

Rare earth metal bis(alkyl) complexes bearing a monodentate arylamido ancillary ligand: Synthesis, structure, and Olefin polymerization catalysis

Yunjie Luo¹, Masayoshi Nishiura, Zhaomin Hou^{*}

Organometallic Chemistry Laboratory, RIKEN (The Institute of Physical and Chemical Research) and PRESTO, Japan Science and Technology Agency (JST), Hirosawa 2-1, Wako, Saitama 351-0198, Japan

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Abstract

The reaction of $\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{thf})_2$ with 1 equiv. of the amine ligand $2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{NH}(\text{SiMe}_3)$ gave the corresponding amido-ligated rare earth metal bis(alkyl) complexes $[2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)]\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})$ ($\text{Ln} = \text{Sc}$ (**1**), Y (**2**), Ho (**3**), Lu (**4**)), which represent rare examples of bis(alkyl) rare earth metal complexes bearing a monodentate anionic ancillary ligand. In the case of Gd, a similar reaction gave the bimetallic complex $\text{Gd}_2(\mu\text{-CH}_2\text{SiMe}_2\text{NC}_6\text{H}_3^i\text{Pr}_2\text{-2,6})_3(\text{thf})_3$ (**5**) through intramolecular C–H activation of a methyl group of Me_3Si on the amido ligand by $\text{Gd}\text{-CH}_2\text{SiMe}_3$ and the subsequent ligand redistribution. Complexes **1–5** were structurally characterized by X-ray analyses. On treatment with 1 equiv of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ in toluene at room temperature, complexes **1–4** showed high activity for the living polymerization of isoprene. The $1/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ system showed high activity also for the polymerization of 1-hexene and styrene.

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1. Introduction

Rare earth metal bisalkyl complexes bearing one anionic ancillary ligand have received much current interest because such complexes can be converted to the corresponding cationic monoalkyl species by treatment with an equimolar amount of a borate compound such as $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ or $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$, leading to formation of unique catalyst systems that differ from those derived from the conventional metallocene complexes [1–4]. To prevent possible ligand redistribution, most of the rare earth bisalkyl complexes reported so far were stabilized by multidentate ancillary ligands such as cyclopenta-

dienyls [2], β -diketiminates [3g,5], benzamidinates [3d], triazacyclononane-amido [3h], deprotonated aza-crown [6], anilido-pyridine-imine [7], aminopyridinates [8], and amido-phosphine [9], while monodentate-ligand-supported rare earth metal bisalkyl complexes remained scarce [10]. Changing the ligand environment of a complex to modify its properties is usually an important strategy for the development of more efficient or selective catalysts. During our recent studies on cationic half-sandwich rare earth metal alkyls in polymerization catalysis [1a,1e,2], we became interested in analogous non-metallocene alkyl complexes. We report here the synthesis, structure and olefin polymerization catalysis of the rare earth metal bis(alkyl) complexes bearing a simple monodentate arylamido ligand, $[2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)]\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})$ ($\text{Ln} = \text{Sc}$ (**1**), Y (**2**), Ho (**3**), Lu (**4**)) [11]. Formation and X-ray structure of a related bimetallic Gd complex $\text{Gd}_2\{\mu\text{-CH}_2\text{SiMe}_2\text{NC}_6\text{H}_3^i\text{Pr}_2\text{-2,6}\}_3(\text{thf})_3$ (**5**) is also described.

^{*} Corresponding author.

E-mail address: houz@postman.riken.go.jp (Z. Hou).

¹ Present address: Department of Biological and Pharmaceutical Engineering, Ningbo Institute of Technology, Zhejiang University, Ningbo 315100, China.

2. Results and discussion

2.1. Synthesis and structure of $[2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)]\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})$ ($\text{Ln} = \text{Sc}$ (1), Y (2), Ho (3), Lu (4))

The alkane elimination reaction of $\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{thf})_2$ with 1 equiv. of $2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{NHSiMe}_3$ in benzene or THF at room temperature afforded the mono(arylamido) rare earth metal bis(alkyl) complexes $[2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)]\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})$ ($\text{Ln} = \text{Sc}$ (1), Y (2), Ho (3), Lu (4)) in 54–68% isolated yields (Scheme 1). All these complexes showed good solubility in common organic solvents, such as THF, toluene, and hexane. Formation of a mono(alkyl) bis(arylamido) rare earth metal complex was not observed even when 2 equiv. of $2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{NHSiMe}_3$ were used.

