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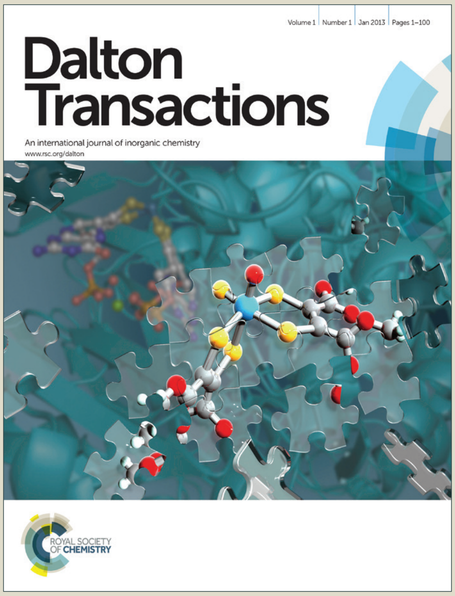

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ARTICLE TYPE

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-2, 6-$Me_2C_6H_3)_2$, RE = Y (**1**), L^2 = HC(N-2,6-$^i Pr_2C_6H_3)_2$, RE = Y (**2**), Er (**3**), Dy (**4**), Sm (**5**), 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 influences of alkylaluminium, metal central, temperature, sequence of addition of alkylaluminium and $[Ph_3C][B(C_6F_5)_4]$ on the polymerization of isoprene were studied. It was interesting to find that addition of the cocatalysts sequence has a great influence of the regioselectivity of the polymerization. High 1,4-regioselectivities polymerization of isoprene (as high as 98%) were observed when the catalysts were added in the order of [RE]/[alkylaluminum]/[borate].

Introduction

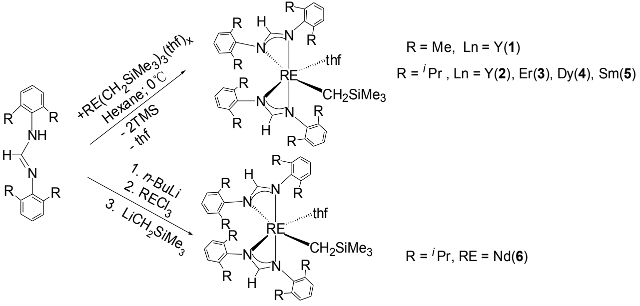
As an alternative to cyclopentadienyl, amidinates have been widely used in the field of coordination and organometallic chemistry because their steric and electronic properties can be easily modulated by the substituents on C and N atoms.[1] Over the past decades, different kinds of amidinate ligands 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, 2b] alkyls,[2e] and hydrides[2c, 2d] with amidinate as supporting ligands have been described and some of them have performed a highly 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 amidinates applied in rare-earth metal chemistry are decorated with bulky groups, such as phenyl,[2a, 2b] cyclohexyl,[2a] 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 more flexible in stereochemistry. The chemistry of formamidinate supported alkaline and alkaline earth metal complexes have 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, Lu).[4]

Monoamidinate rare-earth metal bisalkyls[5] and bisamides[2a, 6] have been found as good precatalysts for olefin polymerization. Herein, we would like to report the synthesis and characterization of a series of rare-earth metal monoalkyl complexes supproted 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-$(CH_3)_2C_6H_3N$=CH-$NHC_6H_3(CH_3)_2$-2,6 (**HL**^{1}) or 2,6-$(^i Pr)_2C_6H_3N$=CH-$NHC_6H_3(^i Pr)_2$-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 = ^{i}Pr, RE = Y (**2**), Er (**3**), Dy (**4**), Sm (**5**) in 64% to 73% yields (Scheme 1). This kind of complexes can also be prepared by one-pot salt metathesis reaction of anhydrous $LnCl_3$ with 2 equiv. of formamidinate lithium **L**^{2}Li (formed by *in suit* treatment of formamidinate **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 $[HC(N\text{-}2,6\text{-}^i Pr_2C_6H_3)_2]_2NdCH_2SiMe_3{\cdot}thf$ (**6**) formulated same as those of **2**-**5** was isolated (Scheme 1).



