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Rare-earth metal alkyl complexes bearing alkoxy N-heterocyclic carbene ligand: synthesis, characterization, catalysis for isoprene polymerization

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Treatment of imidazolium iodide [R-NHC-CH$_2$CH(^{n}Bu)OH]I (1a (R= methyl), 1b (R= isopropyl) and benzimidazole iodide [R-NHC(C$_6$H$_4$)-CH$_2$CH(^{n}Bu)OH]I (2a (R=methyl) , 2b(R=isopropyl)), respectively, with ((trimethylsilyl)methyl)lithium (LiCH$_2$SiMe$_3$) followed by rare-earth metal tris(alkyl)s (Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$) (Ln=Sc, Y, Lu), afforded the alkoxy-modified N-heterocyclic carbene ligated rare-earth metal bis(alkyl) complexes {[R-NHC-CH$_2$CH(^{n}Bu)OLn(CH$_2$SiMe$_3$)$_2$]$_2$ (3a(R=methyl, Ln=Sc), 3b(R= methyl, Ln= Lu), 4a(R= isopropyl, Ln=Y), 4b(R= isopropyl, Ln=Lu)) and [(CH$_3$)$_2$CH-NHC(C$_6$H$_4$)-CH$_2$CH(^{n}Bu)OY(CH$_2$SiMe$_3$)$_2$]$_2$ (5)} via double-deprotonation reactions. All complexes were characterized by NMR spectroscopy, elemental analysis and X-ray crystallography. They are dimers in which two rare-earth metal ions are bridged by two μ^2-O atoms. Under the activation of an organoborate, complexes 3a showed cis-1,4 enriched regioselectivity for isoprene polymerization (84.3%).

Introduction

N-heterocyclic carbene (NHC) ligands have drawn more attention due to low toxicity, strong σ-donor in transition metal chemistry over the past few decades.[1] By changing the substituents on the nitrogen atom, it is easy to get N-heterocyclic carbene ligands with various sterics and electronics. Recently, the functionalized N-heterocyclic carbene ligands via modifying the imidazolium salt with a pendant anionic group become one of the most efficient ligands in coordination chemistry. These ligands are hemiliable, anticipated to change the coordination sphere, chirality of the covalently attaching metal centers.[2]

To date, functionalized NHC-supported rare-earth metal complexes have been explored by several groups. Shen Qi *et al*. prepared a tris-phenoxo-tethered N-Heterocyclic carbene supported yttrium complex and the lanthanide bromides bearing the salicylaldiminato functionalized NHC ligand.[3] Arnold *et al*. designed a variety of amino- and alkoxyl-functionalized NHC rare-earth metal complexes.[4] They successfully synthesized the carbene-amine-supported lanthanide bis(amido) complexes through the transamination reaction between the lithium carbene-amine and the homoleptic lanthanide tris(amide). Following the similar method, they obtained the alkoxy NHC ligands[5] stabilized yttrium bis(amido) complexes.

Although a lot of functionalized NHC rare-earth metal complexes having been explored, there are only few reports about the rare-earth metal alkyl complexes bearing functionalized NHC ligands. Neutral NHC coordinated scandium tris(alkyl) complexes $[\{2,6-C_6H_3R_2NCH\}_2CSc(CH_2SiMe_3)_3]$ synthesized by Xiao-bing Lu *et al*. showed excellent activities for polymerization of 1-octene and copolymerization of 1-hexene and 1,5-hexadiene.[6] Okuda *et al*. prepared several steric bulky neutral NHC rare-earth metals tris(alkyl) complexes.[7] Our group reported firstly the indenyl-, fluorenyl- and amidinato-functionalized NHC ligated rare-earth metal bis(alkyl) complexes,[8] which showed high activity and 3,4-regioselectivity (>99%) for isoprene polymerization. We also found that the 3,4-selectivity decreased with the steric hindrance of the ligands decreasing from fluorenyl-NHC and amidino-NHC to indenyl-NHC, suggesting that the more bulky ligand facilitates the 3,4-regio-selectivity. Herein, we report

the alkoxy NHC ligands and the corresponding new rare-earth metal alkyl complexes. The preliminary catalytic performance of the scandium complex for isoprene polymerization was studied, which showed that the less bulky ligand provided a more opening coordination sphere for the active scandium center to afford the enriched 1,4-regioselectivity.

