NJC

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/njc

Rare-earth metal bis(alkyl) complexes bearing pyrrolidinyl-functionalized cyclopentadienyl, indenyl and fluorenyl ligands: synthesis, characterization and ligand effect on isoprene polymerization

Meng Deng,[1] Shuhui Chi,[1] and Yunjie Luo[1,2,*]

1. *Organometallic Chemistry Laboratory, Ningbo Institute of Technology, Zhejiang University, Ningbo 315100, P. R. China*
2. *School of Chemical Engineering, Ningbo University of Technology, Ningbo 315211, P. R. China*

Corresponding author: E-mail: lyj@nit.zju.edu.cn

Tel: +86-574-88130085

Fax: +86-574-88130130

Abstract A series of rare-earth metal bis(alkyl) complexes bearing pyrrolidinyl-functionalized cyclopentadienyl, indenyl and fluorenyl ligands were prepared and characterized. Alkane elimination of $Ln(CH_2SiMe_3)_3(THF)_2$ with 1 equiv of the corresponding ancillary ligand precursors in THF at room temperature afforded the rare-earth metal bis(alkyl) complexes $LLn(CH_2SiMe_3)_2(THF)_2$ (L = $C_5Me_4SiMe_2NC_4H_8$, Ln = Y (**1**), Lu (**2**); L = $C_9H_6SiMe_2NC_4H_8$, Lu (**4**)). Intramolecular C-H activation occured when $Sc(CH_2SiMe_3)_3(THF)_2$ was treated with 1 equiv of $C_5Me_4HSiMe_2NC_4H_8$, leading to the generation of the scandium mono(alkyl) complex $(C_5Me_4SiMe_2NC_4H_7)Sc(CH_2SiMe_3)(THF)$ (**3**). One-pot salt metathesis reaction of $LnCl_3$ with 1 equivalent of fluorenyl lithium

$C_{13}H_8SiMe_2NC_4H_8Li$, followed by addition of 2 equivalents of $LiCH_2SiMe_3$ in THF at room temperature gave the mono-fluorenyl-ligated rare-earth metal bis(alkyl) complexes $(C_{13}H_8SiMe_2NC_4H_8)Ln(CH_2SiMe_3)_2(THF)$ (Ln = Y (**5**), Lu (**6**)). All these complexes were characterized by elemental analysis and NMR spectroscopy. **3**, **5** and **6** were subjected to X-ray single crystal determination. Upon activated with one equivalent of $[Ph_3C][B(C_6F_5)_4]$ and excess Al^iBu_3, the rare-earth metal bis(alkyl) complexes **1**, **2**, **4-6** were active for *cis*-1,4-selective polymerization of isoprene in toluene at room temperature. The ligand effect on the polymerization activity was observed, with a sterically more bulky ligand providing higher activity (Fluorenyl > Indenyl > Cp). Moreover, employing **6**/$[Ph_3C][B(C_6F_5)_4]/Al^iBu_3$ as the catalyst system, the polymerization proceeded in a controllable fashion.

Introduction

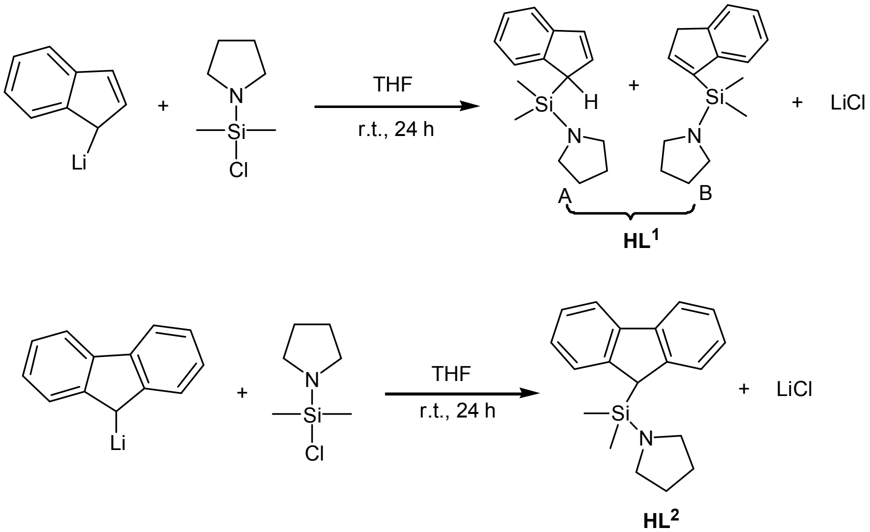
To investigate the relationship between molecular structure and reactivity is a long-standing research topic in organometallic and polymer chemistry.[1] Over the past decade, one of the most attractive outcomes in the field of organo-rare-earth-metal chemistry is employing rare-earth metal bis(alkyl) complexes with a general formula $LLnR_2(S)_x$ (L = monoanionic ancillary ligands, R = alkyl, benzyl, and allyl groups; S = coordinated solvent) as catalyst precursors, for such complexes have demonstrated high efficiency and unique performance in polymerization and organic transformations when activated with an appropriate borate compound such as $[Ph_3C][B(C_6F_5)_4]$ or $[PhNMe_2H][B(C_6F_5)_4]$.[2] Upon to date, much attention is still ongoing to cationic rare-earth metal alkyl complexes aiming at designing efficient catalysts and developing novel reactions. Due to the unique chemical and physical properties of rare-earth metal elements, the reactivity of rare-earth metal complexes can be tuned not only by modifying the ancillary ligands but also by changing the ion size of the central metals, however, in most cases changing the ligand environment of a complex to modify its properties is usually an important strategy for the development of more efficient and selective catalysts.[1]

On the other hand, to meet the shortage of natural rubber and the increasing demand for high-performance rubbers, *cis*-1,4-polyisoprene is recognized as a promising candidate to replace natural rubber for tires manufacture.[3] Contrary to heterogeneous rare-earth-metal-based Zieglar-Natta catalysts,[4] structurally well-defined homogeneous single-site rare-earth metal catalysts are beneficial to mechanistic investigation. For example, rare-earth metal metallocene complexes,[5] non-Cp ligated rare-earth metal complexes,[6,7] and pincer-type rare-earth metal complexes[8] have displayed distinguished *cis*-1,4-selectivity in isoprene polymerization. To understand the ligand effect on the polymerization performance, we prepared a series of rare-earth metal bis(alkyl) complexes bearing pyrrolidinyl-functionalized cyclopentadienyl, indenyl and fluorenyl ligands, and employed them as catalyst precursors in isoprene polymerization. It was found that the fluorenyl-ligated rare-earth metal bis(alkyl) complexes, upon activated by $[Ph_3C][B(C_6F_5)_4]$ and Al^iBu_3, showed highly *cis*-1,4-selective polymerization of isoprene in a controllable fashion. Here we report these results.

