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1. Introduction

Since the first structural characterization of a half sandwich rareearth bis(alkyl) complex was reported by Schaverien in 1989,1 rareearth dialkyl complexes have demonstrated great potential applications in synthetic chemistry and polymerization.² The reported results indicated that the proper design of the coligand is of great importance and can not only improve the stability of rareearth bis(alkyl) complexes but also influence their reactivity.^{2c,3} Recently, myriads of rare-earth complexes with non-Cp ancillary ligands were explored.^{3,4} Among various non-Cp ligands, amidinate and guanidinate stand out and are widely employed in lanthanide chemistry because of their tunable steric and electronic properties, rich coordination mode and easy accessibility.⁵ Guanidinate scaffolds are of tremendous popularity in lanthanide chemistry and numerous rare-earth complexes bearing guanidiante ligands have been reported. However, just a handful of neutral mono(guanidinate) bis(alkyl) rare-earth complexes were synthesized. And neither their reactivity towards small molecules nor their performance as precatalyst towards conjugated diene polymerization have been unveiled so far.6

Recently, our group reported the reactions of amidinate rareearth dialkyl complexes⁷ with various small molecules, which not only shed some light on the reaction chemistry of amidiante rare-earth dialkyl complexes, but also provided different options for the synthesis of some organolanthanide derivatives.

Synthesis, structure and reactivity of guanidinate rare earth metal bis(o-aminobenzyl) complexes*

Feng Kong, D Meng Li, D Xigeng Zhou and Lixin Zhang *

A series of guanidinate rare-earth metal complexes $[(PhCH_2)_2NC(NC_6H_4^{i}Pr_2-2,6)_2]RE(CH_2C_6H_4NMe_2-o)_2$ (RE = Y (2a), La (2b), Dy (2c), Lu (2d)) were synthesized by the acid-base reaction of RE(CH_2C_6H_4NMe_2-o)_3 with (PhCH_2)_2N[C(NHR)=(NR)] (R = 2,6^{-i}Pr_2-C_6H_3) (1) in THF. Treatment of complexes 2 with two equivalents of carbon dioxide, sulfur and phenyl isothiocyanate gave the corresponding insertion products {[(PhCH_2)_2NC(NC_6H_4^{i}Pr_2-2,6)_2]RE(μ - η^2 : η^1 -O_2CCH_2C_6H_4NMe_2-o)(μ - η^1 : η^1 -O_2CCH_2C_6H_4NMe_2-o)]_2 (RE = Y (3a), La (3b), Dy (3c), Lu (3d)), {[(PhCH_2)_2NC(NC_6H_4^{i}Pr_2-2,6)_2]RE[μ -S(CH_2C_6H_4NMe_2-o)]_2]_2 (RE = Y (4a), La (4b), Dy (4c), Lu (4d)) and {[(PhCH_2)_2NC(NC_6H_4^{i}Pr_2-2,6)_2]RE{SC(CH_2C_6H_4NMe_2-o)NPh}_2 (RE = Y (5a), La (5b), Dy (5c), Lu (5d)) in good yields, respectively. All new complexes were fully characterized by NMR spectroscopy and elemental analysis. The structures of 1, 2d, 3, 4a, 4c-d, 5a, and 5c-d were established by X-ray diffraction studies. Complexes 2 were found to have a high activity and excellent 3,4-selectivity for isoprene polymerization in the presence of [Ph₃C][B(C₆F₅)₄].

> In order to further explore the effect of subtle ligand change on the reaction patterns of rare-earth bis(alkyl) complexes, we designed a new bulky tetraalkylated guanidinate with two benzyl groups at the axis N atom. Herein, we report the synthesis of this new guanidine and the corresponding rareearth bis(alkyl) complexes. The reactions of the dialkyl species with small molecules, such as CO_2 , S_8 , and PhNCS are also disclosed. Moreover, the catalytic performance of the mono(guanidiante) rare-earth bis(alkyl) complexes for isoprene polymerization will be discussed as well.

2. Results and discussion

2.1 Synthesis of $(PhCH_2)_2N[C(NHR)=(NR)](R = 2,6^{-i}Pr_2C_6H_3)(1)$

The neutral guanidinate compound (PhCH₂)₂N[C(NHR)=NR] $(R = 2.6^{-i} Pr_2 C_6 H_3)$ (1) was synthesized in good yield by the reaction of lithium dibenzylamido with one equivalent of carbodiimide (Scheme 1). Compound 1 was characterized by NMR spectroscopy and X-ray structural analysis. The X-ray diffraction reveals that the Δ CN parameter of complex **1** is 0.102 Å (Fig. 1), which shows the difference in interatomic distance in the supposed "double" and "single" bonds is very evident. This compound is very easy to dissolve in hexane, toluene and THF. In the ¹H NMR spectrum (in CDCl₃) of **1**, four doublets at $\delta =$ 1.34, 1.25, 1.05 and 0.91 ppm can be assigned to methyl protons, and the multiples appear at 3.31-3.20 assignable to methine protons. After scrutiny of the ¹H NMR spectrum (in CDCl₃), we found that the multiples were formed by two sets of overlapped multiples. And this was further confirmed by the ¹³C NMR spectrum (in CDCl₃): two resonances at $\delta = 29.0$ and 28.4 ppm can be assigned to methine carbons of the -CHMe₂



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Department of Chemistry, Fudan University, Shanghai 200433, China. E-mail: lixinzh@fudan.edu.cn; Fax: +86-21-5566-5702

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Scheme 1



Fig. 1 Molecular structure of complex 1 with thermal ellipsoids at 30% probability. All of the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): C(1)-N(1) 1.269(3), C(1)-N(2) 1.371(3), C(1)-N(3) 1.389(3), C(26)-N(3) 1.454(3), C(33)-N(3) 1.474(3), N(2)-C(1) 1.371(3); C(1)-N(1)-C(2) 121.1(2), C(1)-N(2)-C(14) 132.7(2), N(1)-C(1)-N(2) 122.8(2), N(1)-C(1)-N(3) 119.1(2), N(2)-C(1)-N(3) 118.1(2), C(1)-N(3)-C(26) 121.61(19), C(1)-N(3)-C(33) 115.15(18), C(26)-N(3)-C(33) 114.26(18).

units. Besides, we further collected the NMR spectra of **1** in C_6D_6 , and in the ¹H NMR spectrum (in C_6D_6) of **1**, the signals of methine protons in -CHMe₂ units appear as multiple peaks at $\delta = 3.50$ and 3.35 ppm. In its ¹³C NMR spectrum (in C_6D_6), corresponding carbon resonances appear at $\delta = 29.3$ and 28.6 ppm respectively.

2.2 Synthesis of $[(PhCH_2)_2NC(NC_6H_4^{i}Pr_22,6)_2]RE$ (CH₂C₆H₄NMe₂-o)₂ (RE = Y (2a), La (2b), Dy (2c), Lu (2d))

As shown in Scheme 2, treatment of $\text{RE}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)_3$ with 1 afforded the guanidinate-stabilized bis(aminobenzyl) complexes $[(\text{PhCH}_2)_2\text{NC}(\text{NC}_6\text{H}_3^{i}\text{Pr}_2\text{-}2,6)_2]\text{RE}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)_2$ (RE = Y (2a), La (2b), Dy (2c), Lu (2d)) in moderate yields. All the new compounds were characterized by elemental analysis, NMR spectroscopy (except for 2c). In ¹H NMR spectra of 2, the resonances of the methylene protons in aminobenzyl group appear as



Scheme 2



Fig. 2 Molecular structure of complex 2d with thermal ellipsoids at 30% probability. All of the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Lu(1)-N(1) 2.318(3), Lu(1)-N(1) 2.318(3), Lu(1)-N(3) 2.624(3); N(1)-C(1)-N(1A) 109.4(4), N(1)-C(1)-N(2) 125.31(19), N(1A)-C(1)-N(2) 125.31(19), N(1)-Lu(1)-N(1A) 57.07(11).

sharp singlets at $\delta = 1.81(2a)$, 1.84(2b) and 1.80(2d) ppm respectively. And the signals at $\delta = 48.0(2a)$, 61.6(2b) and 53.3(2d)in their ¹³C NMR spectra can be assigned to their corresponding methylene carbons. And the signals of methine protons in the guanidinate ligand of the complexes 2 are observed at $\delta =$ 4.12 ppm for 2a, 3.93 ppm for 2b and 4.20 ppm for 2d, while their corresponding carbon resonances almost remain unchanged, the similar phenomenon was observed in $[(CH_3)_2NC(NC_6H_4^{i}Pr_2-2,6)_2]$ Y(CH₂SiMe₃)₂ (THF) and the corresponding neutral ligand $(CH_3)_2N[C(NHR)=(NR)]$ (R = 2,6^{-*i*}Pr₂C₆H₃).^{6c} Other characteristic peaks can also be assigned clearly. Single crystal X-ray structural analysis of complex 2d established the distorted-octahedral geometry of its core structure. The structure of 2d is depicted in Fig. 2; selected bond lengths and angles are listed in the caption. The lutetium atom was coordinated by six atoms: two nitrogen atoms from the guanidinate ligand, two carbon atoms and two amino nitrogen atoms. The guanidinate ligand coordinates symmetrically to the Lu atom. Because of the better symmetry of the coordinated guanidinate ligand, the numbers of the methine and methyl resonances of the ligand decrease in the NMR spectra of complexes 2 in comparison with the neutral ligand.6 The bond length of Lu–N (2.318(3) Å) is very close to the Lu–N distance in $[CyC(N-2,6^{-l}Pr_2C_6H_3)_2]Lu(CH_2SiMe_3)_2(THF)$ (average 2.313 Å)⁸ and slightly shorter than Y-N distance (2.373 Å) in [PhC(NC₆H₄^{*i*}Pr₂-2,6)₂]Y(CH₂C₆H₄NMe₂-*o*)₂,^{7b} after taking into consideration of the difference between metal radii.