Results and Discussion

The mixture of 1,2-epoxyhexane with 1 equivalent of imidazole was stirred for 12 h at 50 °C, which was further treated with 1 equivalent of iodomethane and 2-iodopropane to give ligands 1a and 1b, respectively, in high isolated yields.[5] Following the same procedure compounds 2a and 2b were prepared by using benzimidazole to replace imidazole (Scheme 1). These ligands have similar structures, showing the similar topologies in the ^1H and ^{13}C NMR spectra. Taking compound 1a as an example, the ylidene proton NHC-*H* shows a typical singlet resonance at δ 9.38 ppm; while the triplet resonance at δ 0.89 and multiple resonances at δ 1.32 and 1.54 ppm are attributed to the *n*-butane protons; the resonance of ylidene carbon appears at δ 135.99 ppm, consistent with the previous report.[5]
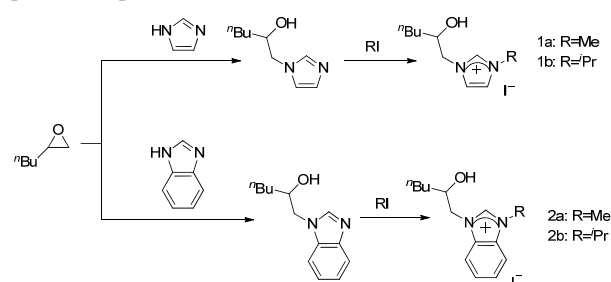
Scheme 1. Synthesis of the alkoxy NHC ligands

The alkoxy NHC ligands 1a, 1b, 2a and 2b reacted with one equimolar of $LiCH_2SiMe_3$ in toluene for 20 min at room temperature to give the neutral carbene intermediates, respectively. The resulting carbene mixtures were added into the toluene solution of rare-earth metal tris(alkyl)s $Ln(CH_2SiMe_3)_3(THF)_2$ and maintained stirring for 2h. Concentration, filtration and cooling at –30 °C afforded colorless crystals of the corresponding bi(alkyl) complexes $[R\text{-}NHC\text{-}CH_2CH(^nBu)OLn(CH_2SiMe_3)_2]_2$ (**3a**(R=methyl, Ln=Sc), **3b**(R= methyl, Ln= Lu), **4a**(R= isopropyl, Ln=Y), **4b**(R= isopropyl, Ln=Lu)) and $[(CH_3)_2CH\text{-}NHC(C_6H_4)\text{-}CH_2CH(^nBu)OY(CH_2SiMe_3)_2]_2$ (**5**)} in 47.7%-61.6% isolated yields (Scheme 2).
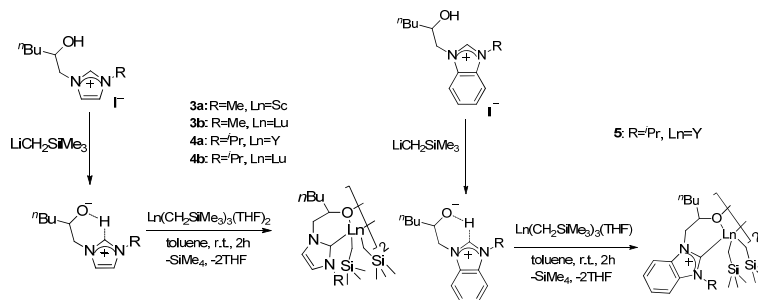
Scheme 2. Synthesis of NHC-ligated rare-earth metal bis(alkyl)s complexes

The complexes were confirmed by ^{1}H and ^{13}C NMR spectrum analyses. Since the overall molecular structure of complexes **3a**, **3b**, **4a**, **4b** and **5** is similar, complex **3b** was chosen to be discussed in detail. Compared with the ligand precursor 1a, the disappearance of ylidene proton suggested the completeness of the reaction. The singlet resonances at δ 0.25 and 0.53ppm are assignable to the methyl protons of CH_2SiCH_3, which is analogous to complex $(Ind\text{-}NHC)Lu(CH_2SiMe_3)_2$ we reported previously.[8a] The characteristic signal of ylidene carbon at δ 198.00, which is consistent with the result reported,[8] confirms the formation of a direct $Lu\text{-}C_{carbene}$ linkage.