Results and discussion

Synthesis and characterization of the pyrrolidinyl-functionalized indene and fluorene

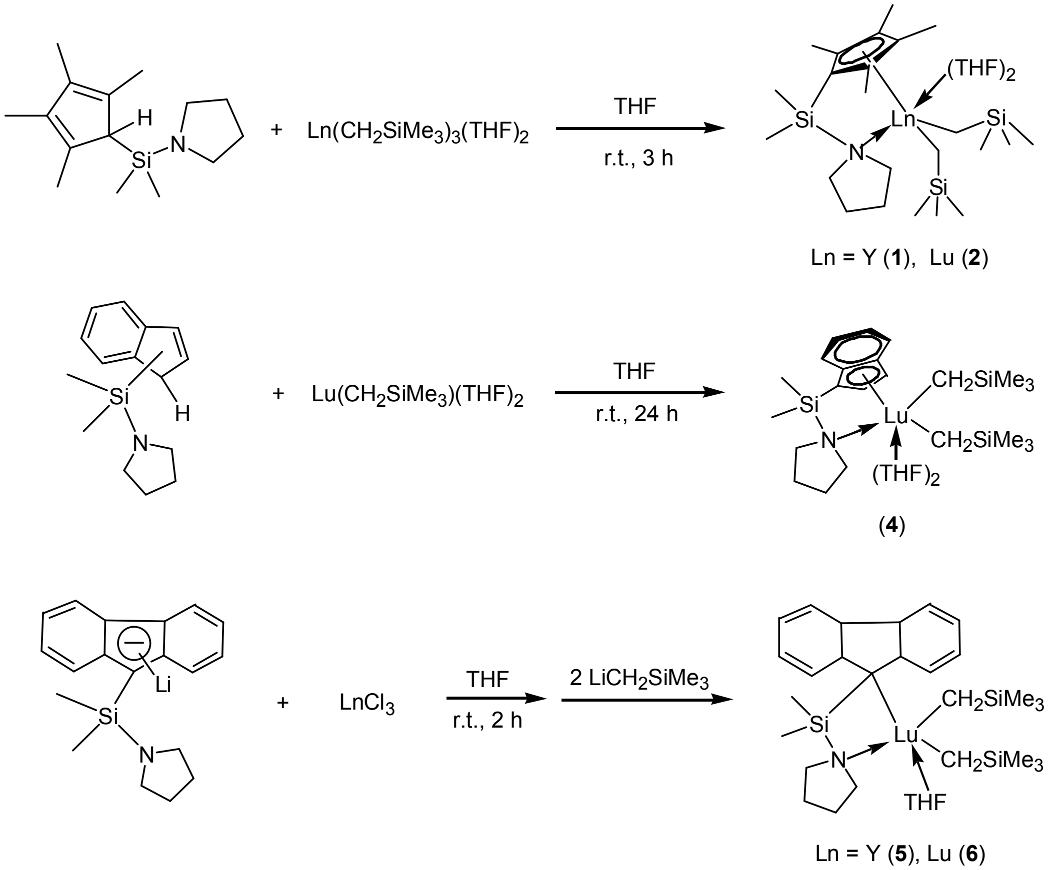
The pyrrolidinyl-functionalized indenyl ligand $C_9H_7SiMe_2NC_4H_8$ (**HL^1**) and fluorenyl ligand $C_{13}H_9SiMe_2NC_4H_8$ (**HL^2**) were synthesized by treatment of 1-(chlorodimethylsilanyl)-pyrrolidine $C_4H_8NSiMe_2Cl$ with 1 equivalent of indene lithium C_9H_7Li or fluorene lithium $C_{13}H_9Li$ in THF at room temperature, respectively (Scheme 1). **HL^1** was obtained in 65% isolated yield as yellow oil, which contains a mixture of isomers in nearly 20:1 molar ratio (A:B = 20:1). **HL^2** was obtained as yellowish brown powder in 95% isolated yield. **HL^1** and **HL^2** were confirmed by elemental analysis and NMR spectroscopy.



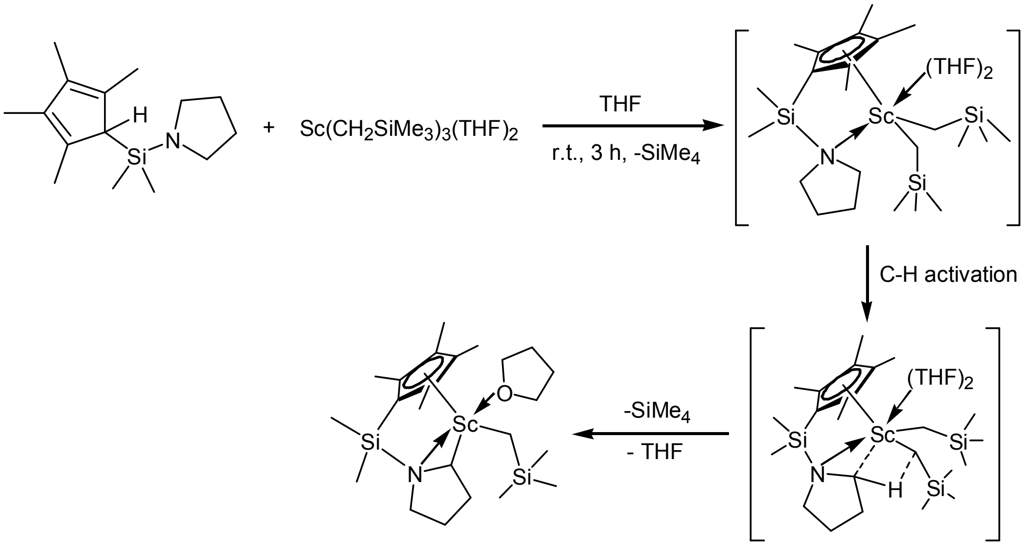
Scheme 1 Preparation of the pyrrolidinyl-functionalized indene and fluorene

Synthesis and characterization of the rare-earth metal bis(alkyl) complexes

Alkane elimination of $Ln(CH_2SiMe_3)_3(THF)_2$ (Ln = Y, Lu) with 1 equiv of the pyrrolidinyl-functionalized cyclopentadiene $C_5Me_4HSiMe_2NC_4H_8$ in THF at room temperature for 3 h, after workup, afforded the neutral mono-Cp-ligated rare-earth metal bis(alkyl) complexes $(C_5Me_4SiMe_2NC_4H_8)Ln(CH_2SiMe_3)_2(THF)_2$ (Ln = Y (**1**), Lu (**2**)) in 82-86% isolated yields, as shown in Scheme 2. In contrast, employing the same synthetic route, if the central meter being Sc^{3+}, only mono-Cp-ligated scandium mono(alkyl) complex $(C_5Me_4SiMe_2NC_4H_7)Sc(CH_2SiMe_3)(THF)$ (**3**) was isolated. The proposed mechanism for the formation of **3** is illustrated in Scheme 3. The generation of **3** instead of the aimed product scandium bis(alkyl) complex $(C_5Me_4SiMe_2NC_4H_8)Sc(CH_2SiMe_3)_2(THF)_x$ may contribute to the intramolecular C-H σ bond activation at α-position of the pyrrolidinyl ring,[9] as illustrated in Scheme 3.



Scheme 2 Preparation of the rare-earth metal bis(alkyl) complexes **1**, **2**, **4-6**



(**3**)

Scheme 3 Proposed mechanism for the generation of the pyrrolidinyl-functionalized Cp-ligated scandium mono(alkyl) complex **3**

Deprotonation of a mixture of isomers of the pyrrolidinyl-functionalized indene $C_9H_7SiMe_2NC_4H_8$ with one equivmolar amount of $Lu[CH_2SiMe_3]_3(THF)_2$ in THF at room temperature, after workup, gave the mono-indenyl-ligated lutetium bis(alkyl) complex $(C_9H_6SiMe_2NC_4H_8)Lu(CH_2SiMe_3)_2(THF)_2$ (**4**) as pale yellow powder in 86% isolated yield, as shown in Scheme 2.

However, due to the low acidity of fluorene, salt metathesis strategy was adopted to prepare fluorenyl-ligated rare-earth metal bis(alkyl) complexes. One-pot reaction of $LnCl_3$ with 1 equivalent of fluorenyl lithium $C_{13}H_8SiMe_2NC_4H_8Li$, followed by addition of 2 equivalents of $LiCH_2SiMe_3$ in THF at room temperature, after workup, produced the mono-fluorenyl-ligated rare-earth metal bis(alkyl) complexes $(C_{13}H_8SiMe_2NC_4H_8)Ln(CH_2SiMe_3)_2(THF)$ (Ln = Y (**5**), Lu (**6**)) in 53-54% isolated yields (Scheme 2).