The solid structures of complexes 1–4 were determined by X-ray diffraction analyses. Selected bond lengths and angles are shown in Table 1. All these complexes are isostructural and isomorphous, and therefore only the structure of 1 is given in Fig. 1. The metal atom is four-coordinated by one nitrogen atom, two CH_2SiMe_3 ligands, and one THF molecule, forming a slightly distorted tetrahedral geometry. The phenyl ring of the amido ligand is oriented almost parallel to the plane formed by C(1), C(5), and O(1). The average Sc– CH_2SiMe_3 bond distance in 1 (2.211(2) Å) is very close to those found in other scandium bis(alkyl) complexes such as $[\text{PhC}(\text{N}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2]\text{Sc}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})$ (2.212(3) Å) [3d], $(1,3\text{-}(\text{SiMe}_3)_2\text{C}_5\text{H}_3)\text{Sc}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})$ (2.215(1) Å) [2c], $[(\text{SiMe}_2\text{CH}_2\text{P}^i\text{Pr}_2)_2\text{N}]\text{Sc}(\text{CH}_2\text{SiMe}_3)_2$ (2.214(5) Å) [9], and $(\text{C}_5\text{Me}_4\text{SiMe}_3)\text{Sc}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})$ (2.223(2) Å) [2d]. The bond distances of the Sc–N (2.035(2) Å) and Sc–O (2.147(2) Å) bonds in 1 are comparable with those in $(\text{BDPPoxyl})\text{ScCH}_2\text{SiMe}_3(\text{thf})$ ($\text{BDPPoxyl} = o\text{-C}_6\text{H}_4(\text{CH}_2\text{NC}_6\text{H}_3\text{-}2,6)_2$) (av. 2.027(1) Å and 2.161(1) Å), respectively [12]. The bond lengths around the metal center in 2 and 3 are very close to each other, in consistence with the similarity of the ionic radius of these two metal ions (Y: 0.900 Å, Ho: 0.901 Å) [13]. The average bond length of the Y– CH_2SiMe_3 bonds (2.367(3) Å) in 2 is comparable to that found in $(\text{C}_5\text{Me}_4\text{SiMe}_3)\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})$ (2.381(4) Å) [14]. The Y–N bond distance in 2 (2.190(2) Å) can be compared with the average bond distance of the Y–N bonds observed in $\text{Y}(\text{ArN}(\text{CH}_2)_3\text{NAr})\text{CH}(\text{SiMe}_3)_2(\text{thf})$ ($\text{Ar} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$) (2.173(3) Å) [15]. The average Lu– CH_2SiMe_3 bond distance in 4 (2.318(3) Å) is comparable with those found in $(\text{C}_5\text{Me}_5)\text{Lu}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})$

Table 1
Selected bond distances (Å) and angles (deg) for complexes 1–4

	Ln = Sc (1)	Ln = Y (2)	Ln = Ho (3)	Ln = Lu (4)
Ln–N(1)	2.035(2)	2.190(2)	2.176(3)	2.153(2)
Ln–C(1)	2.210(2)	2.366(2)	2.366(4)	2.314(3)
Ln–C(5)	2.211(2)	2.367(3)	2.367(4)	2.322(3)
Ln–C(9)	2.837(2)	2.886(2)	2.872(3)	2.889(3)
Ln–O(1)	2.147(2)	2.309(2)	2.311(2)	2.256(2)
N(1)–Ln–C(1)	110.02(8)	109.59(8)	108.9(1)	107.1(1)
N(1)–Ln–C(5)	108.05(8)	106.85(8)	106.1(1)	109.0(1)
N(1)–Ln–O(1)	115.11(7)	117.96(7)	118.4(1)	116.60(8)
C(1)–Ln–C(5)	111.7(1)	108.7(1)	108.3(1)	109.7(1)
C(1)–Ln–O(1)	110.01(8)	110.93(8)	111.3(1)	102.5(1)
C(5)–Ln–O(1)	101.70(8)	102.22(8)	103.0(1)	111.5(1)
Ln–N(1)–C(9)	109.0(1)	104.0(1)	103.9(2)	105.8(2)

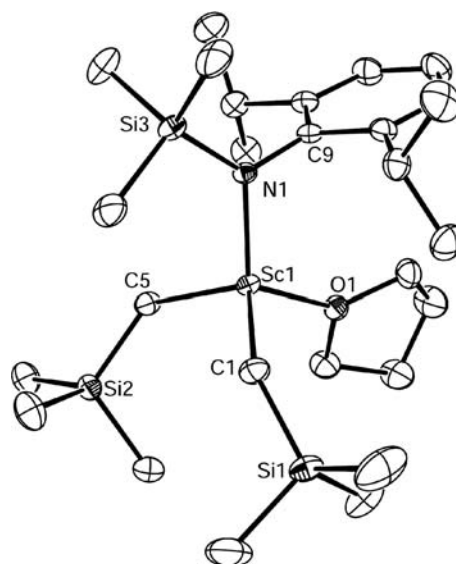
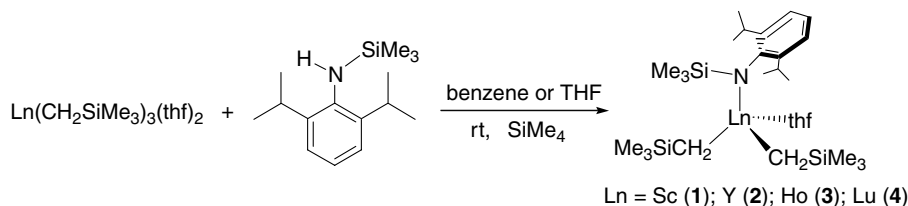


Fig. 1. ORTEP structure of 1 (thermal ellipsoids at the 30% level, hydrogen atoms are omitted for clarity).

(2.332(4) Å) [16] and $(\text{C}_5\text{Me}_4\text{SiMe}_3)\text{Lu}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})$ (2.335(3) Å) [17]. The Lu–N bond (2.153(2) Å) in 4 can be compared with that in $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{NC}_6\text{H}_3\text{Me}_2\text{-}2,6)\text{Lu}(\text{CH}_2\text{SiMe}_3)(\text{thf})$ (2.188(2) Å) [18].

The diamagnetic Sc (1), Y (2), and Lu (4) complexes showed well-resolved NMR spectra, while the paramagnetic Ho complex 3 did not give an informative ^1H NMR spectrum. Ligand redistribution was not observed in solution, as shown by the NMR spectra of 1, 2 and 4. ^1H NMR and ^{13}C NMR spectra of complexes 1, 2 and 4 in C_6D_6 showed one set of signals for the NSiMe_3 ,



Scheme 1.