2.3 Reaction of $[(PhCH_2)_2NC(NC_6H_4^{i}Pr_2-2,6)_2]RE$ (CH₂C₆H₄NMe₂-o)₂ (RE = Y (2a), La (2b), Dy (2c), Lu (2d)) with CO₂

To explore the ligand effect on the structure and reactivity of complexes, reactions of complexes 2 with CO_2 were conducted firstly. The THF solution of complexes 2 was stirred under an atmosphere of CO_2 (0.1 MPa), an immediate colour change from yellow to colourless was observed for complexes 2b and 2c, while the colour change was not observed in the reaction of 2a



and 2d (Scheme 3). Expected insertion products $\{[(PhCH_2)_2 -$ NC(NC₆H₄^{*i*}Pr₂-2,6)₂]RE(μ - η^{2} : η^{1} -O₂CCH₂C₆H₄NMe₂-o)(μ - η^{1} : η^{1} - $O_2CCH_2C_6H_4NMe_2-0$ (RE = Y (3a), La (3b), Dy (3c), Lu (3d)) were obtained in mediate to excellent yields. In their ¹H NMR spectra, the broad peak observed at $\delta = 3.47(3b)$, 3.50(3d) ppm can be assigned to methylene protons of the aminobenzyl groups. Complex **3b** displays a sharp singlet at $\delta = 2.54$ ppm assignable for the methyl protons of -NMe2 groups, while for 3d, the methyl signal turns into a set of broad multiple peaks at $\delta = 2.52$ ppm. However, in the room temperature ¹H NMR spectrum of 3a, there is only one broad peak at $\delta = 2.47$ ppm that can be assigned to methylene and methyl protons in the aminobenzyl groups. Compared to their corresponding dialkyl complexes, in complexes 3 (except 3c), the methylene protons of the aminobenzyl groups obviously shift to downfield which indicates the insertion of CO₂ molecules. And in their ¹³C NMR spectra, the resonances at $\delta = 186.2(3a)$, 183.6(3b) and 183.7(3d) ppm are assignable to the carbons in carboxyl groups. The structures of complexes 3 were further confirmed by the Xray single crystal diffraction. The X-ray crystallographic analysis indicates that complexes 3a-d are isostructural, and crystal structure of 3a is presented in Fig. 3. The generated carboxyl units coordinate to lanthanide centres in two different fashions: μ - η^2 : η^1 and μ - η^1 : η^1 . And the C–O bond lengths of complexes 3 range from 1.222(9) Å to 1.309(8) Å, which are consistent with typical delocalized carboxylate species.9 The Y-O bond length are generally in the normal range except the Y(1)-O(3A) (2.737(4) Å) bond. The Y(1)–O(3A) bond is remarkably longer than those observed in $[(C_5Me_4)SiMe_2(CH_2CH=CH_2)]Y(\mu-\eta^2:\eta^1 O_2CCH_2SiMe_3)(\mu - \eta^1 : \eta^1 - O_2CCH_2SiMe_3)\}_2$ (ref. 9b) (2.563(2) Å) {[PhC(NC₆H₄^{*i*}Pr₂-2,6)₂]Y(μ - η ²: η ¹-O₂CCH₂C₆H₄NMe₂-*o*)(μ and $\eta^{1}: \eta^{1} - O_2CCH_2C_6H_4NMe_2 - o) \}_2$ (2.53(1) Å).^{7b} This unusual bond length can be ascribed to the bulky size and electronic effect of the guanidinate ligand. The poor solubility of complexes 3 even in THF at room temperature can provide extra evidence for the sterically crowded coordination sphere around the lanthanide centres. The reactions of complexes 2 with CO₂ provide not only an effective way for the activation of CO₂, but also a good synthetic method for guanidinate rare-earth derivatives.

2.4 Reaction of $[(PhCH_2)_2NC(NC_6H_4^{i}Pr_2-2,6)_2]RE$ (CH₂C₆H₄NMe₂-o)₂ (RE = Y (2a), La (2b), Dy (2c), Lu (2d)) with S₈

To further study the reactivity of complexes 2, reactions with S_8 were also carried out. Different from their amidinate



Fig. 3 Molecular structure of complex **3a** with thermal ellipsoids at 30% probability. 2,6-Diisopropylphenyl groups of guanidinate ligand and all of the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Y(1)-N(1) 2.318(4), Y(1)-N(2) 2.354(5), Y(1)-O(3) 2.254(4), Y(1)-O(1) 2.269(4), Y(1)-O(2A) 2.276(4), Y(1)-O(4A) 2.330(4), Y(1)-O(3A) 2.737(4), O(1)-C(40) 1.259(7), O(2)-C(40) 1.276(6), O(3)-C(50) 1.280(6), O(4)-C(50) 1.257(7); O(3)-Y(1)-O(1) 81.80(15), O(1)-Y(1)-O(4A) 85.33(16), O(3)-Y(1)-O(4A) 135.12(15), O(3)-Y(1)-O(3A) 84.96(14), O(1)-Y(1)-O(2A) 141.14(14), N(1)-C(1)-N(2) 110.5(4), N(1)-Y(1)-N(2) 56.38(15), O(1)-C(40)-O(2) 122.2(5), O(4)-C(50)-O(3) 118.5(5).



counterparts,^{7b} the reactions of complexes 2 with 1/4 equivalent S₈ gave dinuclear lanthanide insertion products {[(PhCH₂)₂- $NC(NC_6H_4^{i}Pr_2-2,6)_2]RE[\mu-S(CH_2C_6H_4NMe_2-o)]_2]_2$ (RE = Y (4a), La (4b), Dy (4c), Lu (4d)) in good yields (Scheme 4).^{10d} These complexes are easily soluble in toluene and THF, and slightly soluble in hexane. Complexes 4a, 4b and 4d were characterized by the ¹H and ¹³C NMR spectra in C₆D₆ at 25 °C. The ¹H NMR spectra show multiple signals at $\delta = 3.89(4a)$, 3.77(4b) and 3.95(4d) ppm which are assignable for the methine protons of the CHMe₂ groups. Compared to their corresponding dialkyl complexes, the signals of the methylene protons obviously shift to lower field because of the insertion of the sulfur atoms. For 4b, the signal for the methylene protons of aminobenzyl group appears as a sharp singlet at $\delta = 4.52$ ppm, while for **4a** and **4d**, it becomes a broad peak at $\delta = 4.28$ and 4.46 ppm respectively. And their corresponding carbon signals show up at $\delta = 34.6(4a)$, 33.5(4b) and 34.3(4d) ppm as sharp singlets. The X-ray single crystal diffraction analysis established the bimetallic structure of complexes 4a, 4c and 4d (Fig. 4). Two yttrium ions are connected by four bridging thiolate units which definitely proves the insertion of sulfur atoms into each of Y-C bonds. In lanthanide chemistry, the similar core



Fig. 4 Molecular structure of complex 4a with thermal ellipsoids at 30% probability. 2, 6-Diisopropylphenyl groups of guanidinate ligand and all of the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Y(1)–N(2) 2.320(3), Y(1)–N(1) 2.338(3), Y(1)–S(3) 2.7781(10), Y(1)–S(4) 2.7900(9), Y(1)–S(2) 2.8012(10), Y(1)–S(1) 2.8079(9), Y(2)–N(4) 2.320(3), Y(2)–N(5) 2.323(3), Y(2)–S(1) 2.7947(10), Y(2)–S(2) 2.795(1), Y(2)–S(4) 2.807(1), Y(2)–S(3) 2.8412(9); N(2)–Y(1)–N(1) 56.99(9), S(3)–Y(1)–S(4) 69.31(3), S(4)–Y(1)–S(2) 106.2(1), N(4)–Y(2)–N(5) 57.08(9), S(1)–Y(2)–S(2) 69.28(3), S(2)–Y(2)–S(4) 105.9(1), N(2)–C(1)–N(1) 111.3(3), N(4)–C(40)–N(5) 110.5(3), Y(2)–S(1)–Y(1) 73.84(2), Y(2)–S(2)–Y(1) 73.94(2), Y(1)–S(3)–Y(2) 73.58(2), Y(1)–S(4)–Y(2) 73.93(2).

structure is only observed in complex [{ ${}^{t}BuC(NC_{6}H_{3}-2,6-{}^{i}Pr_{2})_{2}$ } Yb(μ -SCH₂Ph)₂]₂.¹¹ The lengths of Y–S bonds range from 2.778(1) Å to 2.841(1) Å and are comparable to the previously reported Y–S(μ_{2} -SR) bonds.¹⁰ The dihedral angles between the Y1S1Y2 and Y1S3Y2 plane is 179.7°, indicating that the Y1S1Y2S3 is coplanar. Y1S2Y2S4 unit is also coplanar. Besides, the two planes are almost vertical to each other with a dihedral angle of 89.86°.