All these rare-earth metal alkyl complexes were characterized by elemental analysis and NMR spectroscopy. These air- and moisture-sensitive complexes are soluble in common organic solvents such as toluene, THF, even in hexane. In the ^{1}H NMR spectra, the methylene protons of Y–CH_2SiMe_3 in **1** give a doublet resonance with a $J_{Y\text{-}H}$ coupling constant of 3.2 Hz at -0.61 ppm, while those of Lu–CH_2SiMe_3 in **2** display sharp singlet resonance at -0.81 ppm. The methylene protons of Lu–CH_2SiMe_3 in **4** are diastereotopic, and display AB spin resonances in the upfield regions at δ -0.93 and -0.79 ppm. In comparison, the methylene protons arising from Y–CH_2SiMe_3 in **5** and Lu–CH_2SiMe_3 in **6** show doublet resonances around -0.58 and -0.72 ppm, respectively. In comparison, with a same central metal Lu^{3+}, ^{13}C NMR spectra show that the resonances of methylene carbon of Lu–CH_2SiMe_3 in **2**, **4**, and **6** appear at δ 39.7, 41.1, and 44.5 ppm, respectively, reflecting an increase of the interaction between central metal and the CH_2SiMe_3 group in the order of Cp > Indenyl > Fluorenyl for ligand effect.

Single crystals of **3**, **5** and **6** suitable for X-ray diffraction were grown from a mixture solution of toluene and hexane at -30 °C. The crystallographic data are summarized in Table 1. X-ray diffraction showed that **5** and **6** are isomorphous, therefore, only the molecular structure of **3** and **6** are illustrated in Fig. 1 and Fig. 2, respectively. The complexes are mononuclear and donor-solvent-coordinated species. The central metal in **3** is five-coordinated by one Cp ring in η^5-mode, one nitrogen atom and one α-position-carbon atom from the pendant pyrrolidinyl group, one CH_2SiMe_3 group, and one oxygen atom of THF to adopt a distorted-trigonal-bipyramidal geometry, if the Cp ring is regarded as occupying an independent vertex. The average bond distances of Sc–Cp (2.5132 Å) and Sc–CH_2SiMe_3 (2.277(2) Å) are agreement with those in $(C_5Me_5SiMe_3)Sc(CH_2SiMe_3)_2(THF)$ (*av.* Sc–Cp = 2.4979 Å, Sc–CH_2SiMe_3 = 2.223 Å).[10] In contrast, the coordination mode of the fluorenyl moiety to the central metals in **5** and **6** is unexpected. X-ray single crystal structural determination shows that the bonding features of the ligand with the central metal in the most fluorenyl-ligated rare-earth metal complexes are usually in η^3 and η^5.[11] However, the smallest differences of the bond distances of ΔLn–C(fluorenyl) in **5** and **6** are 0.323 and 0.326 Å (Δ(Ln–C(1)/Ln–C(2))), respectively, which show that the bonding mode of the fluorenyl moiety to the central metal in **5** and **6** is in η^1-hapticity through the bridgehead carbon atom of the central ring. Such η^1-bonding mode in rare-earth metal complexes is scarce.[12,13] For instance, in Sm(η^2-$C_{12}H_8CNPh$)(OAr)$(THF)_3$ the fluorenyl moieties is bound to samarium ion via the bridgehead atom in η^1-fashion,[12] while in [(η^3:η^5-Flu-CMe_2-Cp)(η^1:η^5-Flu-CMe_2-Cp)Y][Li(Et_2O)$(THF)_3$], the fluorenyl moiety is coordinated via merely one carbon atom of the phenyl ring, not involves the bridgehead carbon atom of the central ring.[13] The central metal in **6** is five-coordinated by one fluorenyl ligand in η^1, κ^1-mode, two CH_2SiMe_3 groups, and one oxygen atom of THF to adopt a distorted-trigonal-bipyramidal geometry. If the ionic radius is considered,[14] the C_{Flu}–Lu distance (2.529(12) Å) in **6** is comparable with those in Sm(η^2-$C_{12}H_8CNPh$)(OAr)$(THF)_3$,[12] but is much longer than those in ($FluCH_2$-Py)Lu$(CH_2SiMe_3)_2$(THF) (*av.* C_{Flu}–Lu = 2.357 Å), in which the fluorenyl ligand is bound to the central metal in η^5-fashion.[15]

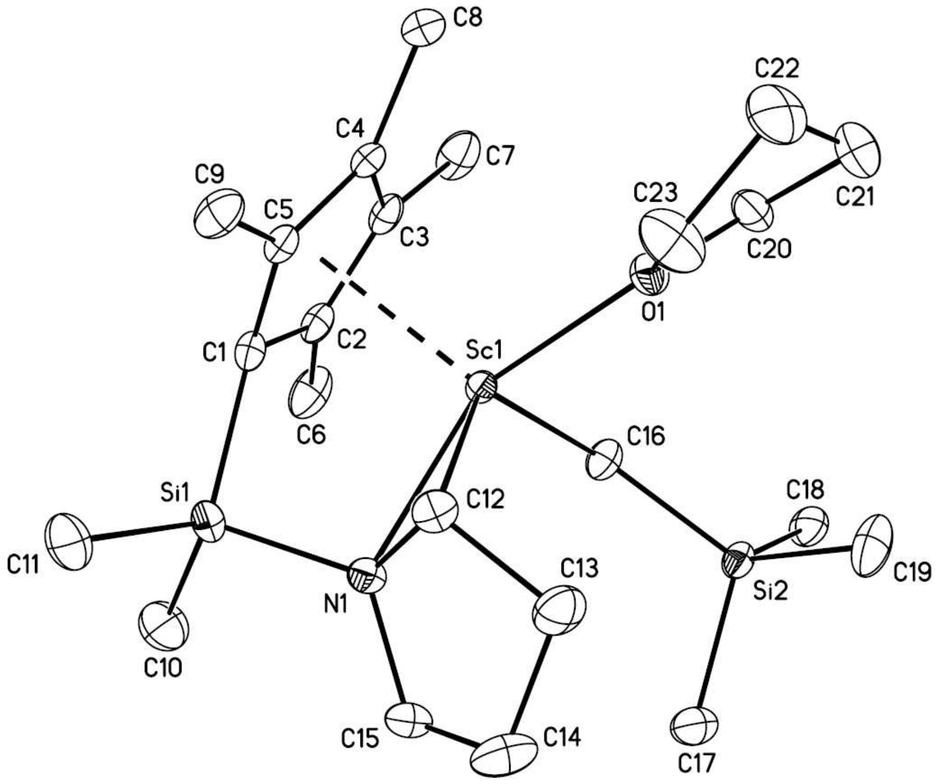


Fig. 1 Molecular structure of **3** with thermal ellipsoids at 20% probability. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and bond angles (°) for **3**: Sc1-C1 = 2.433(2), Sc1-C2 = 2.473(2), Sc1-C3 = 2.556(2), Sc1-C4 = 2.589(2), Sc1-C5 = 2.515(2), Sc1-C12 = 2.190(2), Sc1-C16 = 2.277(2), Sc1-N1 = 2.290(2), Sc1-O1 = 2.2006(16), Sc1-Cp (centroid) = 2.206(7), Cp(centroid)-Sc1-N1 = 101.1(3), Cp(centroid)-Sc1-C12 = 112.6(3), Cp(centroid)-Sc1-C16 = 117.3(3).

