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# Rare-earth alkyl complexes supported by formamidinate ligands: synthesis, structure, and catalytic activity for isoprene polymerization†

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A series of rare-earth metal monoalkyl complexes supported by *N*,*N*′-di(2,6-dialkylphenyl)formamidinate ligand $(L)_2RECH_2SiMe_3{\cdot}thf$ [$L^1$ = $HC(N\text{-}2,6\text{-}Me_2C_6H_3)_2$, RE = Y (**1**), $L^2$ = $HC(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2$, RE = Y (**2**), Er (**3**), Dy (**4**), Sm (**5**), and Nd (**6**)] were synthesized by alkyl elimination reaction or by salt metathesis reaction in good yields. All complexes were characterized by elemental analyses, FT-IR spectroscopy and single crystal X-ray diffraction. In combination with $[Ph_3C][B(C_6F_5)_4]$ and alkylaluminium, these complexes displayed a good activity towards isoprene polymerization to give polyisoprenes with high molecular weight ($M_n > 10^4$) and narrow molecular distribution (PDI < 2.0). The influence of alkylaluminium, central metal, temperature, sequence of addition of alkylaluminium and $[Ph_3C][B(C_6F_5)_4]$ on the polymerization of isoprene was studied. It was interesting to find that addition of the cocatalysts sequence has a great influence on the regioselectivity of the polymerization. High 1,4-regioselectivity polymerizations of isoprene (as high as 98%) were observed when the catalysts were added in the order [RE]/[alkylaluminum]/[borate].

## Introduction

As an alternative to cyclopentadienyl, amidinates have been widely used in the field of coordination and organometallic chemistry because their steric and electronic properties can be easily modulated by the substituents on C and N atoms.[1] Over the past few decades, different kinds of amidinate ligands have been successfully employed in organo rare-earth metal chemistry for the synthesis and characterization of a series of highly reactive species.[2] Rare-earth metal amides,[2a,b] alkyls,[2e] and hydrides[2c,d] with amidinate as supporting ligands have been described and some of them have performed a high catalytic activity in organic transformation and polymerization reaction. In order to improve the stability of those complexes and to gain a full range of species, most of the amidinates applied in rare-earth metal chemistry are decorated with bulky groups, such as phenyl,[2a,b] cyclohexyl,[2a] and terphenyl[2g] on the carbon atom. In contrast to other amidinate ligands, the formamidinate has a low tension of the N–C–N moiety and is more flexible in stereochemistry. The chemistry of formamidinate supported alkaline and alkaline earth metal complexes has been reported.[3] The formamidinate incorporated rare-earth metal complexes were recently reported through reaction of atomic metal, lanthanide(II) intermediate or $Ln(AlMe_4)_3$ (Ln = La, Nd, Y, and Lu).[4]

Monoamidinate rare-earth metal bisalkyls[5] and bisamides[2a,6] have been found to be good precatalysts for olefin polymerization. Herein, we would like to report the synthesis and characterization of a series of rare-earth metal monoalkyl complexes supported by formamidinate as well as their performance as precatalysts for polymerization of isoprene.

## Results and discussion

### Synthesis and characterization of bis(formamidinate) rare-earth metal alkylates

Alkyl elimination reactions of $RE(CH_2SiMe_3)_3(thf)_X$ with 2 equiv. of formamidinates $2,6\text{-}(CH_3)_2C_6H_3N{=}CH\text{–}NHC_6H_3\text{-}(CH_3)_2\text{-}2,6$ (**HL$^1$**) or $2,6\text{-}({}^iPr)_2C_6H_3N{=}CH\text{–}NHC_6H_3({}^iPr)_2\text{-}2,6$ (**HL$^2$**) in hexane at room temperature for three hours, after work-up, afforded the corresponding bis(formamidinate) rare-earth metal alkyls $[HC(N\text{-}2,6\text{-}R_2C_6H_3)_2]_2RECH_2SiMe_3{\cdot}thf$ (R = $CH_3$, RE = Y (**1**), R = ${}^iPr$, RE = Y (**2**), Er (**3**), Dy (**4**), Sm (**5**) in

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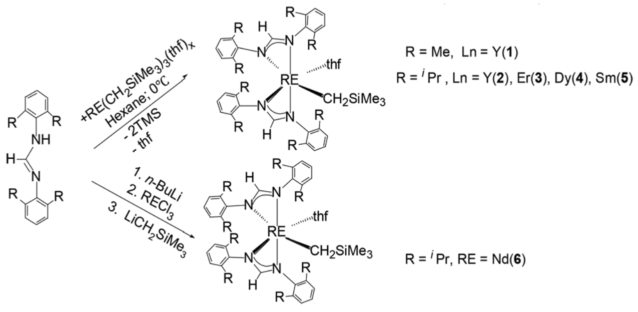