CH_2SiMe_3 , and thf units, and two sets of signals for the isopropyl groups on the phenyl ring, suggesting that rotation of the phenyl ring around the N–C9 bond is highly restricted, which is in consistency with their crystal structures. The methylene protons of the trimethylsilylmethyl groups in complexes **1** and **4** were observed as a singlet peak, while complex **2** showed a doublet (-0.21 ppm) due to Y–H coupling ($J_{\text{Y-H}} = 3.4$ Hz). Similarly, in ^{13}C NMR spectra, the methylene carbon of Ln– CH_2SiMe_3 was observed at 44.38 ppm for **1**, at 46.08 ppm for **4**, and at 38.93 ppm with $J_{\text{Y-C}} = 43.5$ Hz for **2**. The coupling constants of Y–H (3.4 Hz) and Y–C (43.5 Hz) in **2** are very close to those observed in $(\text{C}_5\text{Me}_4\text{SiMe}_3)\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})$ (3.1 and 43.7 Hz), respectively [19].

2.2. Reaction of $\text{Gd}(\text{CH}_2\text{SiMe}_3)_3(\text{thf})_2$ with 2,6- $^i\text{Pr}_2\text{C}_6\text{H}_3\text{NH}(\text{SiMe}_3)$

In an attempt to prepare an analogous gadolinium bisalkyl complex $[2,6-^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)]\text{Gd}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})$, the reaction of $\text{Gd}(\text{CH}_2\text{SiMe}_3)_3(\text{thf})_2$ with an equivalent of 2,6- $^i\text{Pr}_2\text{C}_6\text{H}_3\text{NH}(\text{SiMe}_3)$ was carried out similarly (Scheme 2). However, instead of the expected bisalkyl product, a binuclear Gd complex $\text{Gd}_2(\mu\text{-CH}_2\text{SiMe}_2\text{NC}_6\text{H}_3\text{Pr}_2\text{-2,6})_3(\text{thf})_3$ (**5**), which does not contain a terminal CH_2SiMe_3 group, was isolated in 62% yield (based on Gd). The molecular structure of **5** was unambiguously determined by an X-ray analysis (Fig. 2). Selected bond lengths and angles of **5** are given in Table 2. The two Gd atoms are bridged by three methylene units derived from the SiMe_3 groups of the amido ligands. In addition, one Gd atom (Gd1) is coordinated by two nitrogen atoms

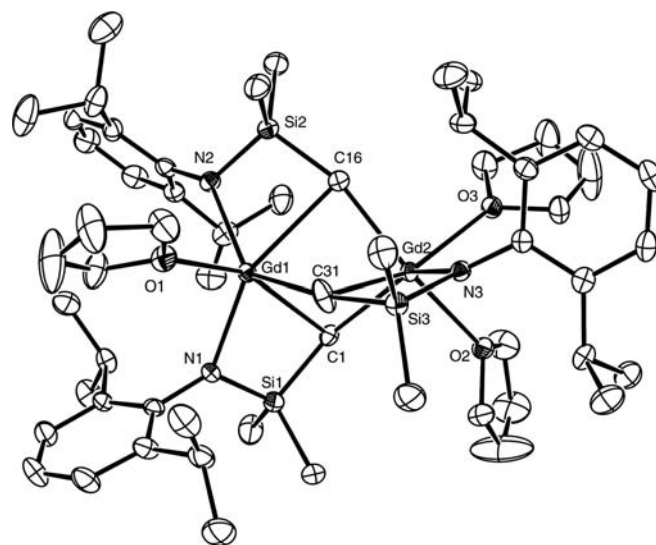
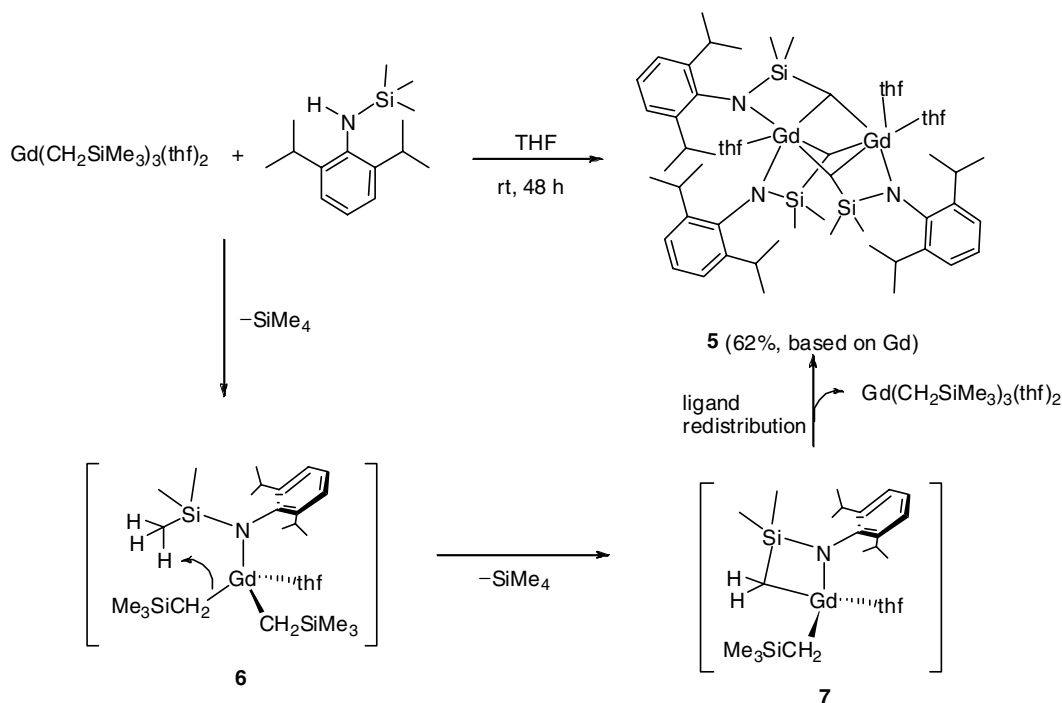