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

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 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 κ^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 structure of **1**, **2** are shown in Fig. 1, and Fig. 2, respectively. Selected bond parameters are listed in Table 1.

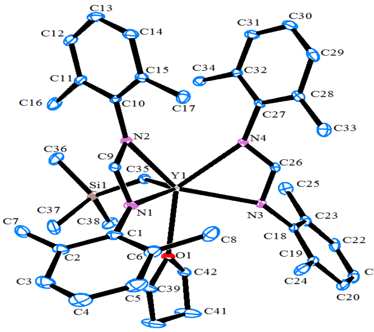


Fig. 1. Molecular structure of complex **1**. Hydrogen atoms are omitted for clarity.

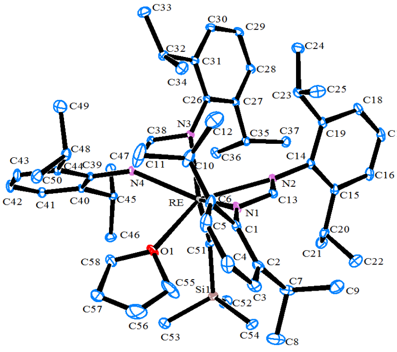


Fig. 2. Molecular structure of complex **2**. Hydrogen atoms are omitted for clarity.

The two C-N bond lengths from the same formamidinate ligand are similar and fall in the intervals of the typical single bonds and double bonds lengths (e.g., C(13)-N(1) = 1.313(4) Å and C(13)-N(2) = 1.323(4) Å in **2**) indicated that the negative charges of anionic formamidinates are delocalized on the NCN cores. The length of Y-C$_{\mathrm{alkyl}}$ bond in **2** (2.376 Å) is slightly longer than that of found in **1** (2.371 Å), this might be 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 $\mathrm{Y(CH_2SiMe_3)_3(thf)_3}$.[9] The length of Y-C$_{\mathrm{alkyl}}$ in **1** and **2** fall into the intervals of distances typical for six-coordinated alkyl yttrium complexes $[(^i\mathrm{Pr})_2\mathrm{TACN(CH_2)_2N}^t\mathrm{Bu]Y(CH_2SiMe_3)_2}$ (2.476(5), and 2.421(7) Å),[7a] $\mathrm{[Me_3SiNC(Ph)N(CH_2)_3NC(Ph)NSiMe_3]YCH(SiMe_3)_2(thf)}$ (2.410(8) Å),[7b] $\mathrm{Ap'_2YCH_2SiMe_3(thf)}$ (2.342(5)Å) (Ap′-H = 2,6-(diisopropylphenyl)-[6-(2,6-dimethylphenyl)pyridin-2-yl]amine).[7c] For the complexes **2**, **4**, **5**, **6**, which were crystallized in the same space group and crystal system, the length of RE-C$_{\mathrm{alkyl}}$ increased with increasement of the size of the central metal, are well in accordance with the lanthanide contraction (Table 1). The angles between the two bulkly formamidines 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**), 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 $\mathrm{C_6H_4\text{-}1,2\text{-}\{NC(^tBu)N(2,6\text{-}Me_2C_6H_3)\}_2Y(CH_2SiMe_3)(thf)}$ (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 $\mathrm{[HC(N\text{-}2,6\text{-}^iPr_2C_6H_3)_2]_2NdBr(thf)}$ [4a] (54.77(14)° and 55.03(14)°), as a result of the steric effect of the bulky $\mathrm{CH_2SiMe_3}$ group.

Table 1. Selected bond length (Å) and bond angle (°) of complexes **1-6**.

