

# Synthesis of the First Rare Earth Metal Bis(alkyl)s Bearing an Indenyl Functionalized N-Heterocyclic Carbene

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Received January 30, 2007

Treatment of indenyl-modified imidazolium bromide [ $C_9H_7CH_2CH_2(NCHCHN(C_6H_2Me_3-2,4,6)CH)Br$ ] ((IndH-NHC-H)Br) with rare earth metal tetra(alkyl) lithium ( $Ln(CH_2SiMe_3)_4Li(THF)_4$ ) or with (trimethylsilylmethyl)lithium ( $LiCH_2SiMe_3$ ) and rare earth metal tris(alkyl)s ( $Ln(CH_2SiMe_3)_3(THF)_2$ ) sequentially afforded the first NHC-stabilized monomeric rare earth metal bis(alkyl) complexes (Ind-NHC)Ln( $CH_2SiMe_3$ )<sub>2</sub> (**1**, Ln = Y; **2**, Ln = Lu; **3**, Ln = Sc) via double-deprotonation reactions. Complexes **1–3** are THF-free isostructural monomers. The monoanionic Ind-NHC species bond to the central metal ion in a  $\eta^5:\kappa^1$  constrained geometry configuration (CGC) mode, which combine with the two *cis*-located alkyl moieties to form a tetrahedron ligand core, leading to the chirality of the complexes. Under the presence of activators  $AlEt_3$  and  $[Ph_3C][B(C_6F_5)_4]$ , complex **2** showed catalytic activity toward the polymerization of isoprene to afford 3,4-regulated polyisoprene (91%).

## Introduction

Thermally stable N-heterocyclic carbenes (NHCs) originated by Arduengo in 1991 have garnered an upsurge in interest in the past decade and become versatile ligands to stabilize and activate metal centers in quite different key catalytic steps of organic syntheses, for example, C–C coupling, aryl and amide amination, hydrosilylation, and olefin metathesis.<sup>1</sup> In these complexes, the NHC mainly plays the role of organophosphane as a solvate albeit with more robust coordination.<sup>2</sup> Functionalization of the imidazolium salt with alkoxide or alkylamides leads to polydentate ligands in combination with NHC with a pendant anionic functionality. The resulting NHCs are hemilabile and covalently bond to the metal center, anticipated to tune the coordination sphere and rigidity and chirality of a complex, and have attracted more attention due to their potential in the area of homogeneous catalysts.<sup>3</sup> The tripodal and “pincer” systems of bisphenolate- or amido-functionalized NHC allowed the isolation of Ti, Zr, and Hf complexes;<sup>4,5</sup> the phenoxy-

modified NHC was used to stabilize Ni bromide species.<sup>6</sup> Recently, indenyl- or fluorenyl-functionalized NHC moiety-supported Ti and V mixed amide/halogen complexes and Ni bromide have been reported.<sup>7</sup> Comparatively, rare earth metal complexes bearing functionalized NHC ligands have remained less explored, although the strongly nucleophilic NHC ligands of two-electron donors are anticipated to stabilize the highly unsaturated Lewis acidic lanthanide ions. Breakthroughs have been achieved by the Arnold group, who have successful isolated carbene-amine-supported lanthanide bis(amido) complexes via a unique reaction pathway, the transamination of the lithium carbene-amine with homoleptic lanthanide tris(amide)s.<sup>8</sup> However, NHC-supported rare earth metal bis(alkyl) complexes have not been known to date.<sup>9</sup> On the other hand, rare earth metal bis(alkyl) complexes are highly active single-component catalysts or crucial precursors of the cationic counterparts after being activated by MAO or borates and have shown tremendous catalytic activities toward polymerizations of olefin,<sup>10</sup> conjugated monomers,<sup>11</sup> and polar monomers.<sup>12</sup> Therefore, exploration of new lanthanide bis(alkyl) complexes has been a research

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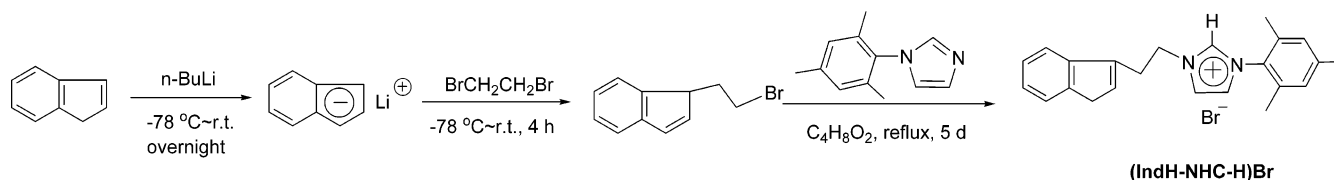
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(9) Functionalized NHC-stabilized bis(alkyl) complexes based on metals of the entire range of the periodic table are also scarce. The bisphenolate-functionalized NHC-ligated titanium bis(alkyl) complex is one of the rare examples reported to date; see ref 3.