**Scheme 1** Synthesis of rare-earth metal alkyl complexes **1–6**.

64% to 73% yields (Scheme 1). This kind of complex can also be prepared by one-pot salt metathesis reaction of anhydrous $LnCl_3$ with 2 equiv. of formamidinate lithium $\mathbf{L^2}Li$ (formed by *in situ* treatment of formamidinate $\mathbf{HL^2}$ with 1 equivalent of *n*-BuLi in THF at room temperature) followed by treatment of 1 equivalent of $LiCH_2SiMe_3$ in THF at room temperature for three hours. A THF coordinated complex $[HC(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2]_2\text{-}NdCH_2SiMe_3\cdot thf$ (**6**) formulated the same as those of **2–5** was isolated (Scheme 1).

All complexes are extremely sensitive to air and moisture and soluble in hexane, toluene and THF. They were characterized by elemental analyses, FT-IR spectroscopy and single crystal X-ray diffraction. FT-IR spectroscopy of these complexes are devoid of any N–H stretching around 3300 $cm^{-1}$ and showed a strong absorption of C═N stretch at approximately 1650 $cm^{-1}$ (**1**) and 1664 $cm^{-1}$ (**2–6**) indicating the delocalized double bond of the N–C–N linkage.[4] Complexes **1** and **2** were also characterized by NMR spectroscopic techniques.

X-ray diffraction revealed that all bis(formamidinate) rare-earth metal alkyl complexes **1–6** adopted the same coordination environment, involving one carbon of the alkyl group, one oxygen atom of the coordinated THF molecule and four nitrogen atoms. Both formamidinate ligands in those complexes are $\kappa^2$-bonded to the metal ion through two nitrogen donor atoms. The coordinated geometry of these complexes can be described as a distorted tetrahedron if the formamidinate ligand can be considered to be a single-point donor located on the backbone carbon (NCN carbon). The representative molecular structures of **1** and **2** are shown in Fig. 1 and 2, respectively. Selected bond parameters are listed in Table 1.

The two C–N bond lengths from the same formamidinate ligand are similar and fall in the intervals of the typical single bond and double bond lengths (*e.g.*, C(13)–N(1) = 1.313(4) Å and C(13)–N(2) = 1.323(4) Å in **2**) indicating that the negative charges of anionic formamidinates are delocalized on the NCN cores. The length of the Y–$C_{alkyl}$ bond in **2** (2.376 Å) is slightly longer than that found in **1** (2.371 Å); this might have resulted from the steric effect of the bulky ${}^i$Pr group, but they are both shorter than the length of Y–C (2.427(19) Å) in