Fig. 1 X-ray structure of **3a** (35% probability of thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sc1–C9 2.3846(17), Sc1–O1 2.0986(11), Sc1– C2 2.2464(17), Sc1–C1 2.2340(17), N1–C9 1.357(2), N2–C9^i 1.360(2); O1–Sc1–O1^i 73.87(5), C1–Sc1–C2 111.30(7), N1–C9–N2^i 103.11(14), N2^i–C9–Sc1 124.60(11), N1–C9–Sc1 132.16(12), C1–Sc1–C9 97.47(6), C2–Sc1–C9 90.40(6), O1^i–Sc1–C2 135.77(6), O1^i–Sc1–C1 112.83(5).

Fig. 2 X-ray structure of **3b** (35% probability of thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Lu–C2 2.487(2), C1–N1 1.460(6), C2–N2 1.351(3), Lu–O 2.2200(14), C11–Lu 2.346(2), C12–Lu 2.355(2); N2–C2–N1 103.94(18), O^i–Lu–O 72.86(6), O–Lu–C11 112.78(7), O–Lu–C12 135.09(7), C11–Lu–C12 112.00(8).
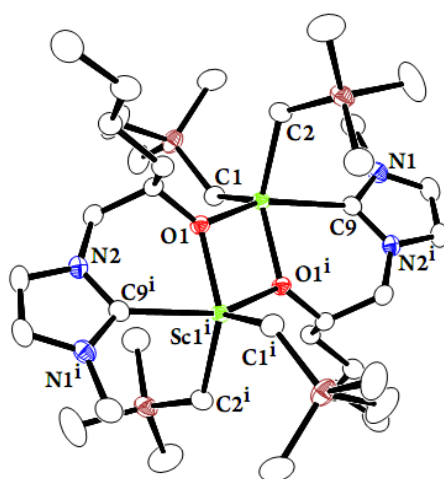