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

Isoprene polymerization

Cationic alkyl species of rare-earth metal (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 borate, this phenomenon was ascribed to the absence of metal alkyl initiator after dealkylated by the borate [Ph$_3$C][B(C$_6$F$_5$)$_4$].[5a] The bis(formamidinate) rare-earth metal monoalkyl complex **3** was tested as an initiator for the polymerization of isoprene (IP) with the activition of aluminum alkyls (AlR$_3$, R = Me, Et, ^{i}Bu) and borates B(C$_6$F$_5$)$_3$, [Ph$_3$C][B(C$_6$F$_5$)$_4$] or [PhNMe$_2$H][B(C$_6$F$_5$)$_4$]. The complex **3** alone was inactive to the polymerization of isoprene, which was still inert by the reaction with one equivalent of [Ph$_3$C][B(C$_6$F$_5$)$_4$] or [PhNMe$_2$H][B(C$_6$F$_5$)$_4$], respectively (Table 2, Entry 1). Upon addition of the third component aluminum alkyls, homogeneous catalytic systems were generated and showed an good activity. Various AlR$_3$ (R = Me, Et, ^{i}Bu), 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 aluminum-to-lanthanide ratio. For example, addition 1000 equivalents of isoprene to a mixture of **3** mixed with 1 equivalent of [Ph$_3$C][B(C$_6$F$_5$)$_4$] 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^{i}Bu$_3$ 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 steric effect of alkylaluminum on the regioselectivity of these homogeneous catalytic systems. When the amount of Al^{i}Bu$_3$ was reduced to 5 equivalents, the 3,4-regioselectivity can be reached to 66% (Table2, entry 6). The borates [Ph$_3$C][B(C$_6$F$_5$)$_4$] and [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] showed little effect on the polymerization activity and regioselectivity when the Al^{i}Bu$_3$ was used (Table 2, entries 4-5).

Table 2 Isoprene polymerization by **3**/Borate/AlR$_3$ system[a]

Entry	Bortate[b]	AlR$_3$ [equiv][a]	*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^{i}Bu$_3$ (10)	30	100	12.4	1.8	39/61
5	[B]$_N$	Al^{i}Bu$_3$ (10)	30	100	12.3	1.8	37/63
6	[B]$_C$	Al^{i}Bu$_3$ (5)	30	99	10.9	1.7	34/66
7	[B]$_C$	Al^{i}Bu$_3$ (20)	30	100	12.2	1.8	50/50

[a] Condition: (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$_3$C][B(C$_6$F$_5$)$_4$]; [B]$_N$ = [PhNMe$_2$H][B(C$_6$F$_5$)$_4$]. [c] Determined by means of GPC against polystyrene standards in THF at 30°C. [d] Determined by ^{1}H 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 equivalent of isoprene to the system of **3** mixed with 10 equivalent of AlMe$_3$ and 1 equivalent of [Ph$_3$C][B(C$_6$F$_5$)$_4$] 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 above catalytic system, the 1,4- regioselectivity of polymers dramatically decreased from 98% to 80% (Table 3, entry 2). However, using Al^{i}Bu$_3$ instead of AlMe$_3$ resulted in disadvantage of 1,4- regioselectivity of polymers (Table 3, entry 3).. This homogeneous catalytic system showed high catalytic activites when the polymerization reaction was run at elevate temperature. For examples, the monomer were almost completely transferred (96% and 98%) when the temperature were increased to 50 °C and 70 °C in short times (45 min and 35 min). To date, few catalytic systems are known to be so stable at such a high temperature.[2c,2d] However, the molar weight of the resulting polyisoprene, 1,4-regioselectivity decreased and the molar weight distribution became wide (Tabel 3, entries 5-6). This might be attributed to the combined effects of 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, 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**, **6** displayed a similar catalytic activity to give polymers having 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 precatalyst, polyisoprene having low 1,4-regioselectivity (72%) was obtained (Tabel 3, entry 10). It is suprisingly found that addition of Al^{i}Bu$_3$ instead of AlMe$_3$ to the catalytic systems **3** or **6**, respectively, different regioselectivity of polymerizations were observed, addition of Al^{i}Bu$_3$ to catalyst **3** followed by addition of [Ph$_3$C][B(C$_6$F$_5$)$_4$] or [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] produced polymer with a low 1,4-regioselectivity (Table 3, entries 3, 4), however, addition of Al^{i}Bu$_3$ to catalyst **6** system followed by addition of [Ph$_3$C][B(C$_6$F$_5$)$_4$] produced polymer with the 1,4-regioselectivity as high as 92% (Table 3, comparison of entry 3 and entry 15). The results might be attributed to ionic radii difference between Er^{3+} and Nd^{3+}, the larger neodymium catalyst can hold more sterically bulky Al^{i}Bu$_3$ 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), 9% (3,4-) polymers (see supporting information), which was in accordance with the ^{1}H NMR spectroscopy (92% 1,4-regioselectivity). Catalyst **6** also displayed high activity when the monomer was fractionally added producing polymer with a high 1,4-regioselectivity and narrow molecular weight distribution, but the molecular weight did not increased dramatically. Different borates slightly influence the regioselectivity of the catalytic system (Table 3, entries 3 and 4).