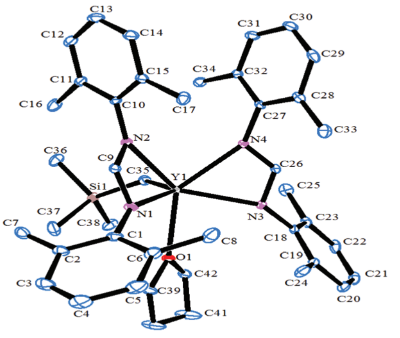

**Fig. 1** Molecular structure of complex **1**. Hydrogen atoms are omitted for clarity.

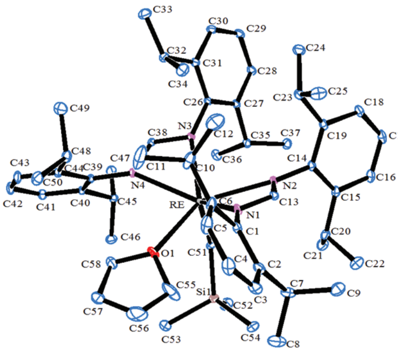

**Fig. 2** The representative molecular structure of complexes **2–6**. Hydrogen atoms are omitted for clarity.

**Table 1** Selected bond lengths (Å) and bond angles (°) of complexes **1–6**

| | **1** | **2** | **3** | **4** | **5** | **6** |
|---|---|---|---|---|---|---|
| Ln(1)–N(1) | 2.388(3) | 2.390(2) | 2.365(6) | 2.4051(19) | 2.519(4) | 2.550(3) |
| Ln(1)–N(2) | 2.411(3) | 2.443(2) | 2.439(6) | 2.4776(17) | 2.456(4) | 2.482(3) |
| Ln(1)–N(3) | 2.400(3) | 2.475(3) | 2.423(6) | 2.3936(19) | 2.437(4) | 2.467(3) |
| Ln(1)–N(4) | 2.378(3) | 2.391(3) | 2.367(5) | 2.4539(17) | 2.494(4) | 2.519(3) |
| Ln(1)–$N_{av}$ | 2.394(3) | 2.425(3) | 2.398(6) | 2.4326(18) | 2.477(4) | 2.505(3) |
| Ln(1)–$C_{alkyl}$ | 2.371(4) | 2.376(3) | 2.365(8) | 2.375(2) | 2.388(6) | 2.440(4) |
| Ln(1)–O(1) | 2.396(2) | 2.406(2) | 2.402(5) | 2.4224(17) | 2.482(4) | 2.519(3) |
| C(13)–N(1) | | 1.313(4) | 1.323(9) | 1.326(3) | 1.305(6) | 1.307(4) |
| C(13)–N(2) | | 1.323(4) | 1.332(9) | 1.306(3) | 1.321(7) | 1.319(4) |
| C(38)–N(3) | | 1.303(4) | 1.322(8) | 1.324(3) | 1.321(6) | 1.315(4) |
| C(38)–N(4) | | 1.319(4) | 1.335(9) | 1.318(3) | 1.316(6) | 1.314(4) |
| N(1)–Ln(1)–N(2) | 56.44(10) | 56.18(8) | 56.5(2) | 55.39(6) | 54.39(14) | 53.74(9) |
| N(3)–Ln(1)–N(4) | 56.40(10) | 55.51(9) | 56.65(19) | 56.02(6) | 54.94(13) | 54.33(9) |
| C(13)–Ln(1)–C(38) | | 130.29 | 130.34 | 130.76 | 130.42 | 130.39 |

$Y(CH_2SiMe_3)_3(thf)_3$.[9] The lengths of Y–$C_{alkyl}$ in **1** and **2** fall into the intervals of distances typical for six-coordinated alkyl yttrium complexes $[(^iPr)_2TACN(CH_2)_2N^tBu]Y(CH_2SiMe_3)_2$ (2.476(5) and 2.421(7) Å),[7a] $[Me_3SiNC(Ph)N(CH_2)_3NC(Ph)NSiMe_3]$-$YCH(SiMe_3)_2(thf)$ (2.410(8) Å),[7b] and $Ap'_2YCH_2SiMe_3(thf)$ (2.342(5) Å) (Ap′-H = 2,6-(diisopropylphenyl)-[6-(2,6-dimethylphenyl)pyridin-2-yl]amine).[7c] For complexes **2**, **4**, **5**, and **6**, which were crystallized in the same space group and crystal system, the length of RE–$C_{alkyl}$ increased with the increase of the size of the central metal, and is in good accord with the lanthanide contraction (Table 1). The angles between the two bulky formamidinates in terms of the nonbonding angle C(13)–Ln–C(38) in **2–5** are almost equal (*e.g.*, 130.29° for **2**; 130.34° for **3**; 130.76° for **4**; 130.42° for **5**) and they are larger than that in the less bulky formamidinates (*e.g.*, C(9)–Y1–C(26) 122.73° for **1**). The N(1)–Y(1)–N(2) and N(3)–Y(1)–N(4) bite angles (56.44(10)° and 56.40(10)° for **1**; 56.18(8)° and 55.51(9)° for **2**) are similar to $C_6H_4$-1,2-$\{NC(^tBu)N(2,6\text{-}Me_2C_6H_3)\}_2$-$Y(CH_2SiMe_3)(thf)$ (55.00(5)° and 55.84(5)°).[8] For compound **6**, the N(1)–Nd(1)–N(2) and N(3)–Nd(1)–N(4) bite angles (53.74(9)° and 54.33(9)°) are all slightly smaller than those found in $[HC(N\text{-}2,6\text{-}^iPr_2C_6H_3)_2]_2NdBr(thf)$[4a] (54.77(14)° and 55.03(14)°) as a result of the steric effect of the bulky $CH_2SiMe_3$ group.

