, 6.28.

*Preparation of L^3_3Y (**9**).* This complex was obtained as yellow crystals in 75% yield by treatment of $Y(CH_2SiMe_3)_3(thf)_2$ (0.668 g, 1.35 mmol) with **HL**^{3} (0.86 g, 2.7 mmol) following procedures similar to those used for preparation **1**, and the color of the solution changed from pistachio to yellow during the reaction. ^1H NMR (300 MHz, C_6D_6): δ 8.63 (s, 1H, CH═N), 7.62 (d, J = 6.0 Hz, 1H), 7.08−7.29 (m, 3H), 6.95−7.03 (m, 3H), 6.54−6.57 (m, 2H), 4.78, 4.90 (AB, J = 15.0 Hz, 4H, $CH_2C_6H_5$), 1.16 (s, 9H, CMe_3). ^{13}C NMR (75 MHz, C_6D_6): δ 30.9, 53.1, 55.9, 101.7, 116.3, 120.1, 120.7, 123.8, 125.9, 126.2, 127.6, 130.1, 139.1, 141.0, 162.2, 206.7 (d, J_{Y-C} = 45.0 Hz, 2-indolyl). Mp: 252−253 °C. IR (KBr pellets, cm^{-1}): ν 2962 (w), 2877 (s), 1631 (w), 1535 (s), 1456 (w), 1392 (s), 1355 (s), 1168 (w), 806 (s), 736 (w). Anal. Calcd For $C_{60}H_{63}N_6Y$: C, 75.30; H, 6.62; N, 8.78. Found: C, 75.31; H, 6.65; N, 8.75.

*Preparation of L^3_3Er (**10**).* This complex was obtained as yellow crystals in 78% yield by treatment of $Er(CH_2SiMe_3)_3(thf)_2$ (0.543 g, 0.95 mmol) with **HL**^{3} (0.55 g, 1.9 mmol) following procedures similar to those used for preparation **1**, and the color of the solution changed from pink to yellow in the process. Mp: 255−256 °C. IR (KBr pellets, cm^{-1}): ν 2962 (w), 2877 (s), 1631 (w), 1535 (w), 1456 (w), 1392 (s), 1355 (s), 1168 (w), 806 (s), 736 (w). Anal. Calcd For $C_{60}H_{63}N_6Er$: C, 69.60; H, 6.13; N, 8.12. Found: C, 69.69; H, 6.15; N, 8.10.

Isoprene Polymerization. The procedures for isoprene polymerization catalyzed by these complexes were similar; a typical polymerization procedure is given below. A 50 mL Schlenk flask, equipped with a magnetic stirring bar, was charged the desired amount of solvent, the rare-earth metal complex, borate, alkyl aluminum, and isoprene. The mixture was stirred vigorously for the desired time, during which an increase of viscosity was observed. The reaction mixture was quenced by addition of 30 mL of acidified methanol. The polymer was coagulated, washed with methanol two times, and finally dried under vacuum to a constant weight.

Crystal Structure Analyses of 1−8. A suitable crystal of complexes **1**−**8** was mounted in a sealed capillary. Diffraction was performed on a Bruker SMART APEX II CCD area detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293(2) K, φ and ω scan technique. An empirical absorption correction was applied using the SADABS program.[18] All structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations based on F^2 using the SHELXTL program package.[19] The hydrogen atom coordinates were calculated with SHELXTL by using an appropriate riding model with varied thermal parameters. The residual electron densities were of no chemical significance. Selected bond lengths and angles are compiled in Table 1, and crystal data and details of the data collection and structure refinements are given in the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystal data in CIF format, figures for complexes **1**−**8**, copies of NMR spectra for characterization of new ligands **HL**^{1}-**HL**^{4}, yttrium complexes, and polyisoprene. CCDC 1019446−1019453 for complexes **1**−**8** contains the supplementary crystallographic data for this paper can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b00308.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: slzhou@mail.ahnu.edu.cn.

*E-mail: swwang@mail.ahnu.edu.cn.

Notes

The authors declare no competing financial interest.

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