Fig. 3 X-ray structure of **4a** (35% probability of thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y1–O1 2.239(4), Y1–O2 2.254(4), Y2–O1 2.250(5), Y2–O2 2.245(4), Y2–C7 2.552(7), Y1–C27 2.549(7), N1–C7 1.353(8), N2–C7 1.355(8), N3–C27 1.362(8), N4–C27 1.357(8), Y1–C13 2.420(7), Y1–C14 2.412(9), Y2–C33 2.371(9), Y2–C34 2.416(7) ; N1–C7–N2 103.6(6), N3–C27–N4 103.5(6), O1–Y1–O2 72.07(15), O2–Y1–C27 77.50(19), O1–Y1–C27 146.44(19), O2–Y2–O1 72.03(14), Y1–O1–Y2 108.12(19), Y2–O2–Y1 107.77(18), C14–Y1–C13 112.9(3), C33–Y2–C34 112.1(3).
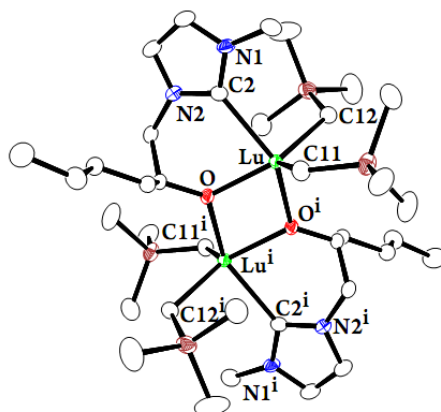
Fig. 4 X-ray structure of **4b** (35% probability of thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Lu1–C9 2.477(12), Lu1–O1 2.195(7), Lu1–C1 2.373(14), Lu1–C2 2.319(12), N2–C9 1.343(16), N1–C9 1.360(14); C1–Lu1–C9 93.0(5), O1–Lu1–O1^i 73.2(3), C2–Lu1–C1 111.9(5), C2–Lu1–C9 100.0(4).
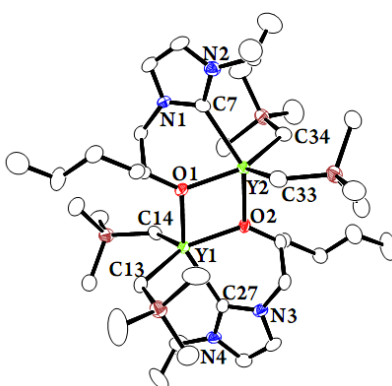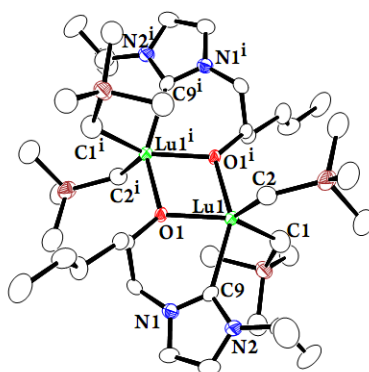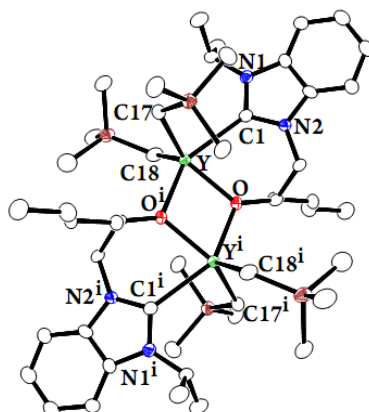

Fig. 5 X-ray structure of **5** (35% probability of thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): O–Y 2.240(3), C1–Y 2.557(4), C1–N1 1.354(5) , C1–N2 1.362(5), C17–Y 2.412(4), C18–Y 2.482(4) ; N1–C1–N2 105.3(3), O–Y–C1 77.28(12), C18–Y–C17 113.78(15), O–Y–O^i 72.01(11).

X-ray diffraction analysis reveals that all these complexes are binuclear tetra(alkyl) (Fig.s 1–5, the crystallographic data are summarized in Table S1), where the two rare-earth metal ions are bridged by two μ^2-O atoms. The dimerization may be caused by the small radius of hydroxyl and the flexibility of n-butane spacer. Each metal center is coordinated by one carbene fraction, two alkyls and two μ^2-O atoms, generating a twisted trigonal bipyramid geometry. For **3a**, **3b**, **4b** and **5**, it could be easily found that two central metal ions and two oxygen atoms constitute a parallelogram. However, for **4a**, the

central metal ion and the oxygen atom are not located in the same plane. The bond length of Y–C$_{carbene}$ (2.552(7) Å for **4a** and 2.557(4) Å for **5**) is similar to that in the alkoxy NHC yttrium bis(amindo) complexes (Y-C$_{carbene}$ = 2.599(2) Å).[4e] Bond length of Ln-C$_{carbene}$ is 2.3846(17) Å for **3a** and 2.487(2) Å for **3b**, which increases with the Ln (Sc, Lu) ionic radius. [9] The bond angles of C$_{carbene}$–Y–O (**4a** 77.50(19) °, **5** 77.28(12) °) are comparable to those found in Cp$_2$Y(L) (79.90(15)°), L=[OCMe$_2$CH$_2$(1-C{NCHCHN^{i}Pr})].[4g]