2.5 Reaction of $[(PhCH_2)_2NC(NC_6H_4^{i}Pr_2-2,6)_2]RE$ (CH₂C₆H₄NMe₂-o)₂ (RE = Y (2a), La (2b), Dy (2c), Lu (2d)) with PhNCS

The reactivity of complexes 2 towards phenyl isothiocynate was also studied. These reactions provided insertion products $[(PhCH_2)_2NC(NC_6H_4^{i}Pr_2-2,6)_2]RE{SC(CH_2C_6H_4NMe_2-0)NPh}_2$

 $(\text{THF})_n$ $(n = 1, \text{RE} = \text{La}(5\mathbf{b}); n = 0, \text{RE} = \text{Y}(5\mathbf{a}), \text{Dy}(5\mathbf{c}), \text{Lu}(5\mathbf{d}))$ in 46–77% yields (Scheme 5). Compared to the guanidinate dialkyl complexes 2, the resonances of methylene protons in aminobenzyl groups of these insertion products shift from upfield to downfield $\delta = 4.14$ for 5a, 4.17 for 5b and 4.15 for 5d ppm respectively. In their ¹³C NMR spectra, the



Scheme 5



Fig. 5 Molecular structure of complex **5a** with thermal ellipsoids at 30% probability. All of the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Y(1)-N(2/2A) 2.329(2), Y(1)-N(3/3A) 2.405(3), Y(1)-S(1/1A) 2.7154(9), N(1)-C(1) 1.359(5), N(1)-C(2) 1.468(3), N(2)-C(1) 1.351(3), S(1)-C(21) 1.735(3), N(3)-C(21) 1.287(4); N(2)-Y(1)-N(2A) 56.81(11), N(2)-Y(1)-S(1A) 128.56(6), N(3)-Y(1)-S(1) 60.70(6), N(3)-C(21)-S(1) 118.0(2), N(3A)-Y(1)-N(3) 120.99(12), C(21)-N(3)-Y(1) 99.6(2).

corresponding signals were observed at $\delta = 42.4(5a), 43.2(5b)$ and 42.6(5d) ppm as singlets. Complex 5b is of high solubility even in hexane while 5a, 5c and 5d are sparingly soluble in hexane. Noticeably, the larger lanthanum bears one coordinated THF molecule, while complexes 5a, 5c and 5d are all solvent free mononuclear complexes. As shown in Fig. 5, the yttrium ion of 5a is surrounded by four nitrogen atoms, two from the guanidinate ligand, two from the NCS fragments and two sulfur atoms from the NCS moieties. The Y-S bond length of 2.7154(9) Å is identical with the corresponding distances in $1,4-C_6H_4[C(NR)_2Y{SC(CH_2C_6H_4NMe_2-o)NPh}_2]_2$ (ref. 7*a*) (2.71 Å) and {(CH₃C₅H₄)₂Y[η^2 -SC(NPh₂)NPh]}₂ (2.7847(8) Å).¹² The S1-C21 and N3-C21 distances, 1.735(3) and 1.287(4) Å, are between the corresponding single and double bond lengths, respectively, indicating that the negative charge is delocalized over the N-C-S moiety.13

2.6 Polymerization of isoprene

Complexes 2 were also evaluated as precatalysts for the polymerization of isoprene, and the results are presented in Table 1. Complexes 2 were inert towards the polymerization of isoprene. The binary system comprised of 2a (2c or 2d)/[Ph₃C][B(C₆F₅)₄] (1 : 1) displayed a high catalytic activity and predominant 3,4regioselectivity for isoprene polymerization at room temperature (entries 1 to 4). But significant catalytic activity drop was observed for the lanthanum binary system (entry 2), probably due to the lower Lewis acidity compared to Y, Dy and Lu ions. Molecular weight distributions of all the polymers obtained from these binary systems are very narrow and unimodal (1.03– 1.05) (entries 1 to 8). Further kinetics study on yttrium binary system was carried out and displayed in Fig. 6. It is noteworthy that the number-average molecular weight (M_n) of the yielded

Entry	Precat.	Al reagent ([Al] _o /[RE] _o)	<i>t</i> [min]	$T_{\mathrm{p}} \left[^{\circ} \mathrm{C}\right]$	Conversion [%]	Microstructures ^b [%]				
						3,4	<i>cis</i> -1,4	trans-1,4	$M_{ m n}~(imes 10^4)^c$	$M_{\rm w}/M_{\rm n}^{\ c}$
1	2a	_	10	25	100	91	2.3	6.7	7.15	1.03
2	2b	_	300	25	100	70	11.8	18.2	7.50	1.04
3	2 c	_	12	25	100	83	3.9	13.1	9.04	1.03
4	2d	_	35	25	100	80	2.3	17.2	7.13	1.05
5	2a	_	8	25	94	91	2.3	6.7	6.70	1.04
6	2a	_	5	25	83	91	2.3	6.7	6.00	1.04
7	2a	_	3	25	41	91	2.3	6.7	3.08	1.07
8	2a	_	2	25	30	91	2.3	6.7	2.38	1.05
9	2a	_	180	0	100	95	0.6	4.4	7.10	1.03
10	2a	_	1440	-20	100	99	0.6	0.3	8.43	1.06
11	2a	_	1080	-20	90	99	0.6	0.3	7.95	1.05
12	2a	_	720	-20	80	99	0.6	0.3	7.04	1.03
13	2a	_	360	-20	53	99	0.6	0.3	4.66	1.06
14	2a	_	180	-20	30	99	0.6	0.3	2.95	1.06
15	2a	$AlMe_3(5)$	40	25	100	7	87.5	5.5	17.90	1.93
16	2a	$Al^{i}Bu_{3}(5)$	40	25	100	53	42	5	9.9/3.36	3.1/1.16

^{*a*} Conditions: 2 20 μmol, [Ph₃C][B(C₆F₅)₄] 20 μmol, [IP]₀/[RE]₀ 750, chlorobenzene 10 mL. ^{*b*} Determined by ¹H NMR and ¹³C NMR spectroscopy in CDCl₃. ^{*c*} Determined by GPC in THF at 40 °C against polystyrene standard.



Fig. 6 Polymerization of isoprene with 2a/[Ph₃C][B(C₆F₅)₄]: molecular weight vs. conversion ([Y]₀ = 2.0 μ mol mL⁻¹, [IP]₀/[Y]₀ = 750, chlorobenzene, 25 °C).

polymer samples was linearly relative to the conversion. In the meanwhile, the molecular weight distribution (M_w/M_n) was almost constant (1.03 to 1.07). The kinetics study indicated that the binary system $2a/[Ph_3C][B(C_6F_5)_4]$ demonstrated characteristics of living polymerization. To the best of our knowledge, examples of isoprene living polymerization with high 3,4regioselectivity remain relatively rare.14 Moreover, the reaction temperature also influenced the polymerization performance. When the polymerization was carried out at 0 °C (entry 9), the yielded polymer showed the higher proportion of 3,4 units (95%). At -20 °C (entries 10–14), although the activity apparently dropped, it took 24 hours for $2a/[Ph_3C][B(C_6F_5)_4]$ system to get 100% conversion, the higher 3,4-regioselectivity (99%) was achieved and the yttrium binary system still demonstrates characteristics of living polymerization (Fig. 7). Interestingly, in contrast to the binary system comprised of $2a/[Ph_3C][B(C_6F_5)_4]$,



Fig. 7 Polymerization of isoprene with 2a/[Ph₃C][B(C₆F₅)₄]: molecular weight vs. conversion ([Y]₀ = 2.0 μ mol mL⁻¹, [IP]₀/[Y]₀ = 750, chlorobenzene, -20 °C).

it was found that the ternary system $2a/[Ph_3C][B(C_6F_5)_4]/AlMe_3$ (1:1:5) showed a high *cis*-1,4-regioselectivity (entry 15).¹⁵ However, the introduction of AlⁱBu₃ to the $2a/[Ph_3C][B(C_6F_5)_4]$ system led to the formation of polymer blend (entry 16).