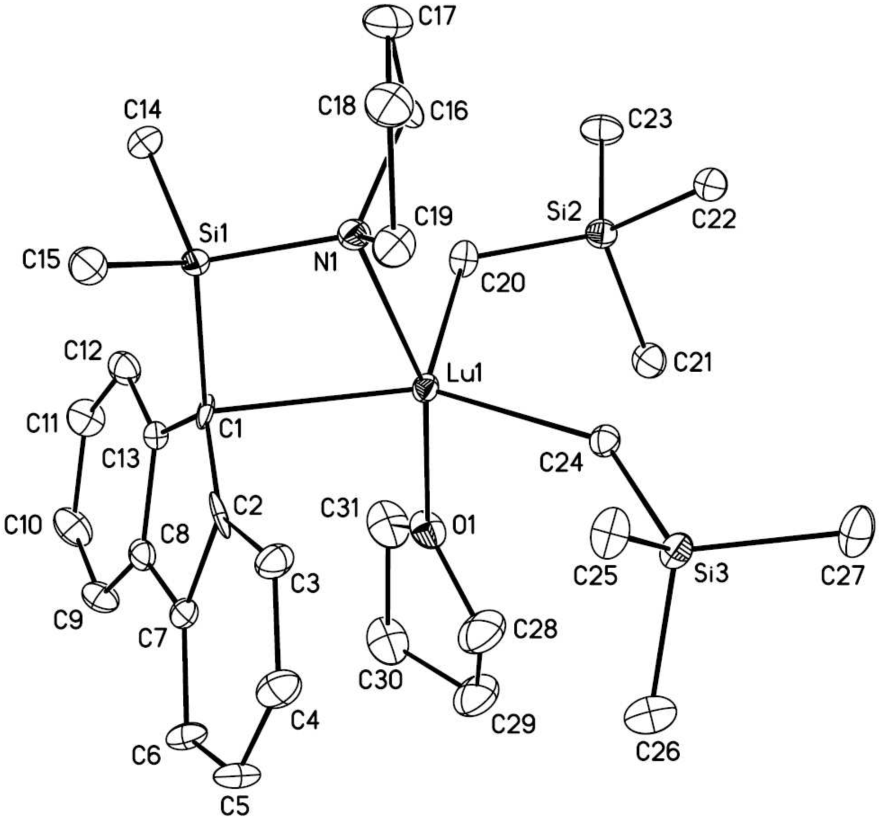


Fig. 2 Molecular structure of **6** with thermal ellipsoids at 20% probability. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and bond angles (°) for **6**: Lu1-C1 = 2.529(12), Lu1-C2 = 2.855(12), Lu1-C3 = 3.297(16), Lu1-C7 = 3.758(13), Lu1-C8 = 3.995(13), Lu1-C12 = 4.152(15), Lu1-C13 = 3.338(12), Lu1-C20 = 2.322(14), Lu1-C24 = 2.321(12), Lu1-N1 = 2.469(11), Lu1-O1 = 2.275(10), C1-Lu1-N1 = 70.4(4), C20-Lu1-C24 = 109.1(5).

Table 1 Details of the crystallographic data and refinements of complexes **3**, **5**, and **6**

	3	**5**	**6**
Empirical formula	$C_{23}H_{44}NOScSi_2$	$C_{31}H_{52}NOSi_3Y$	$C_{31}H_{52}LuNOSi_3$
Formula weight	451.73	627.92	713.98
Temperature (K)	223(2)	220(2)	220(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P\,2_1/c$	$P\,2_1/c$	$P\,2_1/c$
a (Å)	10.7306(5)	10.1323(4)	10.0861(5)
b (Å)	16.1771(7)	11.1789(4)	11.1647(6)
c (Å)	15.2453(7)	30.7457(11)	30.639(2)
α (°)	90	90	90
β (°)	95.132(4)	96.195(4)	96.377(5)
γ (°)	90	90	90
Volume (Å^3)	2635.8(2)	3462.2(2)	3428.8(3)
Z	4	4	4
Density (g·cm^{-3})	1.138	1.205	1.383
μ (mm^{-1})	0.383	1.811	3.006
F (000)	984	1336	1464
Crystal size (mm)	0.80×0.30×0.20	0.60×0.40×0.30	0.70×0.50×0.30
θ range (°)	3.15 to 25.50	3.17 to 25.50	3.14 to 25.50
Limiting indices	$-12 \le h \le 10$ $-19 \le k \le 18$ $-17 \le l \le 18$	$-9 \le h \le 12$ $-13 \le k \le 13$ $-32 \le l \le 37$	$-12 \le h \le 10$ $-13 \le k \le 11$ $-37 \le l \le 36$
Reflection collected	12252	15358	14287
R_{int}	0.0304	0.0376	0.0416
Reflection unique	4908	6443	6386
Data/restraints/param.	4908 / 0 / 262	6443 / 0 / 330	6386 / 0 / 330
GOF on F^2	1.028	1.024	1.133
R_1, wR_2 [$I > 2\sigma(I)$]	$R_1 = 0.0447$, $wR_2 = 0.1096$	$R_1 = 0.0418$, $wR_2 = 0.0847$	$R_1 = 0.0741$, $wR_2 = 0.2001$
R_1, wR_2 (all data)	$R_1 = 0.0605$, $wR_2 = 0.1164$	$R_1 = 0.0673$, $wR_2 = 0.0912$	$R_1 = 0.0874$, $wR_2 = 0.2048$
Largest diff. (e·Å^{-3})	0.352 and -0.355	0.469 and -0.521	4.897 and -2.229

Isoprene polymerization

To investigate the effect of ancillary ligand on polymerization behavior, **1**, **2**, **4-6** were employed as catalyst precursors for isoprene polymerization. These neutral complexes alone showed no activity toward isoprene polymerization in toluene at room temperature, neither did the binary catalyst systems formed from the neutral complex/$Al^{i}Bu_3$. On activation with one equivalent of $[Ph_3C][B(C_6F_5)_4]$, it was found that **5** and **6** became active for isoprene polymerization, whist **1**, **2** and **4** were still inert to isoprene polymerization even the polymerization was prolonged to 24 h. NMR spectra show that the binary catalyst systems of **5** or **6**/$[Ph_3C][B(C_6F_5)_4]$ in toluene at room temperature produce poly(isoprene)s with *cis*-1,4-selectivity > 95%. As the results summarized in Table 2, the activity is also somewhat dependent on the central metal (Table 2, runs 4 and 5).

Notably, addition of excess $Al^{i}Bu_3$ to **1**, **2**, **4-6**/$[Ph_3C][B(C_6F_5)_4]$ catalyst systems improves the polymerization activity, albeit **1**, **2** and **4** still show poor activity. As illustrated in Table 2, with the same central metal Lu^{3+}, the polymerization activity is in the order of **2** < **4** < **6**, indicative of an obvious ligand effect on the polymerization. The catalytic activity trend follows Fluorenyl > Indenyl > Cp. GPC curves indicate that the polymer samples produced by either the binary catalyst systems or the ternary catalyst systems are all unimodal, indicative of a single-site polymerization behavior.

Remarkably, using **6** as the catalyst precursor, the polymerization can complete in 10 min even the molar ratio of [M]/[Lu] is increased upon to 2000. Furthermore, a controllable polymerization fashion is observed in the molar ratio range of [M]/[Lu] from 500 to 2000 with **6**/$[Ph_3C][B(C_6F_5)_4]/Al^iBu_3$ as a catalyst system, for the molecular weights of the resulting polymers increase almost linearly with the increase of the molar ratio of monomer-to-Lu while the molecular weight distributions kept nearly constant (Table 2, runs 11-14).