Fig. 2. ORTEP structure of **5** (thermal ellipsoids at the 30% level, hydrogen atoms and crystal solvent are omitted for clarity).

and one thf ligand, while the other Gd atom (Gd2) is coordinated by one nitrogen atom and two thf ligands. Both Gd atoms form a distorted trigonal prism geometry. The average bond lengths of Gd–N (2.301(3) Å) and Gd–O (2.477(3) Å) in **5** are comparable to those of the Gd–N(SiMe_3)₂ (2.287(2) Å) and Gd–O (2.441(2) Å) bonds in $\{[(\text{Me}_3\text{Si})_2\text{N}]_2(\text{thf})\text{Gd}\}_2(\mu\text{-N}_2)$, respectively [20]. The Gd–C bond lengths in **5** range broadly from 2.471(4) Å to 2.757(4) Å, in which the shortest Gd–C bond distance (2.471(4) Å) is similar to that of the terminal Gd–benzyl bond in $(\text{C}_5\text{Me}_5)\text{Gd}(\text{CH}_2\text{C}_6\text{H}_5)_2(\text{thf})$ (2.470(7) Å) [21].



Scheme 2.

Table 2
Selected bond distances (Å) and angles (°) for complex **5**

Gd(1)–N(1)	2.274(3)	Gd(1)–N(2)	2.345(3)
Gd(2)–N(3)	2.284(3)	Gd(1)–C(1)	2.616(4)
Gd(1)–C(16)	2.757(4)	Gd(1)–C(31)	2.543(5)
Gd(2)–C(1)	2.635(4)	Gd(2)–C(16)	2.471(4)
Gd(2)–C(31)	2.609(5)	Gd(1)–O(1)	2.475(3)
Gd(2)–O(2)	2.479(3)	Gd(2)–O(3)	2.476(3)
Gd(1)⋯Gd(2)	3.3835(5)		
(C1)–Gd(1)–(C16)	78.9(1)	(C1)–Gd(1)–(C31)	85.2(2)
(C16)–Gd(1)–(C31)	79.4(2)	(C1)–Gd(2)–(C31)	83.9(1)
(C1)–Gd(2)–(C31)	83.5(2)	(C16)–Gd(2)–(C31)	83.7(2)
(Gd1)–C(1)–(Gd2)	80.2(1)	(Gd1)–C(16)–(Gd2)	80.5(1)
(Gd1)–C(31)–(Gd2)	82.1(2)		

The formation of **5** could be explained by the reaction path shown in Scheme 2. The alkane elimination reaction of $\text{Gd}(\text{CH}_2\text{SiMe}_3)_3(\text{thf})_2$ with 1 equiv. of 2,6-*i*-Pr₂C₆H₃NH-SiMe₃ should afford the mono(arylamido)-ligated bis(alkyl) complex $[\text{2,6-}i\text{-Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)]\text{Gd}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})$ (**6**), as observed in the synthesis of **1–4**. Intramolecular C–H bond activation of a methyl group of Me₃Si on the amido ligand by CH₂SiMe₃ would give the silylene-linked amido-methyl complex **7**, which could undergo ligand redistribution to give **5** and $\text{Gd}(\text{CH}_2\text{SiMe}_3)_3(\text{thf})_2$. The less stability of the Gd complex **6** compared to its Sc, Y, Ho, and Lu analogues **1–4** must be due to the larger ion radius of Gd.

2.3. Polymerization of isoprene, 1-hexene and styrene

When treated with 1 equiv. of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, complexes **1–4** showed high activity for the polymerization of isoprene at room temperature, with the activity being in the order of **4** > **2** > **3** > **1** (Table 3). The average number molecular weight (M_n) of the resulting polymers increased linearly as the isoprene conversion was raised, while the molecular weight distribution remained very narrow ($M_w/M_n = 1.04–1.06$) during the whole period of the polymerization (Fig. 3, Table 3), demonstrating the excellent “livingness” of the polymerization system [22].

Table 3
Polymerization of isoprene by **1–4**/ $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]^a$

Run	Complex	Ln	<i>t</i> (min)	Conversion ^b (%)	Activity ^c	$M_n^d \times 10^{-4}$	M_w/M_n^d
1	1	Sc	10	15	32	1.53	1.53
2	2	Y	5	12	49	0.73	1.06
3	2	Y	10	42	86	3.65	1.04
4	2	Y	20	74	76	6.16	1.05
5	2	Y	30	100	69	8.73	1.05
6	3	Ho	10	28	58	5.35	1.27
7	4	Lu	5	100	412	2.89	1.12

^a Conditions: Ln, 21 μmol; [Ln]/[B] = 1/1 (mol/mol); [M]/[Ln] = 500 (mol/mol); toluene, 5 mL; 25 °C. Polyisoprene microstructure: 1,4-unit:3,4-unit ≈ 30:70.

^b Weight of polymer obtained/weight of monomer used.

^c Given in kg of polymer/(mol[−] Ln · h).

^d Determined by GPC in THF at 40 °C against polystyrene standard.

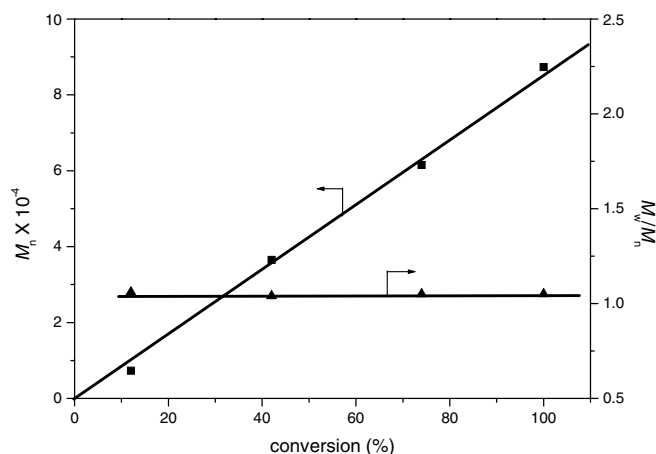


Fig. 3. Plots of M_n and M_w/M_n versus isoprene conversion with **2**/ $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ at 25 °C.