3. Conclusions

In summary, a series of neutral mono(guanidinate) rare-earth bis(alkyl) complexes have been synthesized *via* the protonolysis reaction of homoleptic rare-earth alkyl complexes with one equimolar amount of a new bulky guanidine. The reactions of bis(aminobenzyl) complexes with CO_2 , S_8 and PhNCS provide some new options for effective synthetic routes for guanidinate lanthanide derivatives. Moreover, upon activation of an organoborate, such as [Ph₃C][B(C₆F₅)₄], complexes 2 show excellent activity and predominant 3,4-selectivity towards isoprene

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polymerization in a living fashion, whereas the ternary system $2a/[Ph_3C][B(C_6F_5)_4]/AlMe_3$ (1:1:5) showed a high *cis*-1,4-regioselectivity.

4. Experiment section

4.1 Materials and general procedures

All manipulations involving air- and moisture sensitive compounds were performed under an inert atmosphere of purified nitrogen with rigorous exclusion of air and moisture using standard Schlenk techniques and a nitrogen filled glove box operating at less than 1 ppm oxygen and 1 ppm moisture. Solvents (toluene, hexane, and THF) were distilled from sodium/benzophenone ketyl, and dried over fresh Na chips in the glove box. Bis(2,6-diisopropylphenyl)carbodiimide was obtained from Tokyo Chemical Industry Co., Ltd and used without purification. CH₃C₆H₄NMe₂-o was purchased from Acros and used without purification. ⁿBuLi (2.5 mol L⁻¹ in hexane), AlMe₃ (1 mol L^{-1} in hexane) and $Al^{i}Bu_{3}$ (1 mol L^{-1} in hexane) were purchased from J&K and used without purification. Phenyl isothiocyanate were purchased from Dar Rui and distilled from CaH₂ before being used. Highly pure CO₂ gas (99.99%) was purchased from Pujiang Gas and dried by passing through activated 4 Å molecular sieves. Isoprene was obtained from Tokyo Chemical Industry Co., Ltd and purified by distillation over CaH₂ under a nitrogen atmosphere. C₆D₆ and CDCl₃ was obtained from Cambridge Isotope and dried by sodium chips. $RE(CH_2C_6H_4NMe_2-o)_3$ (ref. 16) were prepared according to the literature procedures. ¹H NMR and ¹³C NMR spectra were recorded on a JEOL ECA-400 NMR spectrometer (FT, 400 MHz for ¹H; 100 MHz for ¹³C) in C_6D_6 at room temperature. GPC data were collected on a Waters 1515 Breeze GPC system using a polystyrene standard in THF.

4.2 X-ray crystallographic analysis

Suitable crystals were sealed in thin-wall glass capillaries 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 MoK α radiation (λ = 0.71073 Å). The determination of crystal class and unit cell was carried out by the SMART program package. The raw frame data were processed using SAINT¹⁷ and SADABS¹⁸ to yield the reflection data file. The structure was solved by using SHELXTL program.¹⁹ Refinement was performed on F^2 anisotropically by the full-matrix least-squares method for all the non-hydrogen atoms. The analytical scattering factors for neutral atoms were used throughout the analysis. Except for the hydrogen atoms on bridging-carbons, hydrogen atoms were placed at the calculated positions and included in the structure calculation without further refinement of the parameters. The hydrogen atoms on bridging carbons were located by difference Fourier syntheses and their coordinates and isotropic parameters were refined. The disordered toluene and THF molecules within the crystal lattice are not crystallographically well defined and are squeezed by the PLATON program. Details of this SQUEEZE are given in the cif files. Residual electron densities were of no chemical significance. Crystal data, data collection, and processing parameters for complexes 2b, 3a, 4a and 5a are summarized in Table 2. CCDC - 1542242 (1), 893571 (2d), 1541968 (3a), 1541967 (3b), 1541964 (3c), 1541970 (3d), 1541962

Table 2 Crystallographic data for complexes 2d, 3a, 4a, 5a									
	2d	3a	4a	5a					
Formula	C ₅₇ H ₇₂ LuN ₅	$C_{59}H_{72}N_5O_4Y$	$C_{114}H_{144}N_{10}S_4Y_2\\$	$C_{71}H_{82}N_7S_2Y$					
Formula weight	1002.17	1004.13	1960.44	1186.47					
Temperature (K)	293(2)	296(2)	273(2)	296(2)					
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073					
Crystal system	Rhombohedral	Triclinic	Monoclinic	Monoclinic					
Space group	R3c	$P\bar{1}$	P21/n	C2/c					
a (Å)	24.986(7)	13.041(5)	15.488(2)	13.050(2)					
b (Å)	24.986(7)	16.053(6)	23.909(3)	26.302(5)					
<i>c</i> (Å)	47.359(9)	16.979(11)	31.418(4)	19.537(4)					
α (deg)	90	103.789(10)	90	90					
β (deg)	90	104.711(10)	98.781(2)	104.170(3)					
γ (deg)	120	112.479(7)	90	90					
$V(Å^3)$	13 025(9)	2945(3)	11 497(3)	6502(2)					
Ζ	18	2	4	4					
$\mu (\mathrm{mm}^{-1})$	1.771	1.036	1.125	1.007					
<i>F</i> (000)	9360	1064	4160	2512					
θ range (°)	1.63 to 25.50	1.48 to 25.05	1.075 to 25.050	1.79 to 25.04					
h, k, l range	$-24 \le h \le 30$,	$-15 \le h \le 15$	$-18 \le h \le 18$	$-15 \le h \le 14$					
	$-29 \le k \le 30$	$-19 \le k \le 18$	$-28 \le k \le 24$	$-29 \le k \le 31$					
	$-57 \le l \le 56$	$-14 \le l \le 20$	$-28 \le l \le 37$	$-23 \le l \le 23$					
Reflections collected	27 469	16 741	56 587	19 415					
Reflections unique	5296[R(int) = 0.0484]	$10\ 159[R(int) = 0.0594]$	$20\ 283[R(int) = 0.0538]$	5746[R(int) = 0.0538]					
Goodness-of-fit on F^2	1.002	1.044	1.042	1.032					
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0600, wR_2 = 0.1539$	$R_1 = 0.0819, wR_2 = 0.2077$	$R_1 = 0.0491, wR_2 = 0.1116$	$R_1 = 0.0440, wR_2 = 0.1154$					
R indices (all data)	$R_1 = 0.1189, wR_2 = 0.1834$	$R_1 = 0.1219, wR_2 = 0.2282$	$R_1 = 0.0915, wR_2 = 0.1212$	$R_1 = 0.0702, wR_2 = 0.1348$					

(4a), 1541966 (4c), 1541963 (4d), 1541969 (5a), 1541965 (5c), 1541961 (5d) contain the supplementary crystallographic data for this paper.[†]

4.3 Synthesis of $(PhCH_2)_2N[C(NHR)=(NR)]$ (R = 2,6-^{*i*}Pr₂-C₆H₃) (1)

A ⁿBuLi solution (10.0 mmol, 4 mL, 2.5 M in hexane) was added slowly to a stirred solution of (PhCH₂)₂NH (1.97 g, 10.0 mmol) in THF (30 mL) at room temperature, then stirred for 2 h. Subsequently, the solution of the in situ (PhCH₂)₂NLi was added to stirred THF solution of bis(2,6-diisopropylphenyl) а carbodiimide (3.63 g, 10.0 mmol) at room temperature, the mixture was stirred for 4 h and added slowly the distilled water to afford a clear orange solution. All volatiles were removed under vacuum. The residue was washed with water, and the product was extracted with hexane (3 \times 25 mL), all volatiles were removed under vacuum, and the yellowish powder was recrystallized in hexane at -35 °C to give colourless crystals (4.53 g, 81%). ¹H NMR (400 MHz, CDCl₃, 25 °C): 7.25–6.97 (m, 16H, Ar), 5.17 (s, 1H, -NH-), 4.29 (s, 4H, -CH₂Ph), 3.31-3.20 (m, 4H, $-CHMe_2$, 1.34 (d, I = 8 Hz, 6H, $-CHMe_2$), 1.25 (d, I = 8 Hz, 6H, -CHMe₂), 1.03 (d, J = 8 Hz, 6H, -CHMe₂), 0.91 (d, J = 8 Hz, 6H, -CHMe₂), ¹³C NMR (100 MHz, CDCl₃, 25 °C): $\delta = 149.8$ (NCN), 146.0 (Ar), 144.7 (Ar), 140.2 (Ar), 138.6 (Ar), 128.7 (Ar), 128.2 (Ar), 127.3 (Ar), 123.0 (Ar), 122.5 (Ar), 51.0 (-CH₂Ph), 29.0 (-CHMe2), 28.4 (-CHMe2), 25.6 (-CHMe2), 24.6 (-CHMe2), 22.6 (-CHMe₂), 21.9 (-CHMe₂); ¹H NMR (400 MHz, C₆D₆, 25 °C): 7.28 (s, 1H, Ar), 7.26 (s, 1H, Ar), 7.14-7.09 (m, 9H, Ar), 7.06-7.03 (m, 3H, Ar), 6.95 (s, 1H, Ar), 6,94 (s, 1H, Ar), 5.40 (s, 1H, -NH-), 4.43 (s, 4H, -CH₂Ph), 3.50 (m, 2H, -CHMe₂), 3.35 (m, 2H, -CHMe₂), 1.42 (d, J = 4 Hz, 6H, -CHM e_2), 1.38 (d, J = 8 Hz, 6H, -CHM e_2), 1.03 (d, J = 4 Hz, 6H, -CHMe₂), 0.83 (d, J = 4 Hz, 6H, -CHMe₂), ¹³C NMR (100 MHz, C₆D₆, 25 °C): δ = 150.1 (NCN), 146.1 (Ar), 145.1 (Ar), 140.3 (Ar), 138.9 (Ar), 135.5 (Ar), 128.8 (Ar), 128.5 (Ar), 127.2 (Ar), 124.1 (Ar), 123.5 (Ar), 123.4 (Ar), 51.5 (-CH₂Ph), 29.3 (-CHMe₂), 28.6 (-CHMe₂), 25.6 (-CHMe₂), 24.9 (-CHMe₂), 22.7 (-CHMe₂), 22.0 (-CHMe₂). Calcd for C₃₉H₄₉N₃ (%): C, 83.67; H, 8.82; N, 7.51; found: C, 83.96; H, 8.77; N, 7.48.