Table 2 Polymerization of isoprene by **1**, **2**, **4**, **5** and **6**/$[Ph_3C][B(C_6F_5)_4]/Al^iBu_3$[a]

Run	complex	[M]/[Ln]/[Al]	t (min)	conv.[b] (%)	M_n[c] $\times 10^{-4}$	M_w/M_n[c]	*cis*-1,4[d] (%)
1	**1**	500/1/0	1440	0	-	-	-
2	**2**	500/1/0	1440	0	-	-	-
3	**4**	500/1/0	1440	0	-	-	-
4	**5**	500/1/0	720	97	12.63	1.69	95.8
5	**6**	500/1/0	360	96	8.68	1.61	97.6
6	**1**	500/1/10	10	12	6.8	1.67	95.5
7	**2**	500/1/10	10	24	6.2	1.84	97.2
8	**4**	500/1/10	10	36	8.2	1.65	97.9
9	**5**	500/1/10	10	75	10.2	1.81	98.1
10	**5**	500/1/10	20	100	14.3	1.78	97.8
11	**6**	500/1/10	10	100	7.49	1.76	96.6
12	**6**	1000/1/10	10	100	15.16	1.73	97.4
13	**6**	1500/1/10	10	100	21.98	1.79	95.8
14	**6**	2000/1/10	10	100	29.85	1.81	96.1

[a] Polymerization conditions: in toluene; Ln, 20 μmol; solvent/monomer = 3/1 (v/v); [Ln]/[B] = 1/1 (mol/mol); B = $[Ph_3C][B(C_6F_5)_4]$, T_p = 25 ºC. [b] conv. = weight of polymer obtained/weight of monomer used. [c] Determined by GPC in THF at 40 °C against polystyrene standard. [d] Determined by ^{1}H NMR and ^{13}C NMR in $CDCl_3$.

Conclusion

With the aim of investigating ligand effect on the structure-reactivity relationship, a series of rare-earth metal bis(alkyl) complexes bearing pyrrolidinyl-functionalized cyclopentadienyl, indenyl and fluorenyl ligands were prepared and characterized. The substituted cyclopentadienyl- or indenyl-ligated rare-earth metal bis(alkyl) complexes $LLn(CH_2SiMe_3)_2(THF)_2$ (L = $C_5Me_4SiMe_2NC_4H_8$, Ln = Y (**1**), Lu (**2**); L = $C_9H_6SiMe_2NC_4H_8$, Lu (**4**)) could be prepared via alkane elimination between $Ln(CH_2SiMe_3)_3(THF)_2$ and 1 equiv of the corresponding ligand precursor at room temperature in THF. The alkane elimination synthetic strategy could not be applied to access fluorenyl-ligated rare-earth metal bis(alkyl) complexes for the low acidity of fluorene. Mono-fluorenyl-ligated rare-earth metal bis(alkyl) complexes $(C_{13}H_8SiMe_2NC_4H_8)Ln(CH_2SiMe_3)_2(THF)$ (Ln = Y (**5**), Lu (**6**)) were prepared by one-pot salt metathesis reaction of $LnCl_3$, $C_{13}H_8SiMe_2NC_4H_8Li$ and $LiCH_2SiMe_3$ in 1:1:2 molar ratio in THF at room temperature. In the presence of excess Al^iBu_3, and upon activated with one equivalent of $[Ph_3C][B(C_6F_5)_4]$, these complexes were active for *cis*-1,4-selective polymerization of isoprene in toluene at room temperature. The activity trend with respect to the ligand effect followed Fluorenyl > Indenyl > Cp. A controllable polymerization fashion was observed with **6**/$[Ph_3C][B(C_6F_5)_4]/Al^iBu_3$ as a catalyst system.

Experimental

Materials and procedures

All manipulations were performed under pure argon with rigorous exclusion of air and moisture using standard Schlenk techniques and argon-filled glovebox. Solvents (toluene, hexane and THF) were distilled from sodium/benzophenone ketyl, degassed by the freeze-pump-thaw method, and dried over fresh Na chips in the glovebox. Anhydrous $LnCl_3$ were purchased from Strem. $LiCH_2SiMe_3$ (1 M in pentane solution) was obtained from Aldrich, dried under vacuum before use. Al^iBu_3

(1.1 M in toluene), *n*-BuLi (2.5 M in hexane solution), and $[Ph_3C][B(C_6F_5)_4]$ were purchased from Acros. Isoprene was dried by stirring with CaH_2, and distilled before polymerization. $C_5Me_4HSiMe_2Cl$, indene, fluorene, Me_2SiCl_2 and pyrrolidine were purchased from Aldrich, and used as received. Deuterated solvents (C_6D_6, $CDCl_3$) were obtained from Aldrich. $Ln(CH_2SiMe_3)_3(THF)_2$ (Ln = Sc, Y, Lu),[10,16] $C_4H_8NSiMe_2Cl$ and $C_5Me_4HSiMe_2NC_4H_8$ were prepared according to the literatures.[17,18]

Samples of rare-earth metal complexes for NMR spectroscopic measurements were prepared in the glovebox using J. Young valve NMR tubes. NMR (^1H, ^{13}C) spectra were recorded on a Bruker AVANCE III spectrometer at 25 °C for the rare-earth metal complexes and the polymer samples, and referenced internally to residual solvent resonances unless otherwise stated. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion on a Carlo-Erba EA-1110 instrument; quoted data are the average of at least two independent determinations. FT-IR spectra were recorded on a Bruker TENSOR 27 spectrometer. Molecular weight and molecular weight distribution of the polymers were measured by PL GPC 50 at 40 °C using THF as eluent against polystyrene standards, flow rate: 1.0 mL/min, sample concentration: 1 mg/mL.

Syntheses

$C_9H_7SiMe_2NC_4H_8$. To a THF solution of C_9H_7Li (2.442 g, 20 mmol), which was prepared from the reaction of C_9H_8 with 1 equivalent amount of *n*-BuLi in hexane at the room temperature, was added slowly one equimolar amount of $C_4H_8NSiMe_2Cl$ (3.275 g, 20 mmol) in THF. The wine-red mixture was stirred at the room temperature for 24 h, and then the volatiles were removed in vacuo. The resulting residue was extracted by hexane (3×10 mL) and filtered. Removal of hexane gave a mixture of isomeric products in nearly 20:1 molar ratio (A:B = 20:1) as pale-yellow oil (3.17 g, 65%). ^{1}H NMR (400 MHz, C_6D_6): (A) δ -0.04 (s, 3H, Si*Me$_2$*), 0.00 (s, 3H, Si*Me$_2$*), 1.47 (m, 4 H, C_4H_8N), 2.72 (m, 2H, C_4H_8N), 2.80 (m, 2H, C_4H_8N), 3.59 (s, 1H, indenyl-*H*), 6.59 (d, 1H, indenyl-*H*), 6.88 (d, 1H, indenyl-*H*), 7.20 (t, 1H, Ar-*H*), 7.26 (d, 1H, Ar-*H*), 7.49 (d, 2H, Ar-*H*). (B) δ 0.40 (s, 0.3H, Si*Me$_2$*), 1.56 (m, 0.2H, C_4H_8N), 2.98 (m, 0.2H, C_4H_8N), 3.16 (s, 0.1H, indenyl-*H*), 6.65 (0.05H, indenyl-*H*), 7.38 (0.05H, Ar-*H*), 7.58 (0.05H, Ar-*H*), 7.71 (0.05H, Ar-*H*). ^{13}C NMR (100 MHz, C_6D_6): δ -3.6, -3.8, -1.9 (Si*Me$_2$*), 27.1 27.3 (C_4H_8N), 40.9 (C_4H_8N), 47.3 (C_4H_8N), 47.4 (C_4H_8N), 48.7 (C_4H_8N), 121.4, 122.7, 122.9, 123.3, 123.9, 124.7, 125.1, 126.6, 135.8, 144.9, 145.2, 145.6 (C_9H_6). Calcd for $C_{15}H_{21}NSi$: C, 74.01; H, 8.70; N, 5.75. Found: C, 74.05; H, 8.76; N, 5.40.