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^{i}Bu$_3$	[B]$_C$	20	360	99	59	1.3	24/76
4	**3**	1000	Al^{i}Bu$_3$	[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^{i}Bu$_3$	[B]$_C$	20	45	97	13	1.8	92/8
16[e]	**6**	1000 +1000	Al^{i}Bu$_3$	[B]$_C$	20	45 + 45	95	19	1.7	92/8

[a] Condition: Ln (10 μmol); isoprene/toluene = 1 : 10 (vol/vol); Ln/Borate/AlR$_3$ = 1 : 1 : 10 (molar ratio). [b][Borate]: [B]$_C$ = [Ph$_3$C][B(C$_6$F$_5$)$_4$]; [B]$_N$ = [PhNMe$_2$H][B(C$_6$F$_5$)$_4$]. [c] Determined by means of GPC against polystyrene standards in THF at 30 °C. [d] Determined by ^{1}H and ^{13}C NMR spectroscopy. [e] 1 mL IP added first follow by addition 1 mL IP in 10 mL toluene after 45 min.

Conclusions

In summary, a series of rare-earth metal alkylates formulated as (HC(N-2, 6-R$_2$C$_6$H$_3$)$_2$)$_2$RECH$_2$SiMe$_3$·thf (R = CH$_3$, ^{i}Pr) were systhesized 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. A high 1,4-regioselectivity (as high as 98%) polymerizations were observed when the catalysts were added in the order of [RE]/[alkylaluminum]/[borate].