4.4 Synthesis of $[(PhCH_2)_2NC(NC_6H_4^{i}Pr_2-2,6)_2]$ Y(CH₂C₆H₄NMe₂-*o*)₂ (2a)

A THF solution (10 mL) of Y(CH₂C₆H₄NMe₂-o)₃ (0.25 g, 0.5 mmol) was added into a stirred solution (20 mL) of (PhCH₂)₂N [C(NHR)=(NR)] (R = 2,6^{-*i*}Pr₂-C₆H₃) (1) (0.28 g, 0.5 mmol) in THF. The reaction solution was left to stir for 3.5 days at 65 °C and all volatiles were removed under vacuum. The oily residue was washed with cold hexane and pale yellow powder was obtained by filtration. The pale yellow powder was recrystallized in toluene at -35 °C for 2 days to give white powder of **2a** 0.30 g (65%). ¹H NMR (400 MHz, C₆D₆, 25 °C): δ = 7.15–7.13 (m, 4H, Ar), 7.02–6.86 (m, 12H, Ar), 6.68 (d, *J* = 8 Hz, 4H, Ar), 6.59 (d, *J* = 12 Hz, 2H, Ar), 6.95–6.87 (m, 10H, Ar), 6.75–6.73 (m, 4H, Ar), 6.68 (d, *J* = 8 Hz, 4H, Ar), 6.52 (m, 2H, Ar), 4.28 (br s, 4H, $-CH_2$ Ph), 4.12 (m, 4H, $-CHMe_2$), 2.19 (s, 12H, $-NMe_2$), 1.81 (s, 4H, $-CH_2$ C₆H₄NMe₂-o), 1.50 (d, *J* = 6 Hz, 12H, $-CHMe_2$), 1.45 (d, *J* = 4 Hz, 12H, $-CHMe_2$), ¹³C NMR (100 MHz, C₆D₆, 25 °C): δ =

161.3 (NCN), 145.4 (d, J = 26 Hz, Ar), 144.2 (s, Ar), 141.8 (s, Ar), 136.0 (s, Ar), 129.9 (s, Ar), 127.4 (s, Ar), 126.7 (s, Ar), 124.4 (s, Ar), 123.8 (s, Ar), 120.8 (s, Ar), 118.2 (s, Ar), 53.2 (s, $-CH_2Ph$), 48.0 (d, J = 20 Hz, $-CH_2C_6H_4NMe_2$ -o), 46.6 (br s, $-NMe_2$), 29.1 (s, $-CHMe_2$), 24.7 (s, $-CHMe_2$), 24.2 (br s, $-CHMe_2$). Calcd for $C_{57}H_{72}N_5Y$ (%): C, 74.73; H, 7.92; N, 7.64; found: C, 75.25; H, 7.76; N, 7.20.

4.5 Synthesis of $[(PhCH_2)_2NC(NC_6H_4^{i}Pr_2-2,6)_2]$ La $(CH_2C_6H_4NMe_2-o)_2$ (2b)

A THF solution (10 mL) of La(CH₂C₆H₄NMe₂-o)₃ (0.27 g, 0.5 mmol) was added into a stirred THF solution (20 mL) of $(PhCH_2)_2N[C(NHR)=(NR)]$ (R = 2,6^{-*i*}Pr₂-C₆H₃) (1) (0.280 g, 0.5 mmol). The reaction solution was left to stir for 12 hours at 50 °C and all volatiles were removed under vacuum. The oily residue was washed with cold hexane and yellow powder was obtained by filtration. The powder was recrystallized in toluene at $-35 \degree$ C for 3 days to give yellow powder of 2b 0.21 g (43%). ¹H NMR (400 MHz, C₆D₆, 25 °C): δ = 7.14 (s, 2H, Ar), 7.12 (s, 2H, Ar), 6.99 (s, 1H, Ar), 6.97 (s, 1H, Ar), 6.95-6.87 (m, 10H, Ar), 6.75-6.73 (m, 4H, Ar), 6.68 (s, 1H, Ar), 6.66 (s, 1H, Ar), 6.61-6.58 (m, 2H, Ar), 4.18 (s, 4H, -CH₂Ph), 3.93 (m, 4H, -CHMe₂), 2.06 (s, 12H, $-NMe_2$), 1.84 (s, 4H, $-CH_2C_6H_4NMe_2-o$), 1.42 (d, J = 8 Hz, 12H, $-CHMe_2$, 1.35 (d, J = 8 Hz, 12H, $-CHMe_2$), ¹³C NMR (100) MHz, C₆D₆, 25 °C): δ = 158.4 (NCN), 145.1 (s, Ar), 143.8 (s, Ar), 141.1 (s, Ar), 141.0 (s, Ar), 136.4 (s, Ar), 130.0 (s, Ar), 129.3 (s, Ar), 128.6 (s, Ar), 128.0 (s, Ar), 127.6 (s, Ar), 127.4 (s, Ar), 124.2 (s, Ar), 122.9 (s, Ar), 119.7 (s, Ar), 119.3 (s, Ar), 61.6 (s, -CH₂C₆H₄NMe₂o), 52.4 (s, -CH₂Ph), 44.8 (s, -NMe₂), 29.1 (s, -CHMe₂), 24.6 (s, -CHMe₂), 24.1 (s, -CHMe₂). Calcd for C₅₇H₇₂N₅La (%): C, 70.86; H, 7.51; N, 7.25; found: C, 70.71; H, 7.43; N, 6.89.

4.6 Synthesis of $[(PhCH_2)_2NC(NC_6H_4^iPr_2-2,6)_2]$ Dy $(CH_2C_6H_4NMe_2-o)_2$ (2c)

A THF solution (10 mL) of Dy(CH₂C₆H₄NMe₂-o)₃ (0.28 g, 0.5 mmol) was added into a stirred solution (20 mL) of (PhCH₂)₂N [C(NHR)=(NR)] (R = 2,6-^{*i*}Pr₂-C₆H₃) (1) (0.28 g, 0.5 mmol) in THF. The reaction solution was left to stir for 3 days at 65 °C, and all volatiles were removed under vacuum. The oily residue was washed with cold hexane and pale yellow powder was obtained by filtration. The powder was recrystallized in toluene at -35 °C for 2 days to give pale yellow powder of **2c** 0.29 g (58%). Calcd for C₅₇H₇₂N₅Dy (%): C, 69.17; H, 7.33; N, 7.08; found: C, 69.25; H, 7.83; N, 6.71.