In the polymerization of 1-hexene, only the Sc complex **1** showed significant activity in combination with an equivalent of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, which converted 650 equivalents of 1-hexene into atactic poly(1-hexene) with $M_n = 7300$ and $M_w/M_n = 2.65$ at room temperature in 30 min. This is a rare example of efficient α -olefin polymerization catalyzed by a rare earth metal catalyst [23]. The polymerization of styrene by **1**/ $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ gave a mixture of syndiotactic and atactic polystyrenes, in contrast with the exclusive formation of syndiotactic polystyrene observed in the case of $(\text{C}_5\text{Me}_4\text{SiMe}_3)\text{Sc}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ [2d]. A neutral bis(alkyl) complex alone did not show activity for the above polymerization.

2.4. Characterization of a cationic scandium alkyl active species

To gain information on the active species in the present polymerization systems, ¹H NMR monitoring of the reaction of **1** with 1 equiv. of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ in $\text{C}_6\text{D}_5\text{Cl}$ was carried out. Rapid formation of $\text{Ph}_3\text{CCH}_2\text{SiMe}_3$ together with disappearance of **1** was observed at room tempera-

ture. However, identification of the resulting cationic scandium alkyl species was not successful because of its instability. From a THF solution, a more stable scandium alkyl species, which could be assigned to $[2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)\text{Sc}(\text{CH}_2\text{SiMe}_3)(\text{thf})_2][\text{B}(\text{C}_6\text{F}_5)_4]$, was obtained (Scheme 3). Addition of one equivalent of THF to a 1:1 reaction mixture of **1** and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ in $\text{C}_6\text{H}_5\text{Cl}$ or toluene also gave the same species. This bis(THF)-coordinated cationic scandium alkyl species, however, did not show activity for the polymerization, probably because of the lack of a vacant coordination site on the metal center. Therefore, the true active species in the present polymerization catalyst system might be a cationic, THF-free, mono-amido-ligated scandium alkyl species such as $[2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)\text{Sc}(\text{CH}_2\text{SiMe}_3)][\text{B}(\text{C}_6\text{F}_5)_4]$ or its mono-THF-coordinated analogue.

3. Conclusion

The acid–base reaction of $\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})_2$ with 1 equivalent of $2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{NH}(\text{SiMe}_3)$ afforded straightforwardly the corresponding mono-amido-ligated rare earth metal bis(alkyl) complexes $[2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)]\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})$ ($\text{Ln} = \text{Sc}$ (**1**), Y (**2**), Ho (**3**), Lu (**4**)), which represent rare examples of the bis(alkyl) rare earth metal complexes bearing a monodentate anionic ancillary ligand. In the case of a larger metal such as Gd , further reactions (intramolecular C–H activation and ligand redistribution) took place to give the bimetallic complex $\text{Gd}_2(\mu\text{-CH}_2\text{SiMe}_2\text{NC}_6\text{H}_3^i\text{Pr}_2\text{-}2,6)_3(\text{thf})_3$. On treatment with 1 equiv. of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ in toluene, complexes **1–4** served as active catalysts for the living polymerization of isoprene at room temperature. The combination of the Sc complex **1** with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ showed high activity also for the polymerization of 1-hexene and styrene. The active catalyst species in the present polymerization systems might be a cationic, THF-free, mono-amido-ligated rare earth metal alkyl species, such as $[2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)\text{Sc}(\text{CH}_2\text{SiMe}_3)][\text{B}(\text{C}_6\text{F}_5)_4]$ or its mono-THF-coordinated analogue.

4. Experimental

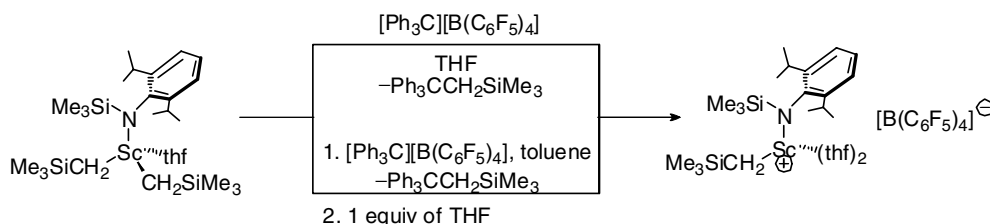
4.1. Materials and procedures

All manipulations were performed under pure argon with rigorous exclusion of air and moisture using standard Schlenk techniques and an Mbraun glovebox. Argon was