Experimental Section

General procedure

All syntheses and manipulations of air- and moisture-sensitive materials were performed under dry argon and oxygen-free atmosphere, using standard Schlenk techniques or a glovbox. All solvents were refluxed and distilled over sodium benzophenone ketyl under argon prior to use unless otherwise noted. [Ph$_3$C][B(C$_6$F$_5$)$_4$], [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] were purchased from STREM. AlMe$_3$, AlEt$_3$, Al^{i}Bu$_3$ were purchaed from Sigma-Aldrich, and used as received. Isoprene was purchased from TCI, dried with CaH$_2$, and distilled before polymerization. Formamidinates HL^1 and HL^2 were prepared according to literature methods.[10] Elemental analyses data were obtained on a Perkin−Elmer Model 2400 Series II elemental analyzer. ^{1}H NMR and ^{13}C NMR spectra for analyses of compounds were recorded on a Bruker Model AV-300 NMR spectrometer (300 MHz for ^{1}H; 75.0 MHz for ^{13}C) in C$_6$D$_6$ for rare-earth metal compexes and in CDCl$_3$ for polyisoprene. Chemical shift (δ) 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** (0.348g, 1.38 mmol) at room temperature. The mixture was stirred for 3 h at room temperature and the color of the solution was 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. The colorless crystals **1** were obtained at 0 °C (0.36g, 71% yield). m.p: 132 °C. δ_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). δ_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. ν_{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 crytals **2** were obtained in 72% yield after recrystallization from the concentrated hexane solution at 0 °C (0.68 g). m.p: 143 °C. δ_H (C_6D_6, ppm): 8.09 (s, 2H, NC(H)=N), 7.18-7.24 (m, 12H, C_6H_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_2Si). δ_C (C_6D_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. ν_{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 $C_{58}H_{89}N_4OSiY$: 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 $Er(CH_2SiMe_3)_3(THF)_2$ (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. ν_{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 $C_{58}H_{89}N_4ErOSi$: 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 $Dy(CH_2SiMe_3)_3(THF)_2$ (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 recrytallization from the concentrated from hexane solution at 0 °C (0.39 g). m.p: 145 °C. ν_{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 $C_{58}H_{89}N_4DyOSi$: 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 $Sm(CH_2SiMe_3)_3(THF)_3$ (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. ν_{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 $C_{58}H_{89}N_4OSiSm$: 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 dropwised to a THF (15.0 mL) solution of **HL^2** (1.177 g, 3.0 mmo) 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 $LiCH_2SiMe_3$ (1.8 mL, 1.5 mmol, 0.82 M in hexane) was added *via* a pipet. The resulting mixture was stirred at room temperature for about 2 h, 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. ν_{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 $C_{58}H_{89}N_4NdOSi$: 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-monochro-mated Mo-Kα radiation (λ = 0.71073 Å), temperature 173(2) K for **1-5**, and 293(2) K for **6**, φ and ω 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 aniso-tropically 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 structure of **3**, two large residual peaks are very close to 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 Table ESI 1 and 2 in Electronic Supplementary Information.

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 quenced by the addition of methanol, and the poured in a large amount of methanol to precipitate the polymer, then dried under vacuum and weighed.

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Notes and references

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1 *(a)* F. T. Edelmann, *Adv. Organomet. Chem*., 2008, **57**, 183; *(b)* Frank T. Edelmann, *Chem. Soc. Rev*., 2012, **41**, 7657-7672.

2 *(a)* Y. J. Luo, S. M. Fan, J. P. Yang, J. H. Fang and P. Xu, *Dalton Trans*., 2011, **40**, 3053; *(b)* J. F. Wang, T. Cai, Y. M. Yao, Y. Zhang and Q. Shen, *Dalton Trans*., 2007, 5275; *(c)* J. H. Cheng, H. Y. Wang, M. Nishiura and Z. M. Hou, *Chem. Sci*., 2012, **3**, 2230; *(d)* J. H. Cheng and Z. M. Hou, *Chem. Commun*., 2012, **48**, 814; *(e)* S. Bambirra, M. W. Bouwkamp, A. Meetsma and B. Hessen, *J. Am. Chem. Soc*., 2004, **126**, 9182; *(f)* Z. J. Yao and G. X. Jin, *Organometallic*., 2012, **31**, 1767; *(g)* J. A. R. Schmidt and J. Arnold, *Chem. Commun*., 1999, 2149.

3 *(a)* M. L. Cole, A. J. Davies, C. Jones, P. C. Junk, *J. Organomet. Chem*., 2004, **689**, 3093; *(b)* M. L. Cole, P. C. Junk, L. M. Louis, *J. Chem. Soc., Dalton Trans*., 2002, 3906; *(c)* M. L. Cole, P. C. Junk, *New J. Chem*., 2005, **29**, 135.