4.7 Synthesis of $[(PhCH_2)_2NC(NC_6H_4^{i}Pr_2-2,6)_2]$ Lu $(CH_2C_6H_4NMe_2-o)_2$ (2d)

A THF solution (10 mL) of Lu(CH₂C₆H₄NMe₂-o)₃ (0.29 g, 0.5 mmol) was added into a stirred THF solution (20 mL) of (PhCH₂)₂N[C(NHR)=(NR)] (R = 2,6-^{*i*}Pr₂-C₆H₃) (1) (0.28 g, 0.5 mmol). The reaction solution was left to stir for 3.5 days at 65 °C and all volatiles were removed under vacuum. The oily residue was washed with cold hexane and white powder was obtained by filtration. The white powder was recrystallized in toluene at -35 °C for 2 days to give a colourless crystalline complex **2d** 0.23 g (45%). ¹H NMR (400 MHz, C₆D₆, 25 °C): δ = 7.14–7.12 (m,

4H, Ar), 7.00–6.96 (m, 8H, Ar), 6.90–6.84 (m, 8H, Ar), 6.97 (s, 1H, Ar), 6.95–6.87 (m, 10H, Ar), 6.75–6.73 (m, 4H, Ar), 6.68 (d, J = 8 Hz, 4H, Ar), 6.52 (m, 4H, Ar), 4.31 (br s, 4H, $-CH_2Ph$), 4.20 (m, 4H, $-CHMe_2$), 2.21 (s, 12H, $-NMe_2$), 1.80 (s, 4H, $-CH_2C_6H_4NMe_2$ - o), 1.53 (d, J = 12 Hz, 12H, $-CHMe_2$), 1.47 (d, J = 8 Hz, 12H, $-CHMe_2$), ¹³C NMR (100 MHz, C₆D₆, 25 °C): $\delta =$ 161.8 (NCN), 145.7 (s, Ar), 145.5 (s, Ar), 142.3 (s, Ar), 136.0 (s, Ar), 129.9 (s, Ar), 127.4 (s, Ar), 126.3 (s, Ar), 124.5 (s, Ar), 124.2 (s, Ar), 121.2 (s, Ar), 117.8 (s, Ar), 53.4 (s, $-CH_2Ph$), 53.3 (s, $-CH_2C_6H_4NMe_2-o$), 47.2 (s, $-NMe_2$), 28.9 (s, $-CHMe_2$), 25.1 (s, $-CHMe_2$), 24.4 (s, $-CHMe_2$). Calcd for C₅₇H₇₂LuN₅ (%): C, 68.31; H, 7.24; N, 6.99; found: C, 69.01; H, 7.19; N, 6.72.

4.8 Synthesis of {[[PhCH₂)₂NC(NC₆H₄^{*i*}Pr₂-2,6)₂]Y(μ - η ²: η ¹-O₂CCH₂C₆H₄NMe₂- σ)(μ - η ¹: η ¹-O₂CCH₂C₆H₄NMe₂- σ)}₂ (3a)

A THF (10 mL) solution of complex 2a (0.46 g, 0.5 mmol) was placed in a tube with a Teflon stopcock and degassed by a freeze pump thaw cycle. One atmospheres of CO2 was introduced into the tube and the solution was concentrated to saturation after 10 minutes. Colourless crystals of 3a (0.45 g, 90%) were harvested after the solution stood at ambient temperature for 3 days. ¹H NMR (400 MHz, C_6D_6 , 25 °C): $\delta = 7.18-7.12$ (m, 8H, Ar), 6.98 (br s, 14H, Ar), 6.94-6.87 (m, 18H, Ar), 6.71-6.69 (m, 8H, Ar), 4.14 (s, 8H, -CH₂Ph), 3.88 (m, 8H, -CHMe₂), 2.47 (br s, 32H, $-OOCCH_2C_6H_4NMe_2-o)$, 1.28 (t, J = 8 Hz, 48H, $-CHMe_2$), ¹³C NMR (100 MHz, C_6D_6 , 25 °C): $\delta = 186.2$ (s, OCO), 165.1 (s, NCN), 152.7 (s, Ar), 143.9 (s, Ar), 142.5 (s, Ar), 136.6 (s, Ar), 131.1 (s, Ar), 130.6 (s, Ar), 129.0 (s, Ar), 127.0 (s, Ar), 126.6 (s, Ar), 123.6 (s, Ar), 123.4 (s, Ar), 123.3 (s, Ar), 123.1 (s, Ar), 122.9 (s, Ar), 119.3 (s, Ar), 52.2 (s, -CH2Ph), 45.1 (br s, -OOCCH2C6H4NMe2-o), 27.9 (s, -CHMe₂), 25.6 (s, -CHMe₂), 23.9 (s, -CHMe₂). Calcd for C₁₁₈H₁₄₄N₁₀O₈Y₂ (%): C, 70.57; H, 7.23; N, 6.97; found: C, 70.52; H, 7.33; N, 6.74.

4.9 Synthesis of {[(PhCH₂)₂NC(NC₆H₄^{*i*}Pr₂-2,6)₂]La(μ - η ²: η ¹-O₂CCH₂C₆H₄NMe₂- σ)(μ - η ¹: η ¹-O₂CCH₂C₆H₄NMe₂- σ)}₂ (3b)

Complex **3b** was obtained as a colourless crystalline product (0.38 g, 73%), similarly to the preparation of **3a** described above. ¹H NMR (400 MHz, C₆D₆, 25 °C): δ = 7.35-7.29 (m, 4H, Ar), 7.22-7.18 (m, 5H, Ar), 7.04-7.00 (m, 12H, Ar), 6.91-6.88 (m, 10H, Ar), 6.86-6.82 (m, 4H, Ar), 6.68 (d, *J* = 4 Hz, 8H, Ar), 4.08 (s, 8H, -CH₂Ph), 3.80 (m, 8H, -CHMe₂), 3.47 (br s, 8H, -OOCCH₂C₆-H₄NMe₂-o), 2.54 (s, 24H, -OOCCH₂C₆H₄NMe₂-o), 1.29 (d, *J* = 4 Hz, 24H, -CHMe₂), 1.25 (d, *J* = 4 Hz, 24H, -CHMe₂), ¹³C NMR (100 MHz, C₆D₆, 25 °C): δ = 183.6 (s, OCO), 163.4 (s, NCN), 153.3 (s, Ar), 143.8 (s, Ar), 142.3 (s, Ar), 131.5 (s, Ar), 129.3 (s, Ar), 128.8 (s, Ar), 119.8 (s, Ar), 52.0 (s, -CH₂Ph), 45.6 (s, -OOCCH₂C₆H₄-NMe₂-o), 38.6 (s, -OOCCH₂C₆H₄NMe₂-o), 28.4 (s, -CHMe₂), 26.6 (s, -CHMe₂), 23.7 (s, -CHMe₂). Calcd for C₁₁₈H₁₄₄N₁₀O₈La₂ (%): C, 67.22; H, 6.88; N, 6.64; found: C, 66.70; H, 7.45; N, 5.97.

4.10 Synthesis of {[[PhCH₂)₂NC(NC₆H₄^{*i*}Pr₂-2,6)₂]Dy(μ - η ²: η ¹-O₂CCH₂C₆H₄NMe₂- σ)(μ - η ¹: η ¹-O₂CCH₂C₆H₄NMe₂- σ)}₂ (3c)

Complex **3c** was obtained as a colourless crystalline product (0.47 g, 88%), similarly to the preparation of **3a** described above.

Calcd for $C_{118}H_{144}N_{10}O_8Dy_2$ (%): C, 65.75; H, 6.73; N, 6.50; found: C, 66.16; H, 6.92; N, 6.56.

4.11 Synthesis of {[[PhCH₂)₂NC(NC₆H₄^{*i*}Pr₂-2,6)₂]Lu(μ - η ²: η ¹-O₂CCH₂C₆H₄NMe₂-*o*)(μ - η ¹: η ¹-O₂CCH₂C₆H₄NMe₂-*o*)}₂ (3d)

Complex **3d** was obtained as a colourless crystalline product (0.50 g, 92%), similarly to the preparation of **3a** described above. ¹H NMR (400 MHz, C₆D₆, 25 °C): δ = 7.36–7.29 (m, 10H, Ar), 7.01–6.87 (m, 30H, Ar), 6.70 (d, J = 4 Hz, 8H, Ar), 4.14 (s, 8H, –CH₂Ph), 3.91 (m, 8H, –CHMe₂), 3.50 (br s, 8H, –OOCCH₂C₆-H₄NMe₂-o), 2.62–2.40 (m, 24H, –OOCCH₂C₆H₄NMe₂-o), 1.31– 1.27 (m, 48H, –CHMe₂), ¹³C NMR (100 MHz, C₆D₆, 25 °C): δ = 183.7 (s, OCO), 164.7 (s, NCN), 153.0 (s, Ar), 144.2 (s, Ar), 143.2 (s, Ar), 136.9 (s, Ar), 131.4 (br s, Ar), 127.3 (br s, Ar), 127.0 (s, Ar), 124.0 (s, Ar), 123.8 (s, Ar), 123.7 (s, Ar), 119.4 (br s, Ar), 52.6 (s, –CH₂Ph), 45.4 (s, –OOCCH₂C₆H₄NMe₂-o), 38.0 (br s, –OOCCH₂C₆H₄NMe₂-o), 28.3 (s, –CHMe₂), 26.0 (s, –CHMe₂), 24.4 (s, –CHMe₂). Calcd for C₁₁₈H₁₄₄N₁₀O₈Lu₂ (%): C, 65.00; H, 6.66; N, 6.50; found: C, 65.68; H, 6.39; N, 6.05.