Table 1. Polymerization of isoprene using functionalized NHC rare-earth metal bis(alkyl) complexes [a]

entry	Cat.	[B]/[cat]	Time (h)	Yield (%)	cis-1,4 [b]	trans-1,4 [b]	3,4- [b]	$M_{n,calcd}$ [c] $\times 10^{-4}$	M_n [d] $\times 10^{-4}$	M_w/M_n [d]
1	**3a**	1	2	trace	–	–	–	–	–	–
2	**3a**	2	2	70.3	68.7	28.0	3.3	2.39	2.16	1.29
3	**3a**	3	2	85.9	84.3	11.9	3.8	2.92	2.75	1.33

[a] Condition: toluene (3.0 ml); Ln (10 μmol); [Ph$_3$C][B(C$_6$F$_5$)$_4$] (10 μmol)；AliBu$_3$ (100 μmol); [IP]/[Lu]=500; T$_p$=25°C. [b] Determined by ^{1}H NMR and ^{13}C NMR spectroscopy in CDCl$_3$. [c] Calculated by ([IP]/[Ln]) × 68.12 × yield. [d] Determined by GPC in THF at 40 °C against polystyrene standard.

The catalytic performance of complex **3a** under the activation of [Ph$_3$C][B(C$_6$F$_5$)$_4$] toward the polymerization of isoprene in toluene was studied. Complex **3a** was inert for polymerization of isoprene under the activation of 1 equivalent of [Ph$_3$C][B(C$_6$F$_5$)$_4$] (Table 1, entry 1), which showed moderate activity and cis-1,4 enriched selectivity when the loading of

[Ph$_3$C][B(C$_6$F$_5$)$_4$] increased to 2 equivalents. Further increasing the amount of [Ph$_3$C][B(C$_6$F$_5$)$_4$] to 3 equivalents, both the activity and the selectivity increased (Table 1, entries 2 and 3). Although the cationic (Ind-NHC)Y(CH$_2$SiMe$_3$)$_2$ was reported to display high activity and 3,4-regioselectivity towards isoprene polymerization, its scandium analogues

(Ind-NHC)Sc(CH$_2$SiMe$_3$)$_2$ and (Flu-NHC)Sc(CH$_2$SiMe$_3$)$_2$ were completely inert.[8] Because the greater hindrance of the indenyl and fluorenyl prevents the coordination of isoprene to the scandium center. The high activity of complex **3a** should be mainly attributed to the steric less bulky alkoxy-NHC ligand. The abstraction of the two alkyl ligands by two [Ph$_3$C][B(C$_6$F$_5$)$_4$] might also provide a more opening coordination sphere around the scandium metal center for the monomer. Both maybe the reason for the *cis*-1,4 enriched regioselectivity of **3a**, since the steric bulky Ind-NHC and Flu-NHC lead to 3,4-selectivity for their attached yttrium metal centers.[8] The above results prove again that a more opening coordination sphere of an active metal species favors to form 1,4-tacticity during the isoprene polymerization.

Conclusion

In summary, we prepared a series of alkoxy-functionalized N-heterocyclic carbene ligands and the corresponding rare-earth metal alkyl complexes. These complexes bearing less bulky ligands are binuclear tetra(alkyl)s, of which the dicationic scandium alkyl species could initiate isoprene polymerization with the moderate *cis*-1,4 selectivity (84.3 %). By comparing with the sterically bulky NHC ligands stabilized rare-metal alkyl complexes that are 3,4-regioselective reported previously, the *cis*-1,4 selectivity of this catalytic system composed of scandium complex should be attributed to the relatively more opening coordination environment around the active metal center. This might direct a new way to efficiently design polymerization catalysts.