$C_{13}H_9SiMe_2NC_4H_8$. To a THF solution of $C_{13}H_9Li$ (3.443 g, 20 mmol), which was prepared from the reaction of $C_{13}H_{10}$ with 1 equivalent amount of *n*-BuLi in toluene at the room temperature, was added slowly one equimolar amount of $C_4H_8NSiMe_2Cl$ (3.275 g, 20 mmol) in THF. The mixture was stirred at the room temperature for one day, and then the volatiles were removed in vacuo. The resulting residue was extracted by hexane (3×10 mL) and filtered. Removal of hexane gave the aimed product as yellowish-brown powder (5.571 g, 95%). ^{1}H NMR (400 MHz, C_6D_6): δ 0.00 (s, 6H, Si*Me$_2$*), 1.40 (m, 4H, C_4H_8N), 2.59 (m, 4H, C_4H_8N), 3.82 (s, 1H, fluorene *H*), 7.27 (m, 4H, Ar*H*), 7.50 (d, *J* = 7.2 Hz, 2H, Ar*H*), 7.79 (d, *J* = 6.8 Hz, 2H, Ar*H*). ^{13}C NMR (100 MHz, C_6D_6): δ -3.5 (Si*Me$_2$*), 27.1 (C_4H_7N), 44.8 (C_4H_7N), 47.4 (fluorene *C*), 120.2, 124.6, 125.5, 126.2, 141.2, 146.1 (Ar*C*). Calcd for $C_{19}H_{23}NSi$: C, 77.76; H, 7.90; N, 4.77. Found: C, 77.55; H, 7.73; N, 4.58.

$(C_5Me_4SiMe_2NC_4H_8)Y(CH_2SiMe_3)_2(THF)_2$ (1). To a THF (10 mL) solution of $C_5Me_4HSiMe_2NC_4H_8$ (0.249 g, 1.0 mmol) was added slowly a THF solution (5 mL) of $Y(CH_2SiMe_3)_3(THF)_2$ (0.495 g, 1.0 mmol) at room temperature. The reaction mixture was stirred for 3 h to give a clear pale yellow solution. Removal of the volatiles under vacuum afforded **1** as pale-yellow oil (0.52 g, 86%). ^1H NMR (400 MHz, C_6D_6): δ -0.61 (d, J = 3.2 Hz, 4H, $\mathrm{C}\mathit{H_2}\mathrm{SiMe_3}$), 0.31 (s, 18H, $\mathrm{CH_2Si}\mathit{Me_3}$), 0.49 (s, 6H, $\mathrm{Si}\mathit{Me_2}$), 1.28 (br s, 8H, β-THF), 1.57 (m, 4H, $\mathrm{C_4}\mathit{H_8}\mathrm{N}$), 2.02 (s, 6H, $\mathrm{C_5}\mathit{Me_4}$), 2.30 (s, 6H, $\mathrm{C_5}\mathit{Me_4}$), 2.87 (m, 4H, $\mathrm{C_4}\mathit{H_8}\mathrm{N}$), 3.50 (br s, 8H, α-THF). ^{13}C NMR (100 MHz, C_6D_6): δ 1.1 ($\mathrm{Si}\mathit{Me_2}$), 4.6 ($\mathrm{CH_2Si}\mathit{Me_3}$), 11.7 ($\mathrm{C_5}\mathit{Me_4}$), 14.7 ($\mathrm{C_5}\mathit{Me_4}$), 25.1 ($\beta$-THF), 26.6 ($\mathit{C_4}\mathrm{H_8N}$), 27.3 ($\mathit{C_4}\mathrm{H_8N}$), 34.3 (d, J = 43.4 Hz, $\mathit{C}\mathrm{H_2SiMe_3}$), 47.4 ($\mathit{C_4}\mathrm{H_8N}$), 69.8 ($\alpha$-THF), 124.1 ($\mathit{C_5}\mathrm{Me_4}$), 126.6 ($\mathit{C_5}\mathrm{Me_4}$). Anal. Calcd for $C_{31}H_{64}NO_2SiY$: C, 62.07; H, 10.75; N, 2.34. Found: C, 61.90; H, 10.42; N, 2.30.

$(C_5Me_4SiMe_2NC_4H_8)Lu(CH_2SiMe_3)_2(THF)_2$ (2). **2** was prepared by a procedure similar to that of **1**. Using $Lu(CH_2SiMe_3)_3(THF)_2$ (0.581 g, 1.0 mmol), $C_5Me_4HSiMe_2NC_4H_8$ (0.249 g, 1.0 mmol), **3** was isolated as pale-yellow powder (0.61 g, 82%). ^1H NMR (400 MHz, C_6D_6): δ -0.81 (s, 4H, $\mathrm{C}\mathit{H_2}\mathrm{SiMe_3}$), 0.32 (s, 18H, $\mathrm{CH_2Si}\mathit{Me_3}$), 0.43 (s, 6H, $\mathrm{Si}\mathit{Me_2}$), 1.27 (br s, 8H, β-THF), 1.53 (m, 4H, $\mathrm{C_4}\mathit{H_8}\mathrm{N}$), 2.04 (s, 6H, $\mathrm{C_5}\mathit{Me_4}$), 2.28 (s, 6H, $\mathrm{C_5}\mathit{Me_4}$), 2.78 (m, 4H, $\mathrm{C_4}\mathit{H_8}\mathrm{N}$), 3.55 (br s, 8H, α-THF). ^{13}C NMR (100 MHz, C_6D_6): δ 0.9 ($\mathrm{Si}\mathit{Me_2}$), 4.7 ($\mathrm{CH_2}\mathit{SiMe_3}$), 11.8 ($\mathrm{C_5}\mathit{Me_4}$), 14.8 ($\mathrm{C_5}\mathit{Me_4}$), 24.9 ($\beta$-THF), 26.1 ($\mathit{C_4}\mathrm{H_8N}$), 39.7 ($\mathit{C}\mathrm{H_2SiMe_3}$), 47.5 ($\mathit{C_4}\mathrm{H_8N}$), 70.2 ($\alpha$-THF), 124.2

(C_5Me$_4$), 126.0 (C_5Me$_4$). Anal. Calcd for $C_{31}H_{64}LuNO_2Si$: C, 52.28; H, 9.40; N, 2.04. Found: C, 52.05; H, 9.75; N, 2.01.

($C_5Me_4SiMe_2NC_4H_7$)Sc(CH_2SiMe_3)(THF) (3). To a THF (10 mL) solution of $C_5Me_4HSiMe_2NC_4H_8$ (0.249 g, 1.0 mmol) was added slowly a THF solution (5 mL) of $Sc(CH_2SiMe_3)_3(THF)_2$ (0.451 g, 1.0 mmol) at room temperature. The reaction mixture was stirred for 3 h to give a clear pale yellow solution. Removal of the volatiles under vacuum afforded yellow oily residue, which was recrystallized from pentane at -30 °C to give **1** as colorless block crystals (0.318 g, 71%). ^{1}H NMR (400 MHz, C_6D_6): δ -0.98 (d, J = 12.0 Hz, 1H, CH_2SiMe$_3$), -0.90 (d, J = 12.0 Hz, 1H, CH_2SiMe$_3$), 0.28 (s, 9H, CH$_2$SiMe_3), 0.42 (s, 3H, SiMe_2), 0.61 (s, 3H, SiMe_2), 1.22 (s, 4H, β-THF), 1.61 (m, 2H, C$_4H_7$N), 1.71 (s, 3H, C$_5Me_4$), 1.79 (s, 3H, C$_5Me_4$), 2.12 (s, 4H, C$_4H_7$N), 2.28 (s, 3H, C$_5Me_4$), 2.34 (s, 3H, C$_5Me_4$), 2.99 (d, J = 36.0 Hz, 1H, C$_4H_7$N), 3.46 (m, 4H, α-THF). ^{13}C NMR (100 MHz, C_6D_6): δ -1.7 (SiMe_2), 1.9 (SiMe_2), 4.5 (CH$_2$SiMe_3), 11.9 (C$_5Me_4$), 15.4 (C$_5Me_4$), 25.3 (β-THF), 27.3 (C_4H$_7$N), 29.2 (C_4H$_7$N), 31.4 (CH$_2$SiMe$_3$), 50.1 (C_4H$_7$N), 70.9 (α-THF), 103.6 (C_5Me$_4$), 124.0 (C_5Me$_4$). Anal. Calcd for $C_{23}H_{44}NOSiSc$: C, 61.50; H, 9.29; N, 3.17. Found: C, 61.15; H, 9.62; N, 3.10.