4.12 Synthesis of {[(PhCH₂)₂NC(NC₆H₄^{*i*}Pr₂-2,6)₂]Y [μ -S(CH₂C₆H₄NMe₂-*o*)]₂}₂ (4a)

To a stirred THF (20 mL) solution of complex 2a (0.46 g, 0.5 mmol) was added slowly a THF (10 mL) solution of S₈ (0.032 g, 0.125 mmol). The reaction solution was left to stir for 3.5 days at 65 °C, and all volatiles were removed under vacuum. After being washed with cold hexane, the oily residue turned to white powder which then was collected by filtration. The white powder was recrystallized in toluene at room temperature for 2 days to give a colourless crystalline complex 4a 0.38 g (77%). ¹H NMR (400 MHz, C_6D_6 , 25 °C): $\delta = 7.76-7.73$ (m, 3H, Ar), 7.15-7.15 (m, 11H, Ar), 7.01-6.95 (m, 12H, Ar), 6.88-6.81 (m, 15H, Ar), 6.51-6.49 (m, 7H, Ar), 4.28 (br s, 8H, -SCH₂C₆H₄NMe₂-0), 4.12 (s, 8H, -CH₂Ph), 3.89 (m, 8H, -CHMe₂), 2.58 (s, 24H, -NMe₂), 1.43 (br s, 24H, $-CHMe_2$), 1.27 (d, J = 4.0 Hz, 24H, $-CHMe_2$), ¹³C NMR (100 MHz, C_6D_6 , 25 °C): $\delta = 166.09$ (s, NCN), 152.6 (s, Ar), 143.3 (s, Ar), 142.7 (s, Ar), 137.8 (s, Ar), 135.9 (s, Ar), 131.3 (s, Ar), 129.4 (s, Ar), 127.2 (s, Ar), 126.5 (s, Ar), 124.6 (s, Ar), 124.2 (s, Ar), 123.0 (s, Ar), 118.3 (s, Ar), 52.5 (s, -CH₂Ph), 45.2 (s, -NMe₂), 34.6 (s, -SCH₂C₆H₄NMe₂-o), 29.0 (s, -CHMe₂), 26.2 (s, -CHMe₂), 24.2 $(s, -CHMe_2)$. Calcd for $C_{114}H_{144}N_{10}S_4Y_2$ (%): C, 69.84; H, 7.40; N, 7.14; found: C, 69.40; H, 7.44; N, 6.73.

4.13 Synthesis of {[(PhCH₂)₂NC(NC₆H₄^{*i*}Pr₂-2,6)₂]La [μ -S(CH₂C₆H₄NMe₂- σ)]₂}₂ (4b)

To a stirred THF (20 mL) solution of complex **2b** (0.48 g, 0.5 mmol) was added slowly a THF (10 mL) solution of S₈ (0.032 g, 0.125 mmol). After it was stirred at room temperature for 12 h, all volatiles were removed under vacuum, and washed with cold hexane, the oily residue turn to white powder which then was collected by filtration. The white powder was recrystallized in toluene at -35 °C for 3 days to give a colourless crystalline complex **4b** 0.31 g (61%). ¹H NMR (400 MHz, C₆D₆, 25 °C): $\delta =$ 7.62 (d, *J* = 4.0 Hz, 3H, Ar), 7.17–7.14 (m, 7H, Ar), 7.10–7.05 (m, 12H, Ar), 6.98–6.92 (m, 8H, Ar), 6.89–6.86 (m, 11H, Ar), 6.61–6.60 (m, 7H, Ar), 4.52 (br s, 8H, –SCH₂C₆H₄NMe₂–*o*), 4.04 (s, 8H,

 $\begin{aligned} -CH_2 \text{Ph}), 3.77 & (\text{m}, 8\text{H}, -CHMe_2), 2.61 & (\text{s}, 24\text{H}, -NMe_2), 1.48 & (\text{d}, J \\ = 4.0 & \text{Hz}, 24\text{H}, -CHMe_2), 1.22 & (\text{d}, J = 4.0 & \text{Hz}, 24\text{H}, -CHMe_2), {}^{13}\text{C} \\ \text{NMR} & (100 & \text{MHz}, \text{C}_6\text{D}_6, 25 \, ^\circ\text{C}): \delta = 164.4 & (\text{s}, \text{NCN}), 152.5 & (\text{s}, \text{Ar}), \\ 142.7 & (\text{s}, \text{Ar}), 142.6 & (\text{s}, \text{Ar}), 138.7 & (\text{s}, \text{Ar}), 136.4 & (\text{s}, \text{Ar}), 131.2 & (\text{s}, \text{Ar}), \\ 129.2 & (\text{s}, \text{Ar}), 128.8 & (\text{s}, \text{Ar}), 127.1 & (\text{s}, \text{Ar}), 126.4 & (\text{s}, \text{Ar}), 124.2 & (\text{s}, \text{Ar}), \\ 124.1 & (\text{s}, \text{Ar}), 123.3 & (\text{s}, \text{Ar}), 118.7 & (\text{s}, \text{Ar}), 51.8 & (\text{s}, -CH_2 \text{Ph}), 45.3 & (\text{s}, \\ -NMe_2), 33.5 & (\text{s}, -SCH_2 \text{C}_6 \text{H}_4 \text{NMe}_2 \text{-}o), 28.8 & (\text{s}, -CHMe_2), 27.6 & (\text{s}, \\ -CHMe_2), 23.6 & (\text{s}, -CHMe_2). & \text{Calcd for } C_{114}\text{H}_{144}\text{N}_{10}\text{S}_4\text{La}_2 & (\%): \text{C}, \\ 66.45; & \text{H}, 7.04; & \text{N}, 6.80; & \text{found: C}, 66.07; & \text{H}, 6.91; & \text{N}, 6.60. \end{aligned}$

4.14 Synthesis of {[(PhCH₂)₂NC(NC₆H₄^{*i*}Pr₂-2,6)₂]Dy $[\mu$ -S(CH₂C₆H₄NMe₂-o)]₂} (4c)

Complex **4c** was obtained as a colourless crystalline product (0.38 g, 73%), similarly to the preparation of **4a** described above. Calcd for $C_{114}H_{144}N_{10}S_4Dy_2$ (%): C, 64.96; H, 6.89; N, 6.65; found: C, 64.84; H, 6.83; N, 6.73.

4.15 Synthesis of {[(PhCH₂)₂NC(NC₆H₄^{*i*}Pr₂-2,6)₂]Lu $[\mu$ -S(CH₂C₆H₄NMe₂- σ)]₂}₂ (4d)

Complex 4d was obtained as a colourless crystalline product (0.36 g, 67%), similarly to the preparation of 4a described above. ¹H NMR (400 MHz, C₆D₆, 25 °C): δ = 7.83-7.80 (m, 3H, Ar), 7.18-7.16 (m, 14H, Ar), 6.87-6.81 (m, 12H, Ar), 6.48 (d, *J* = 4.0 Hz, 6H, Ar), 4.46 (br s, 8H, -SCH₂C₆H₄NMe₂-*o*), 4.13 (s, 8H, -CH₂Ph), 3.95 (m, 8H, -CHMe₂), 2.57 (s, 24H, -NMe₂), 1.41 (d, *J* = 8.0 Hz, 24H, -CHMe₂), 1.30 (d, *J* = 4.0 Hz, 24H, -CHMe₂), ¹³C NMR (100 MHz, C₆D₆, 25 °C): δ = 165.3 (s, NCN), 152.3 (s, Ar), 142.8 (s, Ar), 142.6 (s, Ar), 137.3 (s, Ar), 135.4 (s, Ar), 130.8 (s, Ar), 129.0 (s, Ar), 126.7 (s, Ar), 126.1 (s, Ar), 124.4 (s, Ar), 123.7 (s, Ar), 122.5 (s, Ar), 117.9 (s, Ar), 52.4 (s, -CH₂Ph), 44.7 (s, -NMe₂), 34.3 (s, -SCH₂-C₆H₄NMe₂-*o*), 28.6 (s, -CHMe₂), 25.6 (s, -CHMe₂), 23.8 (s, -CHMe₂). Calcd for C₁₁₄H₁₄₄N₁₀S₄Lu₂ (%): C, 64.20; H, 6.81; N, 6.57; found: C, 64.58; H, 7.51; N, 6.18.