### Isoprene polymerization

Cationic alkyl species of rare-earth metals (group 3 and lanthanide) have been intensively investigated over the past several years because of their crucial importance in catalytic olefin polymerization and unique activities that differ from those of group 4 metal complexes. The cationic species can be generated conveniently by the reaction of neutral alkyl precursors with an equimolar amount of a strong Lewis acid. The complexes of rare-earth metal mono(alkyl) supported by bis-[(7-(N-2,6-diisopropylphenyl)iminomethyl)indole] showed no activity for the polymerization of isoprene with the combination of aluminum alkyls and borates; this phenomenon was ascribed to the absence of a metal alkyl initiator after dealkylation by the borate $[Ph_3C][B(C_6F_5)_4]$.[5a] The bis(formamidinate) rare-earth metal monoalkyl complex **3** was tested as an initiator for the polymerization of isoprene (IP) with the activation of aluminum alkyls ($AlR_3$, R = Me, Et, $^iBu$) and borates $B(C_6F_5)_3$, $[Ph_3C][B(C_6F_5)_4]$ or $[PhNMe_2H][B(C_6F_5)_4]$. Complex **3** alone was inactive to the polymerization of isoprene, which was still inert by the reaction with one equivalent of $[Ph_3C]$-$[B(C_6F_5)_4]$ or $[PhNMe_2H][B(C_6F_5)_4]$, respectively (Table 2, entry 1). Upon addition of the third component aluminum alkyls, homogeneous catalytic systems were generated and showed a good activity. Various $AlR_3$ (R = Me, Et, $^iBu$) and borates have been tested to this ternary catalytic system. The results are summarized in Table 2. The polymerization activities of the system were significantly dependent on both $AlR_3$ and the aluminum-to-lanthanide ratio. For example, addition of 1000 equivalents of isoprene to a mixture of **3** mixed with 1 equivalent of $[Ph_3C][B(C_6F_5)_4]$ and 10 equivalents of $AlMe_3$ in a sequence of borate and alkylaluminum afforded polyisoprene with 98% conversion in 360 min with a ratio (63 : 34) of 1,4- to 3,4-regioselectivity at 20 °C. $AlEt_3$ has a similar activity to $AlMe_3$ but with a decreased 1,4-regioselectivity and an increased 3,4-regioselectivity (Table 2, entry 3). Under the same conditions, using $Al^iBu_3$ instead of $AlMe_3$ or $AlEt_3$, almost 100% conversion with a more improved 3,4-regioselectivity was observed in 30 min (Table 2, entries 2–5), indicating the steric effect of alkylaluminum on the regioselectivity of these homogeneous catalytic systems. When the amount of $Al^iBu_3$ was reduced to 5 equivalents, 66% 3,4-regioselectivity can be reached (Table 2, entry 6). The borates $[Ph_3C][B(C_6F_5)_4]$ and $[PhNMe_2H][B(C_6F_5)_4]$ showed little effect on the polymerization activity and regioselectivity when $Al^iBu_3$ was used (Table 2, entries 4–5).

Table 2 Isoprene polymerization by the **3**/borate/$AlR_3$ system[a]

| Entry | Borate[b] | $AlR_3$ [a] [equiv.] | Time [min] | Conv [%] | $M_n$ [c] [$10^{-4}$] | PDI[c] | 1,4/3,4[d] |
|---|---|---|---|---|---|---|---|
| 1 | $[B]_C$ | — | 360 | — | — | — | — |
| 2 | $[B]_C$ | $AlMe_3$ (10) | 360 | 98 | 14.1 | 2.0 | 66/34 |
| 3 | $[B]_C$ | $AlEt_3$ (10) | 360 | 98 | 7.3 | 1.9 | 47/53 |
| 4 | $[B]_C$ | $Al^iBu_3$ (10) | 30 | 100 | 12.4 | 1.8 | 39/61 |
| 5 | $[B]_N$ | $Al^iBu_3$ (10) | 30 | 100 | 12.3 | 1.8 | 37/63 |
| 6 | $[B]_C$ | $Al^iBu_3$ (5) | 30 | 99 | 10.9 | 1.7 | 34/66 |
| 7 | $[B]_C$ | $Al^iBu_3$ (20) | 30 | 100 | 12.2 | 1.8 | 50/50 |

[a] Conditions: (Ln = Er, 10 μmol); isoprene–toluene = 1 : 10 (vol/vol); *T* = 20 °C; Er–borate–IP = 1 : 1 : 1000; equiv. = $AlR_3$/Er (molar ratio). [b] [Borate]: $[B]_C$ = $[Ph_3C][B(C_6F_5)_4]$; $[B]_N$ = $[PhNMe_2H][B(C_6F_5)_4]$. [c] Determined by means of GPC against polystyrene standards in THF at 30 °C. [d] Determined by $^1H$ and $^{13}C$ NMR spectroscopy.