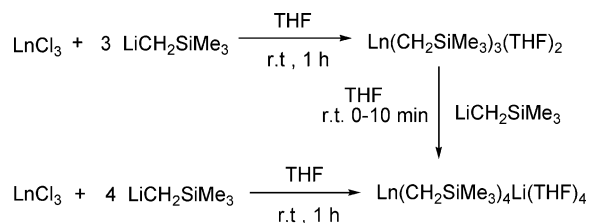
Scheme 1. Synthesis of *N*-Indenyl Imidazolium Bromide, (IndH-NHC-H)Br

concern. Unfortunately, preparation of rare earth metal bis(alkyl) complexes bearing monoanionic ligands has been hindered due to the highly active character of lanthanide alkyl species and the relatively less crowded environment of the metal center, which always result in ligand redistribution, dimerization of the molecule, and the formation of salt or solvent adducts.<sup>13</sup> Thus, investigation of rare earth metal bis(alkyl) complexes chelated by NHC ligands is, obviously, a challenge and attractive. Here we report the preparation of rare earth metal bis(alkyl) complexes bearing *N*-heterocyclic carbene ligands via new synthetic pathways. The preliminary isoprene polymerization data using the lutetium complex are also given.

## Results and Discussion

The indenyl-modified imidazolium bromide, (IndH-NHC-H)Br, was synthesized according to a modified literature procedure.<sup>7</sup> Indene was treated with butyllithium at  $-78\text{ }^{\circ}\text{C}$ , and then the reaction mixture was warmed to room temperature and kept stirring overnight. Addition of the above mixture to bromoethylindene gave bromoethyl indene, which reacted with *N*-mesitylimidazole in dioxane under refluxing for 5 days to generate (IndH-NHC-H)Br in high yield (Scheme 1). The  $^1\text{H}$  NMR spectrum was indicative of the formation of the desired product. The two discrete triplet resonances could be attributed to the ethylene protons, and the signal appearing in the upfield region,  $\delta$  3.32, was assignable to the indenyl nonconjugated protons. The ylidene proton NHC-H displayed a typical singlet resonance in the downfield region,  $\delta$  10.24. The yttrium tetra(alkyl) lithium salt ( $\text{Y}(\text{CH}_2\text{SiMe}_3)_4\text{Li}(\text{THF})_4$ ) was obtained by treatment of yttrium trichlorides with 4 equiv of tris(methylsilylmethyl)lithium ( $\text{LiCH}_2\text{SiMe}_3$ ) at room temperature in THF for 1 h,<sup>14</sup> which could also be *in situ* generated by simply mixing a THF solution of  $\text{LiCH}_2\text{SiMe}_3$  with equimolar  $\text{Y}(\text{CH}_2\text{SiMe}_3)_3$ -

## Scheme 2. Synthesis of Rare Earth Metal Tetra(alkyl) Lithium



( $\text{THF}$ )<sub>2</sub><sup>15</sup> at room temperature (Scheme 2). Reaction of (IndH-NHC-H)Br and  $\text{Y}(\text{CH}_2\text{SiMe}_3)_4\text{Li}(\text{THF})_4$  was carried out at room temperature in toluene for 40 min under vigorous stirring, and then concentration, filtration, and cooling the resultant solution to  $-30\text{ }^{\circ}\text{C}$  afforded the colorless crystalline complex (Ind-NHC)Y( $\text{CH}_2\text{SiMe}_3$ )<sub>2</sub> (**1**) in modest yield (38%) (one step). Alternatively, (IndH-NHC-H)Br reacted with  $\text{LiCH}_2\text{SiMe}_3$  for 40 min at room temperature, and then the reaction mixture was *in situ* added to a  $\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$  solution and maintained for another 20 min, to afford complex **1** in high yield (62.5%) (two steps). The lutetium (**2**) and scandium (**3**) analogues were synthesized following a two-step procedure albeit with longer reaction time at the second step (2 h).