purified by passing through a Dryclean column (4 Å molecular sieves, Nikka Seiko Co.) and a Gasclean GC-RX column (Nikka Seiko Co.). Solvents were distilled from sodium/benzophenone ketyl, degassed by the freeze–pump–thaw method, and dried over fresh Na chips in the glovebox. $\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{thf})_2$ [24], $2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{NH}(\text{SiMe}_3)$ [11b,1c] were prepared according to the literatures. Anhydrous LnCl_3 were purchased from STREM. $\text{LiCH}_2\text{SiMe}_3$ (1 M solution in pentane) was obtained from Aldrich, and used as powder after drying up the solvent under vacuum. $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ was purchased from Tosoh Finechem Corporation and used without purification. $2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{NH}_2$ and Me_3SiCl were purchased from TCI and used without purification. 1-Hexene (TCI), isoprene (TCI), and styrene (Junsei Chemical Co., Ltd.) were dried by stirring with CaH_2 for 24 h, and distilled under reduced pressure prior to polymerization experiments. Deuterated solvents were obtained from ISOTEC. Samples of organo 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 JNM-EX 400 or a JNM-EX 300 spectrometer. The NMR spectra of poly(1-hexene) and poly(isoprene) were recorded in CDCl_3 at 25 °C. The NMR spectra of polystyrene were measured in 1,1,2,2-tetrachloroethane- d_2 at 120 °C. Elemental analyses were performed on a MICRO CORDER JM10 apparatus (J-SCIENCE LAB Co.). Molecular weights and molecular weight distributions of poly(1-hexene) and poly(isoprene) were determined against polystyrene standard by gel permeation chromatography on a HLC-8220 GPC apparatus (Tosoh Corporation) with THF as an eluent at a flow rate of 0.35 mL/min at 40 °C. Molecular weight and molecular weight distributions of polystyrenes were determined against polystyrene standard by high temperature gel permeation chromatography (HT-GPC) on a HLC-8121 GPC/HT apparatus (Tosoh Corporation). 1,2-Dichlorobenzene was used as an eluent at a flow rate of 1.0 mL/min at 145 °C.

4.2. Synthesis of $[2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)]\text{Sc}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})$ (**1**)

To a 10 mL of colorless benzene solution of $\text{Sc}(\text{CH}_2\text{SiMe}_3)_3(\text{thf})_2$ (1.00 g, 2.22 mmol) was added $2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{NH}(\text{SiMe}_3)$ (0.553 g, 2.22 mmol) at room temperature.



Scheme 3.

The mixture was stirred for 2 h at room temperature. The resulting pale yellow solution was filtered. After drying up, the residue was dissolved in 2 mL of hexane, and was cooled at $-30\text{ }^{\circ}\text{C}$ overnight to give $[2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)]\text{Sc}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})$ as colorless cubic crystals (0.82 g, 1.51 mmol, 68% yield). ^1H NMR (C_6D_6 , 400 MHz, $50\text{ }^{\circ}\text{C}$): δ 0.20 (br s, 4H, CH_2SiMe_3), 0.31 (s, 18 H, CH_2SiMe_3), 0.45 (s, 9 H, NSiMe_3), 1.00 (m, 4 H, thf), 1.15 (d, 6 H, $J_{\text{H-H}} = 7.0$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.23 (d, 6 H, $J_{\text{H-H}} = 7.0$ Hz, $\text{CH}(\text{CH}_3)_2$), 3.30 (m, 4 H, thf), 3.81 (m, 2 H, $\text{CH}(\text{CH}_3)_2$), 6.91 (t, $J_{\text{H-H}} = 7.1$ Hz, 1 H, $p\text{-C}_6\text{H}_3$), 7.02 (d, $J_{\text{H-H}} = 7.5$ Hz, 2 H, $m\text{-C}_6\text{H}_3$). ^{13}C NMR (C_6D_6 , 100 MHz, $25\text{ }^{\circ}\text{C}$): δ 3.68, 4.59, 25.35, 25.75, 26.88, 27.86, 44.38, 72.33, 123.69, 124.65, 144.21, 146.46. Anal. Calcd for $\text{C}_{27}\text{H}_{56}\text{NOScSi}_3$: C, 60.05; H, 10.47; N, 2.59. Found: C, 60.07; H, 10.20; N, 2.47%.

4.3. Synthesis of $[2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)]\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})$ (2)

To a 10 mL of colorless benzene solution of $\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{thf})_2$ (1.00 g, 2.02 mmol) was added $2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)$ (0.50 g, 2.02 mmol) at room temperature. The mixture was stirred for 2 h at room temperature. The resulting pale yellow solution was filtered. After drying up, the residue was dissolved in 2 mL of hexane, and was cooled at $-30\text{ }^{\circ}\text{C}$ overnight to give $[2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)]\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})$ as colorless cubic crystals (0.80 g, 1.37 mmol, 68% yield). ^1H NMR (C_6D_6 , 400 MHz, $25\text{ }^{\circ}\text{C}$): δ -0.21 (d, 4 H, $J_{\text{Y-H}} = 3.4$ Hz, CH_2SiMe_3), 0.35 (s, 18 H, CH_2SiMe_3), 0.45 (s, 9 H, NSiMe_3), 1.01 (br s, 4 H, thf), 1.11 (d, 6 H, $J_{\text{H-H}} = 7.0$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.21 (d, 6 H, $J_{\text{H-H}} = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 3.17 (br s, 4 H, thf), 3.85 (m, 2 H, $\text{CH}(\text{CH}_3)_2$), 6.85 (t, $J_{\text{H-H}} = 7.5$ Hz, 1 H, $p\text{-C}_6\text{H}_3$), 7.01 (d, $J_{\text{H-H}} = 7.5$ Hz, 2 H, $m\text{-C}_6\text{H}_3$). ^{13}C NMR (C_6D_6 , 100 MHz, $25\text{ }^{\circ}\text{C}$): δ 3.07, 4.31, 24.81, 25.00, 26.52, 26.92, 38.93 ($J_{\text{Y-C}} = 43.5$ Hz, CH_2SiMe_3), 70.42, 122.60, 124.36, 142.75, 146.80. Anal. Calcd for $\text{C}_{27}\text{H}_{56}\text{NOSi}_3\text{Y}$: C, 55.53; H, 9.69; N, 2.40. Found: C, 56.01; H, 9.20; N, 2.48%.