Experimental

Materials and instrumentation

All reactions were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in an MBraun glovebox. All solvents were purified from the MBraun SPS system. Organometallic samples for NMR spectroscopic measurements were prepared in the glovebox by use of NMR tubes sealed with paraffin film. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV600 (FT, 400MHz for ^{1}H; 100MHz for ^{13}C) spectrometer. NMR assignments were confirmed by ^{1}H-^{1}H COSY and [1]H-[13]CHMQC experiments when necessary. The number-average molecular weights and molecular weight distributions of the polymer samples were measured by means of gel permeation chromatography (GPC) on a TOSOH HLC-8220 GPC apparatus (Column: SuperHZM-Hx3) at 40 °C using THF as eluent (the flowing rate is 0.35 mL/min) against polystyrene standards. Elemental analyses were performed at National Analytical Research Centre of Changchun Institute of Applied Chemistry (CIAC). Isoprene (99%, Acros) was dried over CaH$_2$ with stirring for 48h and distilled before use. Lu(CH$_2$SiMe$_3$)$_3$(THF)$_2$ was prepared by the described procedure earlier. [Ph$_3$C][B(C$_6$F$_5$)$_4$] was prepared according to the literature.[10] LiCH$_2$SiMe$_3$ solution (1.0 M in pentane) was purchased from Aldrich. Imidazole, benzimidazole, iodoMethane, 2-iodopropane and 1,2-epoxyhexanel were purchased from the National Medicine Co. (China) and used without further purification.

Synthesis of ligand 1a

An ampoule was charged with imidazole (2.00 g, 29.38 mmol) and 1,2-epoxyhexanel (2.94 g, 29.38 mmol). The resulting mixture was stirred for 12h at 50℃. Then, iodomethane (4.17 g, 29.38 mmol) and acetonitrile (20 mL) were added and the reaction mixture was stirred for 2h at 80℃. After that, the solvent was removed to yield the crude product as a yellow liquid. The crude product was purified by column chromatography (SiO$_2$, methanol) to produce the yellow viscous liquid product (8.70 g) with a yield of 95.5%.^{1}H NMR (400 MHz, CDCl$_3$, 25 ℃): δ 0.89 (t, 3H, J$_{H-H}$=5.6Hz, C*H$_3$*CH$_2$CH$_2$CH$_2$), 1.32~1.54 (m, 6H, CH$_3$C*H$_2$*C*H$_2$*C*H$_2$*), 4.07 (s, 4H, NC*H$_3$*, OC*H*), 4.23~4.51 (m, 2H, OCHC*H$_2$*N), 7.58, 7.67 (s, s, 2H, NC*H*), 9.38 (s, 1H, imidazolium–H); ^{13}C NMR (100 MHz, CDCl$_3$, 25℃): δ 13.42 (s, 1C, *C*H$_3$CH$_2$CH$_2$CH$_2$), 21.81, 26.90, 33.10(s, CH$_3$*C*H$_2$*C*H$_2$*C*H$_2$), 36.59 (s, 1C, O*C*H), 54.82(s, 1C, OCH*C*H$_2$N), 68.58(s, 1C, N*C*H$_3$)，122.53, 122.89(s, s, 2C, N*C*H), 135.99 (s, 1C, C$_{ylidene}$). Anal. Calcd for C$_{10}$H$_{19}$IN$_2$O (%): C, 38.72; H, 6.17; N, 9.03. Found: C, 38.51; H, 6.07; N, 8.86.

Synthesis of ligand 1b

Following a similar procedure described for the synthesis of ligand 1a, 1b was prepared by using 2-iodopropane to replace iodomethane. The crude product was purified by column chromatography (SiO$_2$, methanol) to produce the yellow viscous liquid product (9.07 g) with a yield of 91.3%. ^{1}HNMR (300 MHz, CDCl$_3$, 25 ℃): δ 0.88 (t, 3H, J$_{H-H}$=7.2Hz, C*H$_3$*CH$_2$CH$_2$CH$_2$), 1.31~1.58 (m, 6H, CH$_3$C*H$_2$*C*H$_2$*C*H$_2$), 1.64 (d, J$_{H-H}$=6.3Hz, 6H, CH(C*H$_3$*)$_2$), 3.68 (b, 1H, O*H*), 4.29~4.36 (s, 1H, OC*H*), 4.46~4.53 (m, 2H, OCHC*H$_2$*N), 4.73 (m, J$_{H-H}$=6.6Hz, 1H, C*H*(CH$_3$)$_2$), 7.46, 7.52 (s, s, 2H, NC*H*), 9.67

(s, 1H, imidazolium-H). Anal. Calcd for $C_{12}H_{23}IN_2O$(%): C, 42.61; H, 6.85; N, 8.28. Found: C, 42.50; H, 6.73; N, 8.31.