It is interesting to find that adjustment of the addition sequence of borate and $AlR_3$ has a dramatic effect on the regioselectivity of polymerization. Addition of 1000 equivalents of isoprene to the system of **3** mixed with 10 equivalents of $AlMe_3$ and 1 equivalent of $[Ph_3C][B(C_6F_5)_4]$ in a sequence of alkylaluminum and borate produced polyisoprene with a 99% conversion having 98% 1,4-regioselectivity and high molar weight $M_n = 44.5 \times 10^4$ in 150 min at 20 °C (Table 3, entry 1). Using $AlEt_3$ instead of $AlMe_3$ in the above catalytic system, the 1,4-regioselectivity of polymers dramatically decreased from 98% to 80% (Table 3, entry 2). However, using $Al^iBu_3$ instead of $AlMe_3$ resulted in decrease of 1,4-regioselectivity of polymers (Table 3, entry 3). This homogeneous catalytic system showed high catalytic activities when the polymerization reaction was run at elevated temperature. For example, the monomers were almost completely transferred (96% and 98%) when the temperatures were increased to 50 °C and 70 °C in short times (45 min and 35 min). To date, few catalytic systems have been known to be so stable at such a high temperature.[2c,d] However, the molar weight of the resulting polyisoprene and 1,4-regioselectivity decreased and the molar weight distribution became wide (Table 3, entries 5–6). This might be attributed to the combined effects of the increased number of active species and rapid chain transfer reactions at high temperatures. It is also found that decreasing the [M]/[Ln] ratio has a little effect on the molecular weight,

**Table 3** Isoprene polymerization by bis(formamidinate) rare-earth metal alkyls/$AlR_3$/borate[a]

| Entry | Precatalyst | [M]/[RE] | $AlR_3$ | Borate[b] | Temp [°C] | Time [min] | Conv [%] | $M_n$ [c] $[10^{-4}]$ | PDI[c] | 1,4/3,4[d] |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | **3** | 1000 | $AlMe_3$ | $[B]_C$ | 20 | 150 | 99 | 44.5 | 1.5 | 98/2 |
| 2 | **3** | 1000 | $AlEt_3$ | $[B]_C$ | 20 | 240 | 82 | 52.4 | 1.5 | 80/20 |
| 3 | **3** | 1000 | $Al^iBu_3$ | $[B]_C$ | 20 | 360 | 99 | 59 | 1.3 | 24/76 |
| 4 | **3** | 1000 | $Al^iBu_3$ | $[B]_N$ | 20 | 150 | 99 | 59 | 1.4 | 30/70 |
| 5 | **3** | 1000 | $AlMe_3$ | $[B]_C$ | 50 | 45 | 96 | 27 | 1.8 | 90/10 |
| 6 | **3** | 1000 | $AlMe_3$ | $[B]_C$ | 70 | 35 | 98 | 22 | 1.9 | 81/19 |
| 7 | **3** | 500 | $AlMe_3$ | $[B]_C$ | 20 | 150 | 100 | 44 | 1.3 | 96/4 |
| 8 | **3** | 2000 | $AlMe_3$ | $[B]_C$ | 20 | 200 | 99 | 57 | 1.3 | 86/14 |
| 9 | **3** | 3000 | $AlMe_3$ | $[B]_C$ | 20 | 250 | 98 | 50 | 1.5 | 76/24 |
| 10 | **1** | 1000 | $AlMe_3$ | $[B]_C$ | 20 | 180 | 99 | 31.4 | 2.2 | 72/28 |
| 11 | **2** | 1000 | $AlMe_3$ | $[B]_C$ | 20 | 180 | 99 | 15 | 2.2 | 94/6 |
| 12 | **4** | 1000 | $AlMe_3$ | $[B]_C$ | 20 | 330 | 99 | 25 | 1.8 | 93/7 |
| 13 | **5** | 1000 | $AlMe_3$ | $[B]_C$ | 20 | 720 | Trace | — | — | — |
| 14 | **6** | 1000 | $AlMe_3$ | $[B]_C$ | 20 | 240 | 96 | 26 | 1.7 | 90/10 |
| 15 | **6** | 1000 | $Al^iBu_3$ | $[B]_C$ | 20 | 45 | 97 | 13 | 1.8 | 92/8 |
| 16[e] | **6** | 1000 + 1000 | $Al^iBu_3$ | $[B]_C$ | 20 | 45 + 45 | 95 | 19 | 1.7 | 92/8 |

[a] Conditions: Ln (10 μmol); isoprene–toluene = 1 : 10 (vol/vol); Ln–Borate–$AlR_3$ = 1 : 1 : 10 (molar ratio). [b] [Borate]: $[B]_C = [Ph_3C][B(C_6F_5)_4]$; $[B]_N = [PhNMe_2H][B(C_6F_5)_4]$. [c] Determined by means of GPC against polystyrene standards in THF at 30 °C. [d] Determined by $^1H$ and $^{13}C$ NMR spectroscopy. [e] 1 mL IP was added first followed by addition of 1 mL IP in 10 mL toluene after 45 min.