The two-step procedure could be explained as shown in Scheme 3. (IndH-NHC-H)Br was deprotonated by  $\text{LiCH}_2\text{SiMe}_3$  with the release of tetramethylsilane (TMS) and LiBr to give the neutral intermediate IndH-NHC. Monitoring the reaction by  $^1\text{H}$  NMR technique demonstrated that the characteristic resonance of the ylidene proton disappeared and the TMS signal showed up (the deuterated  $\text{C}_6\text{H}_6$  contains no TMS standard). The reaction was rapid, and almost no lithium alkyl signal at  $\delta$   $-1.76$  could be observed after 40 min. The following deprotonation of the neutral intermediate IndH-NHC took place immediately upon addition to the  $\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$  solution, evidenced by the loss of the resonance for a nonconjugated proton of the indenyl moiety ( $\delta$  3.32, *vide supra*). The resultant monoanionic Ind-NHC fragment covalently bonded to the rare earth metal bis(alkyl) unit, which was confirmed by NMR spectrum analysis. The ethylene spacer between the indenyl and imidazolyl groups showed four discrete multiple resonances compared with two triplets in the free ligand, indicating that both carbon atoms are chiral (Figure 1). The rotation about the *N*-C<sub>mesityl</sub> bond was restricted, as the *ortho*-methyl of the mesityl fragment gave two discrete resonances at  $\delta$  1.79 and 2.21 compared to the sharp singlet at  $\delta$  1.94 in the free ligand. The methylene protons of  $\text{LnCH}_2\text{SiMe}_3$  species were diastereotopic, displaying interesting and complicated resonances of two independent AB spins in the upfield regions:  $\delta$   $-2.09/-1.81$  and  $-0.86/-0.57$  for **1**,  $\delta$   $-2.44/-2.09$  and  $-1.08/-0.78$  for **2** (Figure S7), and  $\delta$   $-1.82/-1.58$  and  $-0.29/-0.09$  for **3** (Figure S10). Further splitting of the AB spins into doublets due to coupling with the Y atom ( $I = 1/2$ ) was observed for complex **1**. The ylidene carbon in all complexes gave the

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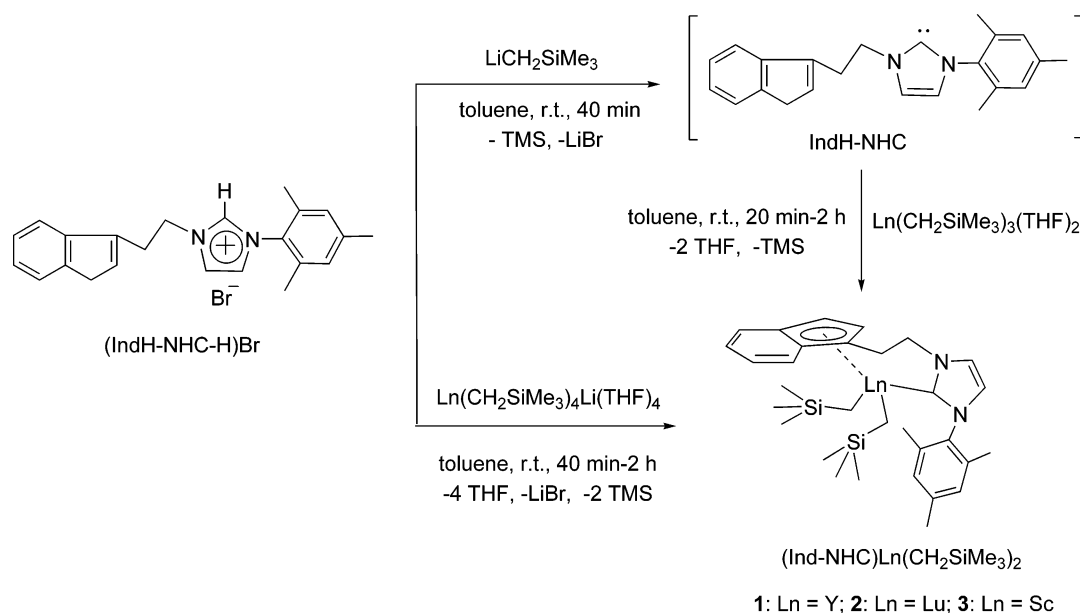
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Table 1. Crystallographic Data and Refinement for 1, 2, and 3