4.16 Synthesis of $[(PhCH_2)_2NC(NC_6H_4^{i}Pr_2-2,6)_2]Y$ {SC(CH₂C₆H₄NMe₂-*o*)NPh}₂ (5a)

A THF (10 mL) solution of PhNCS (0.108 mL, 1 mmol) was added slowly to a stirred THF (20 mL) solution of complex 2a (0.46 g, 0.5 mmol). The reaction solution was left to stir at room temperature for 12 h and all volatiles were removed under vacuum. After being washed with cold hexane, the oily residue turned to white powder which then was collected by filtration and dissolved in toluene. The solution was concentrated to saturation and stood at ambient temperature. Colourless crystals of 5a (0.46 g, 77%) were obtained after 2 days. ¹H NMR (400 MHz, C₆D₆, 25 °C): δ = 7.74–7.71 (m, 2H, Ar), 7.19–7.14 (m, 4H, Ar), 7.04 (br s, 6H, Ar), 6.95–6.92 (m, 2H, Ar), 6.95–6.92 (m, 2H, Ar), 6.89–6.83 (m, 10H, Ar), 6.80–6.76 (m, 2H, Ar), 6.66–6.65 (m, 4H, Ar), 6.39 (d, J = 8.0 Hz, 4H, Ar), 4.20 (s, 4H, $-CH_2Ph$), 4.14 (s, 4H, -CH₂C₆H₄NMe₂-o), 3.94 (m, 4H, -CHMe₂), 2.37 (s, 12H, $-NMe_2$, 1.27 (d, J = 8.0 Hz, 12H, $-CHMe_2$), 1.23 (d, J = 4.0 Hz, 12H, -CHMe₂), ¹³C NMR (100 MHz, C₆D₆, 25 °C): δ = 199.8 (s, NCS), 165.2 (s, NCN), 153.4 (s, Ar), 147.7 (s, Ar), 143.6 (s, Ar), 143.1 (s, Ar), 136.1 (s, Ar), 133.0 (s, Ar), 131.0 (s, Ar), 129.5 (s, Ar), 129.0 (s, Ar), 127.2 (s, Ar), 124.6 (s, Ar), 124.4 (s, Ar), 124.1 (s, Ar), 123.8 (s, Ar), 123.3 (s, Ar), 120.2 (s, Ar), 52.4 (s, -CH₂Ph), 44.9 (s,

-NMe₂), 42.4 (s, -CH₂C₆H₄NMe₂-*o*), 28.7 (s, -CHMe₂), 25.7 (s, -CHMe₂), 24.2 (s, -CHMe₂). Calcd for C₇₁H₈₂N₇S₂Y (%): C, 71.87; H, 6.97; N, 8.26; found: C, 70.97; H, 7.34; N, 8.08.

4.17 Synthesis of [(PhCH₂)₂NC(NC₆H₄^{*i*}Pr₂-2,6)₂]La {SC(CH₂C₆H₄NMe₂-*o*)NPh}₂(THF) (5b)

A THF (10 mL) solution of PhNCS (0.108 mL, 1 mmol) was added slowly to a stirred THF (20 mL) solution of complex 2b (0.48 g, 0.5 mmol). The reaction solution was left to stir at room temperature for 12 h and all volatiles were removed under vacuum. After being washed with cold hexane, the oily residue turned to white powder which then was collected by filtration and dissolved in toluene. The solution was concentrated to saturation and layered with 2 mL hexane solvent. White participate 5b was obtained after the solution stood at -35 °C for 3 days. Yield (0.28 g, 46%). ¹H NMR (400 MHz, C₆D₆, 25 °C): $\delta = 7.72-7.70$ (m, 2H, Ar), 7.13-7.08 (m, 8H, Ar), 7.03-6.82 (m, 22H, Ar), 6.37 (d, J = 8 Hz, 4H, Ar), 4.17 (s, 4H, $-CH_2C_6H_4NMe_2$ o), 4.12 (s, 4H, -CH₂Ph), 3.98 (m, 4H, -CHMe₂), 3.54 (m, 4H, THF), 2.36 (s, 12H, $-NMe_2$), 1.36 (d, J = 8 Hz, 12H, $-CHMe_2$), 1.22 (d & m, J = 8 Hz, 24H, -CH Me_2 & THF & Hex), ¹³C NMR (100 MHz, C_6D_6 , 25 °C): $\delta = 198.9$ (s, NCS), 163.1 (s, NCN), 153.2 (s, Ar), 148.9 (s, Ar), 142.6 (s, Ar), 137.2 (s, Ar), 131.3 (s, Ar), 129.5 (s, Ar), 128.9 (s, Ar), 128.8 (s, Ar), 128.3 (s, Ar), 127.5 (s, Ar), 127.2 (s, Ar), 124.4 (s, Ar), 123.5 (s, Ar), 123.2 (s, Ar), 119.8 (s, Ar), 69.1 (s, THF), 51.7 (s, -CH₂Ph), 45.0 (s, -NMe₂), 43.2 (s, -CH₂C₆H₄NMe₂o), 28.5 (s, -CHMe₂), 27.0 (s, -CHMe₂), 25.3 (s, THF), 24.1 (s, -CHMe₂). Calcd for C₇₅H₉₀N₇S₂OLa (%): C, 68.84; H, 6.93; N, 7.49; found: C, 68.70; H, 7.06; N, 7.73.

4.18 Synthesis of $[(PhCH_2)_2NC(NC_6H_4^{i}Pr_2-2,6)_2]Dy$ {SC(CH₂C₆H₄NMe₂-o)NPh}₂ (5c)

Complex **5c** was obtained as a colourless crystalline product (0.44 g, 70%), similarly to the preparation of **5a** described above. Calcd for $C_{71}H_{82}N_7S_2Dy$ (%): C, 67.67; H, 6.56; N, 7.78; found C, 67.59; H, 6.87; N, 7.80.

4.19 Synthesis of $[(PhCH_2)_2NC(NC_6H_4^{i}Pr_2-2,6)_2]Lu$ {SC(CH₂C₆H₄NMe₂-o)NPh}₂ (5d)

Complex 5d was obtained as a colourless crystalline product (0.41 g, 65%), similarly to the preparation of 5a described above. ¹H NMR (400 MHz, C_6D_6 , 25 °C): $\delta = 7.79-7.76$ (m, 2H, Ar), 7.20-7.14 (m, 5H, Ar), 7.05 (br s, 6H, Ar), 6.95-6.84 (m, 9H, Ar), 6.78-6.75 (m, 2H, Ar), 6.65 (br s, 4H, Ar), 6.38 (d, J = 8.0 Hz, 4H, Ar),4.25 (br s, 4H, -CH₂Ph), 4.15 (s, 4H, -CH₂C₆H₄NMe₂-o), 4.02 (m, 4H, $-CHMe_2$), 2.36 (s, 12H, $-NMe_2$), 1.29 (d, J = 8.0 Hz, 12H, -CHMe₂), 1.23 (br s, 12H, -CHMe₂), ¹³C NMR (100 MHz, C₆D₆, 25 °C): $\delta = 200.2$ (s, NCS), 165.1 (s, NCN), 153.4 (s, Ar), 147.4 (s, Ar), 143.6 (s, Ar), 143.5 (s, Ar), 136.0 (s, Ar), 133.0 (s, Ar), 130.9 (s, Ar), 129.6 (s, Ar), 128.9 (s, Ar), 127.2 (s, Ar), 124.8 (s, Ar), 124.4 (s, Ar), 124.3 (s, Ar), 123.8 (s, Ar), 123.4 (s, Ar), 120.2 (s, Ar), 52.6 (s, -CH₂Ph), 45.0 (s, -NMe₂), 42.6 (s, -CH₂C₆H₄NMe₂-o), 28.6 (s, -CHMe₂), 25.7 (s, -CHMe₂), 24.6 (s, -CHMe₂). Calcd for C₇₁H₈₂N₇S₂Lu (%): C, 67.01; H, 6.49; N, 7.70; found: C, 66.80; H, 6.81; N, 7.60.

4.20 Typical procedure for polymerization of isoprene

The procedures for isoprene polymerization were similar, thus take complex 2a as an example and corresponding polymerization procedure is given below. For $2a/[Ph_3C][B(C_6F_5)_4]$ binary system: in a glovebox, a magnetic stir bar was placed in a 100 mL flask, to which a dropping funnel was attached. Isoprene (1.022 g, 15 mmol), 2a (0.018 g, 0.020 mmol) and C₆H₅Cl (8 mL) were charged into the flask. A C₆H₅Cl solution (2 mL) of [Ph₃C] $[B(C_6F_5)_4]$ (0.0185 g, 0.020 mmol) was charged to the dropping funnel. The reaction apparatus was moved outside and placed in a water bath (25 °C). After 10 min, the C₆H₅Cl solution of $[Ph_3C][B(C_6F_5)_4]$ was dropped into the mixture of 2a and isoprene under rapid stirring. After the mixture was stirred at 25 °C for 10 min, methanol was injected to terminate the polymerization. The reaction mixture was poured into a large quantity (200 mL) of methanol containing a small amount of hydrochloric acid and butylhydroxytoluene (BHT) as a stabilizing agent under stirring. The precipitated polymer was isolated by decantation, washed with methanol, and then dried under vacuum at 60 °C to a constant weight to afford 1.02 g of 3,4-rich polyisoprene (~100% yield). For $2a/[Ph_3C][B(C_6F_5)_4]/$ AlR₃ ternary systems: isoprene (1.022 g, 15 mmol), 2a (0.018 g, 0.020 mmol), AlR₃ (100 μ L, 1 mol L⁻¹ in hexane) and C₆H₅Cl (8 mL) were charged into the flask and other operations are same as above-mentioned binary system.

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