molecular weight distribution and 1,4-regioselectivity (Table 3, entry 7). Increasing the [M]/[Ln] ratio influenced the 1,4-regioselectivity significantly, but molecular weight and molecular distribution changed slightly (Table 3, entries 8 and 9). Other catalysts **2**, **4**, and **6** displayed a similar catalytic activity to give polymers having a high 1,4-regioselectivity (≥90%) and narrow molecular weight distribution under the same conditions except for **5** (Table 3, entries 11–14); however, the produced polyisoprenes have low molecular weight. Using complex **1** as a precatalyst, polyisoprene having a low 1,4-regioselectivity (72%) was obtained (Table 3, entry 10). It is surprisingly found that on addition of $Al^iBu_3$ instead of $AlMe_3$ to the catalytic system **3** or **6**, respectively, different regioselectivities of polymerizations were observed and addition of $Al^iBu_3$ to catalyst **3** followed by addition of $[Ph_3C][B(C_6F_5)_4]$ or $[PhNMe_2H][B(C_6F_5)_4]$ produced a polymer with a low 1,4-regioselectivity (Table 3, entries 3, 4); however, addition of $Al^iBu_3$ to the catalyst **6** system followed by addition of $[Ph_3C][B(C_6F_5)_4]$ produced a polymer with 1,4-regioselectivity as high as 92% (Table 3, comparison of entry 3 and entry 15). The results might be attributed to the ionic radii difference between $Er^{3+}$ and $Nd^{3+}$; the larger neodymium catalyst can hold more sterically bulky $Al^iBu_3$ that favors the 1,4-regioselectivity. In order to estimate the ratio between the *cis*-1,4-PIP and *trans*-1,4-PIP, we used $^{13}C$ NMR spectroscopy to characterize the product of entry 15. The $^{13}C$ NMR spectroscopy results indicated a ratio of 36% (*cis*-1,4), 55% (*trans*-1,4), and 9% (3,4-)polymers (see ESI†), which was in accordance with the $^1H$ NMR spectroscopy (92% 1,4-regioselectivity). Catalyst **6** also displayed high activity when the monomer was fractionally added producing polymers with a high 1,4-regioselectivity and narrow molecular weight distribution, but the molecular weight did not increase dramatically. Different borates slightly influence the regioselectivity of the catalytic system (Table 3, entries 3 and 4).

## Conclusions

In summary, a series of rare-earth metal alkylates formulated as $(HC(N\text{-}2,6\text{-}R_2C_6H_3)_2)_2RECH_2SiMe_3\cdot thf$ (R = $CH_3$, $^iPr$) were synthesized and fully characterized. In combination with alkylaluminum and borate, these complexes displayed a good catalytic activity on polymerization of isoprene. It is found that addition of the cocatalysts sequence has a great influence on the regioselectivity of the polymerization. High 1,4-regioselectivity (as high as 98%) polymerizations were observed when the catalysts were added in the order [RE]/[alkylaluminum]/[borate].

## Experimental section

### General procedure

All syntheses and manipulations of air- and moisture-sensitive materials were performed under a dry argon and oxygen-free atmosphere, using standard Schlenk techniques or a glovebox. All solvents were refluxed and distilled over sodium benzophenone ketyl under argon prior to use unless otherwise noted. $[Ph_3C][B(C_6F_5)_4]$ and $[PhNMe_2H][B(C_6F_5)_4]$ were purchased from STREM. $AlMe_3$, $AlEt_3$, and $Al^iBu_3$ were purchaed from Sigma-Aldrich, and used as received. Isoprene was purchased from TCI, dried with $CaH_2$, and distilled before polymerization. Formamidinates $\mathbf{HL^1}$ and $\mathbf{HL^2}$ were prepared according to literature methods.[10] 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 Model AV-300 NMR spectrometer (300 MHz for $^1H$; 75.0 MHz for $^{13}C$) in $C_6D_6$ for rare-earth metal complexes and in $CDCl_3$ for polyisoprene. Chemical shifts ($\delta$) were reported in ppm. *J* values are reported in Hz. 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$^{-1}$.