4.4. Synthesis of $[2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)]\text{Ho}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})$ (3)

To a 15 mL of pink THF solution of $\text{Ho}(\text{CH}_2\text{SiMe}_3)_3(\text{thf})_2$ (1.00 g, 1.75 mmol) was added $2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)$ (0.437 g, 1.75 mmol) at room temperature. The mixture was stirred for 40 h at room temperature. The resulting solution was dried in vacuum. Then the pink oil residue was extracted with 20 mL of hexane, and the clear hexane solution was concentrated. Cooling at $-30\text{ }^{\circ}\text{C}$ for 2 h gave $[2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)]\text{Ho}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})$ as pink cubic crystals (0.62 g, 0.94 mmol, 54% yield). The ^1H NMR spectrum of **3** was not informative because of the influence of the paramagnetic Ho(III) ion. Anal. Calcd for $\text{C}_{27}\text{H}_{56}\text{HoNOSi}_3$: C, 49.14; H, 8.57; N, 2.12. Found: C, 48.86; H, 7.90; N, 1.87%.

4.5. Synthesis of $[2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)]\text{Lu}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})$ (4)

To a 10 mL of colorless benzene solution of $\text{Lu}(\text{CH}_2\text{SiMe}_3)_3(\text{thf})_2$ (0.90 g, 1.55 mmol) was added $2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)$ (0.39 g, 1.55 mmol) at room temperature. The mixture was stirred for 16 h at room temperature. The resulting pale brown solution was dried in vacuum. After drying up, the residue was extracted with 20 mL of hexane, and concentrated. Cooling at $-30\text{ }^{\circ}\text{C}$ gave $[2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)]\text{Lu}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})$ as colorless cubic crystals (0.65 g, 0.98 mmol, 63% yield). ^1H NMR (C_6D_6 , 400 MHz, $25\text{ }^{\circ}\text{C}$): δ -0.41 (s, 4 H, CH_2SiMe_3), 0.34 (s, 18 H, CH_2SiMe_3), 0.44 (s, 9 H, NSiMe_3), 0.92 (m, 4 H, thf), 1.13 (d, 6 H, $J_{\text{H-H}} = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.23 (d, 6 H, $J_{\text{H-H}} = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 3.09 (m, 4 H, thf), 3.90 (m, 2 H, $\text{CH}(\text{CH}_3)_2$), 6.87 (t, $J_{\text{H-H}} = 7.1$ Hz, 1 H, $p\text{-C}_6\text{H}_3$), 7.01 (d, $J_{\text{H-H}} = 7.5$ Hz, 2 H, $m\text{-C}_6\text{H}_3$). ^{13}C NMR (C_6D_6 , 100 MHz, $25\text{ }^{\circ}\text{C}$): δ 3.27, 4.70, 24.91, 25.18, 26.92, 27.24, 46.08, 71.26, 122.75, 124.34, 143.51, 146.90. Anal. Calcd for $\text{C}_{27}\text{H}_{56}\text{LuNOSi}_3$: C, 48.40; H, 8.44; N, 2.09. Found: C, 48.45; H, 7.96; N, 2.00%.

4.6. Synthesis of $\text{Gd}_2(\mu\text{-CH}_2\text{SiMe}_2\text{NC}_6\text{H}_3^i\text{Pr}_2\text{-}2,6)_3(\text{thf})_3$ (5)

To a 15 mL of colorless THF solution of $\text{Gd}(\text{CH}_2\text{SiMe}_3)_3(\text{thf})_2$ (1.28 g, 2.27 mmol) was added $2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)$ (0.567 g, 2.27 mmol) at room temperature. The mixture was stirred for 48 h at room temperature. The solvent was removed under reduced pressure. The resulting sticky white powder was washed by hexane 2 times to give **5** as white powder (0.897 g, 62% based on Gd). Single crystals suitable for X-ray analysis were obtained by recrystallization from a toluene/hexane solution at $-30\text{ }^{\circ}\text{C}$. The ^1H NMR spectrum of **5** was not informative because of the influence of the paramagnetic Gd(III) ion. Anal. Calcd for $\text{C}_{64}\text{H}_{107}\text{Gd}_2\text{N}_3\text{O}_3\text{Si}_3 \cdot \text{5 toluene}$: C, 56.30; H, 7.90; N, 3.08. Found: C, 55.81; H, 7.52; N, 2.96%.

4.7. Reaction of $[2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)]\text{Sc}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})$ with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$

To a THF solution (5 mL) of $[2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)]\text{Sc}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})$ (51 mg, 94 μmol) was added 1 equiv. of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (87 mg, 94 μmol). The reaction mixture was stirred at room temperature for 5 min, and the solvent was removed under reduced pressure. The residue was washed with hexane, and then dried up under vacuum to give a red solid product, which could be assigned to $\{[2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)]\text{Sc}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})_2\}[\text{B}(\text{C}_6\text{F}_5)_4]$. ^1H NMR (300.40 MHz, $o\text{-C}_6\text{D}_4\text{Cl}_2$, $24.6\text{ }^{\circ}\text{C}$): δ 0.01 (s, 9 H, CH_2SiMe_3), 0.15 (s, 9 H, NSiMe_3), 0.57 (s, 2 H, CH_2SiMe_3), 1.03, 1.10 (d, 12 H, $(\text{CH}_3)_2\text{CH}$), 1.82 (m, 8 H, thf), 3.27 (m, 2 H, $(\text{CH}_3)_2\text{CH}$), 3.78 (m, 8 H, thf). The aromatic protons could not be unequivocally assigned due to overlap with those of the $\text{Ph}_3\text{CCH}_2\text{SiMe}_3$

contamination (see below). Attempts to further purify the cationic species were not successful because of its instability. Evaporation of the hexane extract gave $\text{Ph}_3\text{CCH}_2\text{-SiMe}_3$ as pale-white solid (29 mg, 93%). ^1H NMR ($o\text{-C}_6\text{D}_4\text{Cl}_2$, 400 MHz, 25 °C): δ -0.28 (s, 9 H, CH_2SiMe_3), 2.06 (s, 2 H, CH_2SiMe_3), 6.87–7.26 (m, 15 H, Ph).