($C_9H_6SiMe_2NC_4H_8$)Lu(CH_2SiMe_3)$_2$(THF)$_2$ (4). To a THF solution of $Lu(CH_2SiMe_3)_3(THF)_2$ (0.581 g, 1.0 mmol) was added slowly one equimolar amount of $C_9H_6SiMe_2NC_4H_8$ (0.243 g, 1.0 mmol) in THF. The mixture was stirred at the room temperature for 4 h, and then the volatileS were removed in vacuo. The resulting residue was extracted by hexane (3 × 5 mL) and filtered. Removal of hexane gave **4** as pale-yellow powder (0.64 g, 86%).

^{1}H NMR (500 MHz, C_6D_6): δ -0.93 (d, *J* = 15.0 Hz, 2H, CH_2SiMe$_3$), -0.79 (d, *J* = 10.0 Hz, 2H, CH_2SiMe$_3$), 0.31 (s, 18H, CH$_2$$SiMe_3$), 0.61 (s, 3H, $SiMe_2$), 0.63 (s, 3H, $SiMe_2$), 1.20 (br s, 8H, β-THF), 1.53 (m, 4H, C_4H_8N), 2.91, 2.96 (m, 4H, C_4H_8N), 3.38 (br s, 4H, α-THF), 6.85 (m, 1H, Ar-*H*), 6.92 (m, 2H, Ar-*H*), 7.57 (m, 2H, Ar-*H*), 7.80 (m, 1H, Ar-*H*). ^{13}C NMR (100 MHz, C_6D_6): δ -0.9 (Si*Me*$_2$), 0.2 (Si*Me*$_2$), 4.5 (CH$_2$$SiMe_3$), 25.7 ($\beta$-THF), 27.1 ($C_4H_8N$), 41.1 ($CH_2$SiMe$_3$), 47.5 ($C_4H_8N$), 69.6 ($\alpha$-THF), 103.2 (indene *C*), 121.3, 121.8, 122.9, 124.6, 132.0, 133.5 (Ind-*C* and Ar-*C*). Calcd for $C_{31}H_{58}LuNO_2Si_3$: C, 50.59; H, 7.94; N, 1.90. Found: C, 50.68; H, 8.09; N, 2.16.

$(C_{13}H_8SiMe_2NC_4H_8)Y(CH_2SiMe_3)_2(THF)$ (5). To a THF slurry of YCl_3 (0.196 g, 1.0 mmol) was added slowly 1 equiv of $C_{13}H_8SiMe_2NC_4H_8Li$ (0.299 g, 1 mmol), which was prepared by the treatment of $C_{13}H_9SiMe_2NC_4H_8$ with one equivalent amount of *n*-BuLi in hexane at room temperature. The mixture was stirred at room temperature for 2 h to afford a clear solution, to which $LiCH_2SiMe_3$ (0.188 g, 2.0 mmol) was introduced. The resulting yellow solution was stirred at room temperature for another 2 h. Remove of the volatiles gave a yellow residue, which was extracted by hexane (3 × 10 mL). After filteration and removal of hexane, the crude product **5** was obtained as yellow powder. Recrystallization from hexane/toluene at -20 °C gave **5** as orange block crystals (0.338 g, 54%). ^{1}H NMR (400 MHz, C_6D_6): δ -0.58 (d, *J* = 4.0 Hz, 4H, CH_2SiMe$_3$), 0.22 (s, 18H, CH$_2$SiMe_3), 0.37 (s, 6H, SiMe_2), 1.00 (br s, 4H, C$_4$$H_8$N), 1.56 (m, 4H, β-THF), 2.70 (br s, 4H, C$_4$$H_8$N), 3.21 (m, 4H, α-THF), 7.18 (t, 2H, Ar-*H*), 7.47 (t, 2H, Ar-*H*), 7.75 (d, 2H, Ar-*H*), 8.05 (d, 2H, Ar-*H*). ^{13}C NMR (100 MHz, C_6D_6): δ -1.2 (Si*Me*$_2$), 4.2 (CH$_2$SiMe_3), 25.0 (β-THF), 25.9 (C_4H_8N), 38.6 (CH$_2$SiMe$_3$), 38.9 (C_4H_8N), 69.6 (α-THF), 79.0 (fluorene *C*), 118.3, 118.9, 120.5, 125.5, 132.2, 141.4 (*Ar* C). Calcd for $C_{31}H_{52}NOSi_3Y$: C, 59.29; H, 8.36; N, 2.23. Found: C, 59.36; H, 8.15; N, 2.38.

$(C_{13}H_8SiMe_2NC_4H_8)Lu(CH_2SiMe_3)_2(THF)$ (6). 6 was prepared by a procedure similar to that of **5**. Using $LuCl_3$ (0.282 g, 1.0 mmol), $C_{13}H_8SiMe_2NC_4H_8Li$ (0.299 g, 1.0 mmol), and $LiCH_2SiMe_3$ (0.188 g, 2.0 mmol) to afford the aimed product as yellow block crystals (0.382 g, 53%). ^{1}H NMR (400 MHz, C_6D_6): δ -0.72 (d, 4H, CH_2SiMe$_3$), 0.24 (s, 18H, CH$_2$$SiMe_3$), 0.30 (s, 6H, $SiMe_2$), 0.87 (m, 4H, C$_4$$H_8$N), 1.52 (m, 4H, β-THF), 2.35 (br s, 4H, C$_4$$H_8$N), 3.25 (m, 4H, α-THF), 7.22 (t, 2H, Ar-*H*), 7.52 (t, 2H, Ar-*H*), 7.67 (d, 2H, Ar-*H*), 8.09 (d, 2H, Ar-*H*). ^{13}C NMR (150 MHz, C_6D_6): δ -1.3 (SiMe_2), 4.40 (CH$_2$$SiMe_3$), 25.1 ($\beta$-THF-*C*), 25.7 ($C_4H_8$N), 44.5 (*C*H$_2$SiMe$_3$), 50.6 ($C_4H_8$N), 69.8 ($\alpha$-THF-*C*), 118.3, 118.5, 120.2, 125.1, 133.3, 142.5 (*Ar*-C). Calcd for $C_{31}H_{52}LuNOSi_3$: C, 52.15; H, 7.36; N, 1.96. Found: C, 52.33; H, 7.29; N, 1.81.

Typical procedure for isoprene polymerization. The procedures for isoprene polymerization catalyzed by these rare-earth-metal complexes were similar, and a typical polymerization procedure is given below. A 50 mL Schlenk flask equipped with a magnetic stirring bar was charged in sequence with the desired amount of the scandium complex, toluene, borate (or borate and methyl aluminum) and isoprene. The mixture was stirred vigorously at room temperature for the desired time, during which an increase of viscosity was observed. The reaction mixture was quenched by the addition of ethanol and then poured into a large amount of ethanol to precipitate the polymer, which was dried under vacuum at 60 °C and weighted.

X-ray crystallographic study. Suitable single crystals of complexes were sealed in a thin-walled glass capillary for determining the single-crystal structure. Intensity data were collected with a Rigaku Mercury CCD area detector in ω scan mode using Mo Kα radiation (λ = 0.71070 Å). The diffracted intensities were corrected for Lorentz–polarization effects and empirical absorption corrections. The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. All the non-hydrogen atoms were refined anisotropically. The structures were solved and refined using SHELXL-97 program.