### Synthesis of [HC(N-2,6-Me$_2$C$_6$H$_3$)$_2$]$_2$Y(CH$_2$SiMe$_3$)(THF) (1)

To a hexane (15.0 mL) solution of Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (0.343 g, 0.69 mmol) was added a hexane (15.0 mL) solution of **HL$^1$** (0.348 g, 1.38 mmol) at room temperature. The mixture was stirred for 3 h at room temperature and the color of the solution gradually changed from colorless to faint yellow. The solvent was evaporated under reduced pressure. The residue was extracted with hexane (2 × 8.0 mL). The extractions were combined and concentrated to about 10.0 mL. Colorless crystals **1** were obtained at 0 °C (0.36 g, 71% yield). M.p.: 132 °C. $\delta_H$ (C$_6$D$_6$, ppm): 7.69 (s, 2H, NC(H)=N), 6.92–6.99 (m, 12H, C$_6$H$_3$), 3.61 (s, 4H, thf), 2.32 (s, 24H, CH$_3$), 0.98 (s, 4H, thf), 0.40 (s, 9H, SiCH$_3$), 0.16 (s, 2H, CH$_2$Si). $\delta_C$ (C$_6$D$_6$, ppm): 170.1, 147.0, 131.1, 122.8, 122.4, 68.4, 38.2, 23.5, 18.9, 18.5, 3.3. $\nu_{max}$/cm$^{-1}$: 3155 (s), 2918 (s), 1649 (m), 1587 (m), 1556 (s), 1466 (m), 1367 (s), 1201 (w), 1091 (s), 1033 (s), 758 (s). Anal. calc. for C$_{42}$H$_{57}$N$_4$OSiY: C, 67.18; H, 7.65; N, 7.46. Found: C, 66.97; H, 7.66, N, 7.28.

### Synthesis of [HC(N-2,6-$^i$Pr$_2$C$_6$H$_3$)$_2$]$_2$Y(CH$_2$SiMe$_3$)(THF) (2)

A similar method for preparing complex **1** was used. Complex **2** was prepared by reaction of **HL$^2$** (0.38 g, 1.96 mmol) with Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (0.486 g, 0.98 mmol) in hexane (30.0 mL) for 3 h at room temperature. Colorless crystals **2** were obtained in 72% yield after recrystallization from the concentrated hexane solution at 0 °C (0.68 g). M.p.: 143 °C. $\delta_H$ (C$_6$D$_6$, ppm): 8.09 (s, 2H, NC(H)=N), 7.18–7.24 (m, 12H, C$_6$H$_3$), 3.75 (s, 4H, thf), 3.64 (m, 8H, CH, $^i$Pr), 1.34 (s, 48H, CH$_3$, $^i$Pr), 1.18 (s, 4H, thf), 0.35 (s, 9H, SiMe$_3$), 0.05 (s, 2H, CH$_2$Si). $\delta_C$ (C$_6$D$_6$, ppm): 168.7, 143.3, 142.1, 124.1, 122.7, 122.5, 67.9, 67.6, 38.2, 27.3, 24.2, 24.1, 23.5, 2.9. $\nu_{max}$/cm$^{-1}$: 2960 (w), 2926 (m), 1664 (w), 1587 (s), 1454 (m), 1361 (s), 1330 (s), 1180 (s), 862 (s), 798 (s). Anal. calcd for C$_{58}$H$_{89}$N$_4$OSiY: C, 71.42; H, 9.20; N, 5.74. Found: C, 71.38; H, 9.21; N, 5.71.

### Synthesis of [HC(N-2,6-$^i$Pr$_2$C$_6$H$_3$)$_2$]$_2$Er(CH$_2$SiMe$_3$)(THF) (3)

A similar method for preparing complex **1** was used. Complex **3** was prepared by reaction of **HL$^2$** (0.56 g, 1.434 mmol) with Er(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (0.411 g, 0.717 mmol) in hexane (30.0 mL) for 3 h at room temperature. Pink crystals **3** were obtained in 73% yield after recrystallization from the concentrated hexane solution at 0 °C (0.55 g). M.p.: 145 °C. $\nu_{max}$/cm$^{-1}$: 2960 (w), 2926 (m), 1664 (w), 1587 (s), 1454 (m), 1361 (s), 1330 (s), 1180 (s), 1001 (s), 798 (s), 667 (s). Anal. calcd for C$_{58}$H$_{89}$N$_4$ErOSi: C, 66.11; H, 8.51; N, 5.32. Found: C, 66.07; H, 8.50; N, 5.28.