4.8. Polymerization of isoprene

A typical polymerization reaction is given below (Table 3, run 5). $[2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)]\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})$ (12 mg, 21 μmol) and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (19 mg, 21 μmol) were added to a 100 mL flask with a stirring bar. Then toluene (5 mL) was introduced by a syringe. The mixture was stirred at room temperature for a few minutes, and 0.715 g (10.50 mmol) of isoprene was added under vigorous stirring. After 30 minutes, a large amount of methanol (60 mL) was added to terminate the polymerization. The polymer product was washed with methanol, and dried under vacuum at 60 °C to a constant weight (0.715 g, 100%).

4.9. Polymerization of 1-hexene

To a toluene solution (3 mL) of $[2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)]\text{-Sc}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})$ (11 mg, 21 μmol) in a 100-mL flask was added a toluene solution (7 mL) of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (19 mg, 21 μmol). The mixture was stirred at room temperature for a few minutes, and 1.736 g (20.63 mmol) of 1-hexene was added under vigorous stirring. After 30 min, a large amount of methanol (60 mL) was added to terminate the polymerization. The polymer product was washed with methanol, and dried under vacuum at 60 °C to a constant weight (1.13 g, 65%).

4.10. Polymerization of styrene

To a toluene solution (3 mL) of $[2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)]\text{-Sc}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})$ (11 mg, 21 μmol) in a 100-mL flask was added a toluene solution (7 mL) of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (19 mg, 21 μmol). The mixture was stirred at room temperature for a few minutes, and 2.148 g (21 mmol) of styrene was added under vigorous stirring. A precipitation of polymer product was observed in one minute. After 5 min, a large amount of methanol (60 mL) was added to terminate the polymerization. The white polymer powder was washed with boiling methyl ethyl ketone. The insoluble part was collected by filtration, and dried under vacuum at 60 °C to a constant weight (0.73 g, 34%), which was confirmed to be syndiotactic polystyrene ($r_{\text{rrrr}} > 99\%$) by ^1H and ^{13}C NMR. $M_n = 45.1 \times 10^3$, $M_w/M_n = 1.96$, $T_m = 267$ °C.

4.11. X-ray crystallographic study

The single crystals were sealed in a thin-walled glass capillary under a microscope in the glove box. Data collections were performed on a Bruker SMART APEX diffractometer with a CCD area detector using graphite-monochromated Mo K_α radiation ($\lambda = 0.71069$ Å). The determination of crystal class and unit cell was carried out by SMART program package [25]. The raw frame data were processed using SAINT [26] and SADABS [27] to yield the reflection data file. The structures were solved by using SHELXTL program [28]. Refinement was 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. Hydrogen atoms were placed at the calculated

Table 4
Summary of crystallographic data of 1–5

	1	2	3	4	5 · toluene
Formula	$\text{C}_{27}\text{H}_{56}\text{NOScSi}_3$	$\text{C}_{27}\text{H}_{56}\text{NOSi}_3\text{Y}$	$\text{C}_{27}\text{H}_{56}\text{HoNOSi}_3$	$\text{C}_{27}\text{H}_{56}\text{LuNOSi}_3$	$\text{C}_{64}\text{H}_{107}\text{Gd}_2\text{N}_3\text{O}_3\text{Si}_3$
Molecular weight	539.96	583.91	659.93	669.97	1365.30
Cryst system	Triclinic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2(1)/n$
a (Å)	9.933(2)	10.1085(9)	10.121(1)	10.060(1)	15.172(2)
b (Å)	11.098(3)	11.260(1)	11.236(1)	11.212(1)	19.047(3)
c (Å)	17.233(4)	17.323(2)	17.301(2)	17.296(2)	23.917(3)
α (°)	97.043(3)	97.540(2)	97.495(1)	97.322(2)	90
β (°)	102.430(3)	102.675(2)	102.556(2)	102.560(1)	93.045(2)
γ (°)	110.889(3)	112.066(2)	112.111(1)	111.588(1)	90
V (Å ³)	1691.3(7)	1732.2(3)	1729.4(4)	1723.9(4)	6902(2)
Z	2	2	2	2	4
ρ (g cm ⁻³)	1.060	1.119	1.267	1.291	1.314
μ (Mo K_α) (mm ⁻¹)	0.341	1.804	2.409	2.985	1.999
T (K)	173(1)	173(1)	173(1)	173(1)	173(1)
Number of reflections collected	8855	9149	8354	9014	32847
Number of reflections with $I > 2\sigma(I)$	5822	5997	5948	6572	12137
Number of parameters	317	317	317	317	666
R_1 ($I > 2\sigma(I)$)	0.0397	0.0342	0.0297	0.0248	0.0323
wR_2 ($I > 2\sigma(I)$)	0.0913	0.0638	0.0733	0.0547	0.0678
Goodness-of-fit	1.013	1.056	0.995	1.046	1.002
Maximum/minimum residual density (e Å ⁻³)	0.391/−0.303	0.533/−0.504	1.296/−1.694	1.112/−1.337	0.824/−0.640

positions and were included in the structure calculation without further refinement of the parameters. Crystal data and processing parameters are summarized in Table 4.

5. Supplementary materials

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 295238 for complex **1**, CCDC no. 295239 for complex **2**, CCDC no. 295241 for complex **3**, CCDC no. 295240 for complex **4**, CCDC no. 607633 for complex **5**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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