	1	2	3
formula	C <sub>31</sub> H <sub>45</sub> YN <sub>2</sub> Si <sub>2</sub>	C <sub>31</sub> H <sub>45</sub> LuN <sub>2</sub> Si <sub>2</sub>	C <sub>31</sub> H <sub>45</sub> ScN <sub>2</sub> Si <sub>2</sub>
cryst size, mm	0.37 × 0.24 × 0.13	0.17 × 0.16 × 0.10	0.24 × 0.14 × 0.08
fw	590.78	676.84	546.83
cryst syst	monoclinic	monoclinic	monoclinic
space group	P2(1)/c	P2(1)/c	P2(1)/c
a (Å)	10.5665(7)	10.5025(6)	10.3718(10)
b (Å)	23.2486(16)	23.2946(13)	23.321(2)
c (Å)	13.9158(10)	13.8088(7)	13.6852(13)
α (deg)	90	90	90
β (deg)	107.2620(10)	106.8380(10)	106.253(2)
γ (deg)	90	90	90
V (Å <sup>3</sup> )	3264.5(4)	3233.5(3)	3177.9(5)
Z	4	4	4
D <sub>calcd</sub> (g/cm <sup>3</sup> )	1.202	1.390	1.143
2θ <sub>max</sub> (deg)	52.08	52.10	52.14
μ (cm <sup>-1</sup> )	18.80	31.48	3.28
F(000)	1248	1376	1176
no. of obsd reflns	6430	6374	6277
no. of params refnd	325	334	334
GOOF	1.026	0.956	0.852
R <sub>1</sub> [I > 2σ(I)]	0.0381	0.0260	0.0518
wR <sub>2</sub> [I > 2σ(I)]	0.0878	0.0598	0.0845

Scheme 3. Synthesis of NHC-Ligated Rare Earth Metal Bis(alkyl) Complexes



characteristic signal at  $\delta$  191.23 (doublet) for **1**, 199.92 for **2**, and 188.01 for **3** (Figures S6, S8, and S11), comparable to  $\delta$  186.0, 190.3, and 190.4 found in the NHC-containing complexes (BuNCH<sub>2</sub>CH<sub>2</sub>[C{N(CHCH)N}Bu])Y[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>,<sup>8a</sup> Y[N(SiHMe<sub>2</sub>)<sub>2</sub>]<sub>3</sub>-[C{MeN(CHCH)NMe}], and Y[N(SiHMe<sub>2</sub>)<sub>2</sub>]<sub>3</sub>[C{MeN(CHCH)NMe}]<sub>2</sub>,<sup>2c</sup> respectively, suggesting the formation of a direct Ln-C<sub>carbene</sub> linkage. There was no doubt that the chirality of complexes **1–3** could be significantly influenced by the covalently bonded NHC ligand.

Obviously, the one-step route could also be explained as a double-deprotonation process because the reagent Y(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>4</sub>Li(THF)<sub>4</sub> was the LiCH<sub>2</sub>SiMe<sub>3</sub> adduct of Ln(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> bearing two extra THF molecules. The difference from the two-step procedure was that the resulting neutral compound IndH-NHC was not observable, as it was deprotonated by Ln-CH<sub>2</sub>SiMe<sub>3</sub> species in the system as soon as it was generated. This might be the reason that the one-step procedure was rapid. However, the yield was low owing to the purity of the tetra(alkyl) lithium salt if it was synthesized via treatment of LnCl<sub>3</sub> by LiCH<sub>2</sub>SiMe<sub>3</sub>.

It is noteworthy that all complexes **1–3** could also be accessed by treatment of (IndH-NHC-H)Br with butyllithium, <sup>n</sup>BuLi (20 min), or potassium amide, KN(SiMe<sub>3</sub>)<sub>2</sub> (12 h), respectively, followed by addition to the Ln(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> solution.<sup>16</sup> This confirmed further that the neutral IndH-NHC was the intermediate of these reactions, as indenyl-functionalized imidazolyl bromide deprotonated by KN(SiMe<sub>3</sub>)<sub>2</sub> to yield a neutral carbene compound is an established mechanism.<sup>7a</sup> However, the yields of the complexes were very low in the cases using KN(SiMe<sub>3</sub>)<sub>2</sub>, because the deprotonation reaction was slow and the resultant neutral carbene compound was unstable at room temperature.