Supplementary materials

NMR spectra of **1-6**, Molecular structure of 5, GPC curve and NMR spectra of representative polymer sample, CCDC 1044841-1044843 contain the supplementary crystallographic data for complexes **3**, **5** and **6**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

This work was partly financial supported by the National Natural Science Foundation of China (21172195). The authors are grateful to Mr. Yong Zhang at Suzhou University for X-ray analysis help.

References

1. (a) F. T. Edelmann, *Coord. Chem. Rev.*, 2015, **284**, 124. (b) M. Zimmermann and R. Anwander, *Chem. Rev.*, 2010, **110**, 6194. (c) H. Li and T. J. Marks, *Proc. Natl. Acad. Sci. U.S.A.*, 2006, **103**, 15295. (d) F. T. Edelmann, D. M. M. Freckmann

and H. Schumann, *Chem. Rev*., 2002, **102**, 1851. (e) G. A. Molander and J. A. C. Romero, *Chem. Rev*., 2002, **102**, 2161. (f) W. J. Evans and B. L. Davis, *Chem. Rev.*, 2002, **102**, 2119. (g) H. Schumann, J. A. Meese-Marktscheffel and L. Esser, *Chem. Rev.*, 1995, **95**, 865.

2. (a) M. Nishiura and Z. Hou, *Nat. Chem.*, 2010, **2**, 257. (b) P. M. Zeimentz, S. Arndt, B. R. Elvidge and J. Okuda, *Chem. Rev.*, 2006, **106**, 2404.
3. (a) L. S. Baugh and J. A. M. Canich, *Stereoselective Polymerization with Single-Site Catalysts*, Taylor & Francis: New York, 2008, p447. (b) J. Zhao and G. N. Ghebremeskel, *Rubber Chem. Technol.*, 2001, **74**, 409.
4. (a) Z. Shen, Z. Gong, C. Zhong and J. Ouyang, *Chin. Sci. Bull.*, 1964, **4**, 335. (b) Z. Shen, J. Ouyang, F. Wang, Z. Hu, F. Yu and B. Qian, *J. Polym. Sci., Part A: Polym. Chem.*, 1980, **18**, 3345. (c) C. Shan, Y. Li, S. Pang and J. Ouyang, *Acta Chim. Sin.*, 1983, **41**, 490. (d) C. Shan, Y. Lin and J. Ouyang, *Makromol. Chem.*, 1987, **188**, 629. (e) F. Barbotin, R. Spitz and C. Boisson, *Macromol. Rapid Commun.*, 2001, **22**, 1411. (f) Y. Taniguchi, W. Dong, T. Katsumata, M. Shiotsuki and T. Masuda, *Polym. Bull.*, (Berlin) 2005, **54**, 173. (g) L. Friebe, O. Nuyken and W. Obrecht, *Adv. Polym. Sci.*, 2006, **204**, 1. (h) A. Fischbach and R. Anwander, *Adv. Polym. Sci.*, 2006, **204**, 155. (i) A. Fischbach, C. Meermann, G. Eickerling, W. Scherer and R. Anwander, *Macromolecules*, 2006, **39**, 6811.
5. (a) S. Kaita, Z. Hou and Y. Wakatsuki, *Macromolecules*, 1999, **32**, 9078. (b) W. Evans, T. Champagne and J. Ziller, *Chem. Commun.*, 2005, 5925. (c) W. Evans, T. Champagne and J. Ziller, *Organometallics*, 2005, **24**, 4882. (d) W. Evans, T.

Champagne, D. Giarikos and J. Ziller, *Organometallics*, 2005, **24**, 570. (e) S. Kaita, Z. Hou and Y. Wakatsuki, *Macromolecules*, 2001, **34**, 1539. (f) S. Kaita, Y. Doi, K. Kaneko, A. C. Horiuchi and Y. Wakatsuki, *Macromolecules*, 2004, **37**, 5860. (g) S. Kaita, M.Yamanaka, A. C. Horiuchi and Y. Wakatsuki, *Macromolecules*, 2006, **39**, 1359. (h) S. Kaita, Z. Hou, M. Nishiura, Y. Doi, J. Kurazumi, A. C. Horiuchi and Y. Wakatsuki, *Macromol. Rapid Commun.*, 2003, **24**, 179.

6. (a) A. Fischbach, M. G. Klimpel, M. Widenmeyer, E. Herdtweck, W. Scherer and R. Anwander, *Angew. Chem. Int. Ed.*, 2004, **43**, 2234. (b) S. Arndt, K. Beckerle, P. M. Zeimentz, T. P. Spaniol and J. Okuda, *Angew. Chem. Int. Ed.*, 2005, **44**, 7473. (c) A. Fischbach, F. Perdih, E. Herdtweck and R. Anwander, *Organometallics*, 2006, **25**, 1626. (d) C. Meermann, K. Törnroos, W. Nerdal and R. Anwander, *Angew. Chem. Int. Ed.*, 2007, **46**, 6508. (e) H. Dietrich, C. Zapilko, E. Herdtweck and R. Anwander, *Organometallics*, 2005, **24**, 5767. (f) D. Li, S. Li, D. Cui and X. Zhang, *Organometallics*, 2010, **29**, 2186. (g) S. Liu, G. Du, J. He, Y. Long, S. Zhang and X. Li, *Macromolecules*, 2014, **47**, 3567.
7. (a) S. Sun, H. Ouyang, Y. Luo, Y. Zhang, Q. Shen and Y. Yao, *Dalton Trans.*, 2013, **42**, 16355. (b) Y. Luo, Y. Lei, S. Fan, Y. Wang and J. Chen, *Dalton Trans.*, 2013, **42**, 4040. (c) F. Chen, S. Fan, Y. Wang, J. Chen and Y. Luo, *Organometallics*, 2012, **31**, 3730. (d) Y. Luo, S. Fan, J. Yang, J. Fang and P. Xu, *Dalton Trans.*, 2011, **40**, 3053.
8. (a) W. Gao and D. Cui, *J. Am. Chem. Soc.*, 2008, **130**, 4984. (b) K. Lv and D. Cui,

Organometallics, 2008, **27**, 5438. (c) K. Lv and D. Cui, *Organometallics*, 2010, **29**, 2987. (d) Y. Pan, T. Q. Xu, G. Yang, K. Jin and X. Lu, *Inorg. Chem.*, 2013, **52**, 2802.

9. (a) Z. Jian, D. Cui and Z. Hou, *Chem. Eur. J.*, 2012, **18**, 2674. (b) Y. Mu, W. E. Piers, D. C. MacQuarrie, M. J. Zaworotko and V. G. Young Jr., *Organometallics*, 1996, **15**, 2720
10. Y. Luo, J. Baldamus and Z. Hou , *J. Am. Chem. Soc.*, 2004, **126**, 13910.
11. E. Kirillov, J. Y. Saillard and J. F. Carpentier, *Coord. Chem. Rev.*, 2005, **249**, 1221.
12. Z. Hou, C. Yoda, T. Koizumi, M. Nishiura, Y. Wakatsuki, S. Fukuzawa and J. Takats, *Organometallics*, 2003, **22**, 3586.
13. E. Kirillov, L. Toupet, C. W. Lehmann, A. Razavi, S. Kahlal, J. Y. Saillard and J. F. Carpentier, *Organometallics*, 2003, **22**, 4038.
14. R. D. Shannon, *Acta Cryst.*, 1976, **A32**, 751.
15. Y. Pan, W. Rong, Z. Jian and D. Cui, *Macromolecules*, 2012, **45**, 1248.
16. M. Lappert and R. Pearce, *Chem. Commun.*, 1973, 126.
17. V. Passarelli, F. Benetollo, P. Zanella, G. Carta and G. Rossetto, *Dalton Trans.*, 2003, 1411.
18. Y. Luo, S. Chi and J. Chen, *New J. Chem.*, 2013, **37**, 2675.