4 *(a)* M. L. Cole, G. B. Deacon, C. M. Forsyth, P. C. Junk, K. Konstas, J. Wang, H. Bittig, D. Werner, *Chem. Eur. J*., 2013, **19**, 1410; *(b)* M. L. Cole, G. B. Deacon, P. C. Junk, J. Wang, *Organometallics.,* 2013, **32**, 1370-1378; *(c)* S. Hamidi, L. N. Jende, H. M. Dietrich, C. M. Mossmer, K. W. Tornroos, G. B. Deacon, P. C. Junk, R. Anwander, *Organometallics*., 2013, 32, 1209.

5 *(a)* Y. Yang, Q. Y. Wang, D. M. Cui, *J. Polym. Sci*., *Part A*: Polym. Chem., 2008, **46**, 5251; *(b)* L. X. Zhang, M. Nishiura, M. Yuki, Y. Luo, Z. M. Hou, *Angew. Chem*., *Int. Ed*., 2008, **47**, 2642; *(c)* L. X. Zhang, T. Suzuki, Y. Luo, M. Nishiura, Z. M. Hou, *Angew. Chem*., *Int. Ed*., 2007, **46**, 1909; *(d)* Z. B. Jian, D. M. Cui, Z. M. Hou, X. F. Li, *Chem. Commum*., 2010, **46**, 3022; *(e)* X. F. Li, M. Nishiura, L. H. Hu, K. Mori, Z. M. Hou, *J. Am. Chem*., 2009, **131**, 13870; *(f)* S. H. Li, W. Miao, T. Tang, W. M. Dong, X. Q. Zhang, D. M. Cui, *Organometallics*, 2008, **27**, 718; *(g)* N. Yu, M. Nishiura, X. F. Li, Z. F. Xi, Z. M. Hou, *Chem. Asian. J*., 2008, **3**, 1406; *(i)* V. Y. Rad'Kov, G. G. Skvortov, D. M. Lyubov, A. V. Cherkasov, G. K. Fukin, A. S. Shavyrin, D. M. Cui, A. A. Trifonov, *Eur. J. Inorg. Chem*., 2012, **13**, 2289; *(j)* S. Bambirra, M. W. Bouwkamp, A. Meetsma, B. Hessen, *J. Am. Chem. Soc*., 2004, **126**, 9182.

6 *(a)* C. Doring, W. P. Kretschmer, T. Bauer, R. Kempe, *Eur. J. Inorg. Chem*., 2009, 4255; *(b)* V. Monteil, R. Spitz, C. Boisson, *Polym. Int*., 2004, **53**, 576; *(c)* F. Chen, S. M. Fan, Y. B. Wang, J. Chen, Y. J. Lu, *Organometallics*, 2012, **31**, 3730.

7 *(a)* S. Bambirra, A. Meetsma, B. Hessen, *Organometallics*., 2006, **25**, 3486; *(b)* S. Bambirra, A. Meetsma, B. Hessen, J. H. Teuben, *Organometallics*., 2001, **20**, 782; (c) G. G. Skvortsov, G. K. Fukin, A. A. Trifonov, A. Noor, C. Doring, R. Kempe, *Organometallics,* 2007, **26**, 5770.

8 A. O. Tolpygin, A. S. Shavyrin, A. V. Cherkasov, G. K. Fukin, A. A. Trifonov, *Organometallics*, 2012, **31**, 5405.

9 W. J. Evans, J. C. Brady, J. W. Ziller, *J. Am. Chem. Soc.* **2001**, *123*, 7711-7712.

10 K. Hirano, S.Urban, C. Y. Wang, F. Glorious, *Org. Lett*., 2009, **11**, 1019.

11 G. M. Sheldrick, SADABS: *Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Germany, 1996.

12 G. M. Sheldrick, *SHELXTL 5.10 for Windows NT: Structure Determination Software Programs*, Bruker Analytical X-ray Systems, Inc., Madison, WI, 1997.

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ARTICLE TYPE

Graphical Abstract

Monoalkyl rare-earth metal complexes could be highly active catalysts for 1,4-regioselective polymerization of isoprene in the presence of cocatalysts.