The molecular structures of complexes **1–3** in solution were fairly consistent with those in the solid state, illustrated by X-ray diffraction analysis as shown in Figure 2 (complex **1**). All

(16) When (IndH-NHC-H)Br was deprotonated by using <sup>n</sup>BuLi, the resultant reaction mixture was added *in situ* to the Ln(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> solution, whereas by using KN(SiMe<sub>3</sub>)<sub>2</sub> (12 h), the reaction mixture was vacuumed thoroughly and washed with hexane to extrude the resulting HN(SiMe<sub>3</sub>)<sub>2</sub> before addition to the Ln(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> solution.

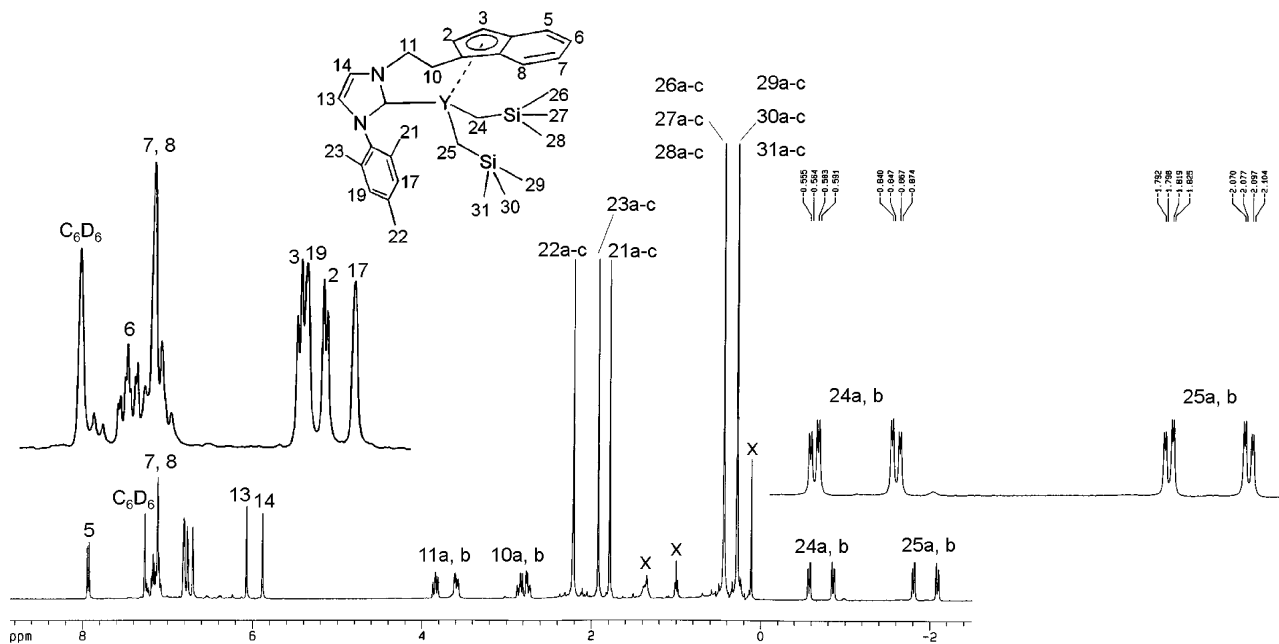


Figure 1.  $^1\text{H}$  NMR spectrum of complex **1**.

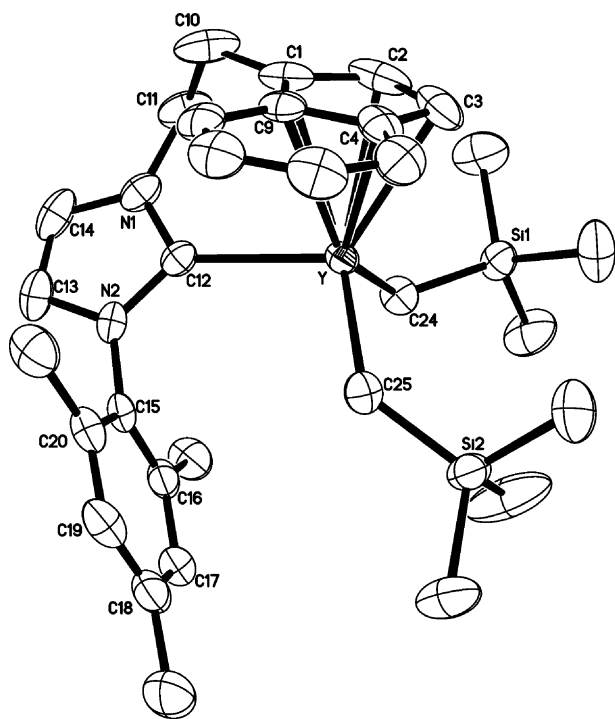


Figure 2. X-ray structure of **1** with 40% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