### Synthesis of [HC(N-2,6-$^i$Pr$_2$C$_6$H$_3$)$_2$]$_2$Dy(CH$_2$SiMe$_3$)(THF) (4)

A similar method for preparing complex **1** was used. Complex **4** was prepared by reaction of **HL$^2$** (0.43 g, 1.096 mmol) with Dy(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (0.312 g, 0.548 mmol) in hexane (30.0 mL) for 3 h at room temperature. Colorless crystals **4** were obtained in 70% yield after recrystallization from the concentrated hexane solution at 0 °C (0.39 g). M.p.: 145 °C. $\nu_{max}$/cm$^{-1}$: 2960 (w), 2866 (m), 1662 (w), 1587 (s), 1456 (m), 1234 (s), 1180 (s), 1001 (s), 798 (s), 667 (s). Anal. calcd for C$_{58}$H$_{89}$N$_4$DyOSi: C, 66.41; H, 8.55; N, 5.34. Found: C, 66.45; H, 8.55; N, 5.29.

### Synthesis of [HC(N-2,6-$^i$Pr$_2$C$_6$H$_3$)$_2$]$_2$Sm(CH$_2$SiMe$_3$)(THF) (5)

A similar method for preparing complex **1** was used. Complex **5** was prepared by reaction of **HL$^2$** (0.192 g, 0.492 mmol) with Sm(CH$_2$SiMe$_3$)$_3$(THF)$_3$ (0.155 g, 0.246 mmol) in hexane (30.0 mL) for 3 h at room temperature. Yellow crystals **5** were obtained in 64% yield after recrystallization from the concentrated hexane solution at 0 °C (0.16 g). M.p.: 149 °C. $\nu_{max}$/cm$^{-1}$: 2960 (w), 2866 (m), 1664 (w), 1587 (s), 1456 (m), 1361 (s), 1180 (s), 1020 (s), 798 (m), 669 (s), 599 (s). Anal. calcd for C$_{58}$H$_{89}$N$_4$OSiSm: C, 67.19; H, 8.65; N, 5.40. Found: C, 67.22; H, 8.68; N, 5.36.

### Synthesis of [HC(N-2,6-$^i$Pr$_2$C$_6$H$_3$)$_2$]$_2$Nd(CH$_2$SiMe$_3$)(THF) (6)

*n*-BuLi (2.0 mL, 3.0 mmol, 1.5 M in hexane) was added dropwise to a THF (15.0 mL) solution of **HL$^2$** (1.177 g, 3.0 mmol) at room temperature. After 30 min, the reaction mixture was transferred to a THF slurry of NdCl$_3$ (0.38 g, 1.5 mmol) at room temperature. The mixture was stirred for 1 h to afford a clear solution, to which LiCH$_2$SiMe$_3$ (1.8 mL, 1.5 mmol, 0.82 M in hexane) was added *via* a pipette. The resulting mixture was stirred at room temperature for about 2 h and then the solvent was removed under reduced pressure to give an oily crude product. The crude product was extracted by hexane (2 × 10 mL). The extractions were combined and concentrated to about 10 mL. The blue crystals **6** were obtained at 0 °C (1.01 g, 65% yield). M.p.: 147 °C. $\nu_{max}$/cm$^{-1}$: 2960 (w), 2866 (m), 1660 (w), 1587 (s), 1456 (m), 1264 (s), 1180 (s), 1010 (s), 798 (m), 665 (s). Anal. calcd for C$_{58}$H$_{89}$N$_4$NdOSi: C, 67.59; H, 8.70; N, 5.44. Found: C, 67.62; H, 8.71; N, 5.41.

### Crystal structure analyses of 1–6

A suitable crystal of complexes **1–6** was each mounted in a sealed capillary. Diffraction was performed on a Bruker SMART APEX II CCD area detector diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda$ = 0.71073 Å), temperatures 173(2) K for **1–5** and 293(2) K for **6**, and the $\varphi$ and $\omega$ scan technique. An empirical absorption correction was applied using the SADABS program.[11] 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.[12] 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. But in the structure of **3**, two large residual peaks are very close to the central metal with distances of 0.84 Å and 0.70 Å, respectively, so they were treated as noise. 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 Tables S1 and S2 in ESI.†

CCDC 982911–982916 for **1–6** contain the supplementary crystallographic data for this paper.

### Isoprene polymerization

A typical polymerization procedure for the isoprene polymerization catalyzed by these complexes is given below. A 50 mL Schlenk flask, equipped with a magnetic stirring bar, was charged the desired amount of toluene, the rare earth metal complex, alkyl aluminium, borate, and isoprene. The mixture was stirred vigorously for a fixed time during which an increase of viscosity was observed. The reaction mixture was quenched by the addition of methanol, and poured in a large amount of methanol to precipitate the polymer and then dried under vacuum and weighed.

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