Synthesis of ligand 2a

Following a similar procedure described for the synthesis of the ligand 1a, 2a was prepared by using benzimidazole to replace imidazole. The crude product was purified by column chromatography(SiO_2, methanol) to produce the yellow solid (9.01 g) with a yield of 85.2%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ℃): δ 0.89 (t, 3H, $J_{H–H}$=7.2Hz, $CH_3CH_2CH_2CH_2$), 1.33~1.66 (m, 6H, $CH_3CH_2CH_2CH_2$), 4.23 (s, 3H, NCH_3), 4.60~5.63 (m, 3H, OCH, OCHCH_2N), 7.62~7.72 (m, 4H, Ar), 10.38 (s, 1H, benzimidazolium-H). Anal. Calcd for $C_{14}H_{21}IN_2O$ (%): C, 46.68; H, 5.88; N,7.78. Found: C, 46.53; H, 5.70; N, 7.66.

Synthesis of ligand 2b

Following a similar procedure described for the synthesis of the ligand 1b, 2b was prepared by using using benzimidazole to replace imidazole. The crude product was purified by column chromatography (SiO_2, methanol) to produce the yellow solid (9.89 g) with a yield of 86.7%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ℃):δ 0.90 (t, 3H, $J_{H–H}$=7.2Hz, $CH_3CH_2CH_2CH_2$), 1.35~1.68 (m, 6H, $CH_3CH_2CH_2CH_2$), 1.82~1.86 (m, 6H, $CH(CH_3)_2$), 4.18~4.21 (m, 1H, OCH), 4.62~4.84 (m, 2H, OCHCH_2N), 4.96 (m, 1H, C$H(CH_3)_2$), 7.73~7.77 (m, 4H, Ar), 10.62 (s, 1H, benzimidazolium–H). Anal. Calcd for $C_{16}H_{25}IN_2O$ (%): C, 49.49; H,6.49; N,7.21. Found: C, 49.41; H, 6.35; N, 7.09.

Synthesis of complex 3b

The toluene solution (5 ml) of $LiCH_2SiMe_3$ (0.035 g, 0.36 mmol) was added dropwise into a toluene solution (5 ml) of 1a, the mixture was stirred for 20 minutes at room temperature. Then the resulting mixture was add to the toluene solution (5 ml) of $Lu(CH_2SiMe_3)_3(THF)_2$ (0.21 g, 0.36 mmol), the reaction mixture remained stirring for 2h. Concentration, filtration, and cooling at -30℃ afforded colorless crystals of complex **3b** (0.12 g) with a yield of 61.6%. ^{1}H NMR(400MHz, C_6D_6, 25℃): δ -0.46, -0.23 (AB, $^2J_{H–H}$=11.6Hz, 2H, Lu-CH_2SiMe$_3$), -0.33 (s, 2H, Lu-CH_2SiMe$_3$), 0.25, 0.53 (s, s, 18H, Lu-CH$_2$SiMe_3), 0.93 (t, $J_{H–H}$=7.2Hz, $CH_3CH_2CH_2CH_2$), 1.30~1.45, 2.10~2.21 (m, 6H, $CH_3CH_2CH_2CH_2$), 3.60 (s, 3H, NCH_3), 3.69, 4.96 (AB, 2H, OCHCH_2N), 4.95 (d, $J_{H–H}$=6.4Hz, 2H, OCH), 5.98, 5.99(s, s, 2H, NCH); ^{13}C NMR (100MHz, C_6D_6, 25℃): δ 5.17, 5.43 (s, s, 2C, Lu-CH$_2$SiMe_3), 14.72 (s, 1C, $CH_3CH_2CH_2CH_2$), 23.51, 29.32, 35.58 (s, 3C,

$CH_3CH_2CH_2CH_2$), 38.36 (s, 1C, NCH_3), 40.86, 41.86 (s, s, 2C, Lu-CH_2SiMe$_3$), 55.26 (s, 1C, OCHCH_2N), 72.28 (s, 1C, OCH), 120.27, 122.43 (s, s, 2C, NCH), 198.00 (s, 1C, Lu-C$_{ylidene}$). Anal. Calcd for $C_{18}H_{39}N_2LuSi_2$ (%): C, 40.74; H,7.41; N, 5.28. Found: C, 40.59; H, 7.29; N, 5.20.

Synthesis of complex 4b

Following the procedure described above, the reaction of 1b (0.12g, 0.366 mmol) with $LiCH_2SiMe_3$ (0.035 g, 0.36 mmol) and $Lu(CH_2SiMe_3)_3(THF)_2$ (0.21 g, 0.36 mmol) afforded complex **4b** (0.12g) with a yield of 60.1%. Anal. Calcd for $C_{20}H_{43}N_2OSi_2Lu$ (%): C, 42.99; H,7.76; N,5.01. Found: C, 42.83; H, 7.64; N, 4.87.

Synthesis of complex 3a

Following the procedure described above, the reaction of 1a (0.11 g, 0.36 mmol) with $LiCH_2SiMe_3$ (0.035 g, 0.36 mmol) and $Sc(CH_2SiMe_3)_3(THF)_2$ (0.16 g, 0.36 mmol) afforded complex **3a** (0.077 g) with a yield of 52.4%. Anal. Calcd for $C_{18}H_{39}N_2OScSi_2$: C, 53.96; H, 9.81; N, 6.99. Found: C, 53.79; H, 9.72; N, 6.88.

Synthesis of the complex 4a

Following the procedure described above, the reaction of 1b (0.12 g, 0.36 mmol) with $LiCH_2SiMe_3$ (0.035 g, 0.36 mmol) and $Y(CH_2SiMe_3)_3(THF)_2$ (0.18 g, 0.36 mmol) afforded **4a** (0.099 g) with a yield of 57.3%. Anal Calcd for $C_{20}H_{43}N_2OSi_2Y$ (%): C, 50.82; H, 9.17; N, 5.93. Found: C, 50.73; H, 9.06; N, 5.88.

Synthesis of complex 5

Following the procedure described above, the reaction of 2b (0.14 g, 0.36 mmol) with $LiCH_2SiMe_3$ (0.035 g, 0.36 mmol) and $Y(CH_2SiMe_3)_3(THF)_2$ (0.18 g, 0.36 mmol) afforded **5** (0.110 g) with a yield of 57.5%. Anal Calcd for $C_{24}H_{45}N_2OSi_2Y$ (%): C, 55.15; H, 8.68; N, 5.36. Found: C, 55.03; H, 8.52; N, 5.31.

Isoprene polymerization

A typical polymerization procedure was as follows (Table 2, entries 2 and 3). In a glovebox, isoprene (1.0 ml, 10 mmol) was added into a 25 ml flask. Then 10 μmol of complex 3a and 2 equiv of $[Ph_3C][B(C_6F_5)_4]$ (19.2 mg, 0.02 mmol) and 10 equiv of Al^{i}Bu$_3$ were added to initiate the polymerization. After stirring for 2h at room temperature. The mixture was poured to ethanol to terminate the polymerization and precipitate the white solid of polyisoprene, which was filtered and dried under vacuum at ambient temperature to constant weight.

X-Ray crystallographic study

Crystals for X-ray analysis were obtained as in the preparation. The crystals were manipulated in a glovebox. Data collections were performed at 86.5 °C on a Bruker SMART APEX diffractometer with a CCD are a detector, using graphite-monochromated Mo K radiation(λ=0.71073Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data was processed using SAINT and SADABS to yield the reflection data file. The structures were solved by using the SHELXTL program Refinement was performed on F^2 anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. CCDC 1054531-1054535 contains the supplementary crystallographic data for **3a**, **4a**, **4b**, **3b** and **5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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