complexes are isomeric solvent-free monomers, adopting tetrahedral geometries (Table 1). THF is extruded from the central metal coordination sphere owing to the strong electron-donating effect of the ylidene carbon. The NHC ligand coordinates to the Ln ion in a  $\eta^5/k^1$  constrained geometry configuration (CGC) mode. The two alkyl species are located in *cis*-positions with one *endo* and the other *exo* with respect to the imidazole ring. The bond length of Ln–C<sub>carbene</sub> is 2.501(3) Å for **1**, 2.443(3) Å for **2**, and 2.350(3) Å for **3**, consistent with the order of Ln ionic radius,<sup>17</sup> comparable to Y–C<sub>carbene</sub>, 2.501(5) Å, in the complex (tBuNCH<sub>2</sub>CH<sub>2</sub>[C{N(CHCH)NtBu}])Y[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>,<sup>8a</sup> however, it is slightly longer than the bond length of Ln–C

Table 2. Selected Bond Lengths [Å] and Angles [deg] for Complexes **1–3**

	Ln = Y	Ln = Lu	Ln = Sc
Ln–C1	2.709(3)	2.661(3)	2.531(3)
Ln–C2	2.672(3)	2.607(4)	2.487(3)
Ln–C3	2.640(3)	2.584(3)	2.482(3)
Ln–C4	2.686(3)	2.653(3)	2.572(3)
Ln–C9	2.700(3)	2.675(3)	2.579(3)
Ln–C24	2.370(3)	2.319(3)	2.209(3)
Ln–C25	2.370(3)	2.319(3)	2.208(3)
Ln–C12	2.501(3)	2.443(3)	2.350(3)
Ln–C <sub>cent</sub>	2.396(2)	2.344(2)	2.227(2)
C24–Ln–C25	107.88(10)	106.60(12)	106.56(10)
C <sub>cent</sub> –Ln–C12	100.10(2)	101.60(4)	104.60(5)
C24–Ln–C12	95.06(9)	94.98(11)	94.04(9)
C25–Ln–C12	107.11(9)	106.35(11)	105.67(10)
C12–N2–C15	123.9(2)	124.0(3)	124.9(2)

formed by the metal ion and the alkyl carbon (2.208–2.370 Å) (Table 2). The Ln–C<sub>pcent</sub> bond lengths averaging 2.322 Å are similar to that in a CGC-type furyl-indenyl yttrium bis(alkyl) complex (Lu–C<sub>pcent</sub> = 2.367(4) Å).<sup>13a</sup> However, the bond angles of C(24)–Ln–C(25) (106.56(10)–107.88(10)°) are much smaller than 124.4° in the latter complex due to the different locating mode for the bis(alkyl) species, but they are larger than the average 101.5° for the other reported C–Ln–C bond angles due to the combined influence of the constrained chelating ligands and noncoordination of the THF solvent.<sup>11c,18</sup> Complexes **1–3** represent the first examples of anionic NHC-ligated rare earth metal bis(alkyl)s, as far as we are aware. In addition, they are also rare examples of such solvent-free complexes,<sup>19</sup> indicating the strong electron-donating nature of the NHC moiety. The number of coordinated solvent molecules, in some cases, is crucial in governing the catalytic activity of the complex; for instance, the two-THF-solvated benzamidinate yttrium bis(alkyl) complex loses its catalytic activity toward

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ethylene polymerization compared to the highly active counterpart of one THF adduct.<sup>20</sup>

Recent reports show that rare earth metal bis(alkyl) complexes are active for isoprene polymerization.<sup>21</sup> Thus, complexes **1**, **2**, and **3** were tested for this activity. The preliminary results showed that they were inert if used alone. Upon activation with equimolar  $[\text{Ph}_3\text{C}][(\text{C}_6\text{F}_5)_4\text{B}]$  and  $\text{AlEt}_3$ , moderate activities but high selectivity were observed. Under the condition of isoprene/**2**/ $[\text{Ph}_3\text{C}][(\text{C}_6\text{F}_5)_4\text{B}]/\text{AlEt}_3 = 1000:1:1:1$ , the polymerization was carried out in toluene for 12 h, affording an 80% yield of polyisoprene with a molecular weight ( $M_n$ ) of 37 000 (PDI = 1.44) and 91% 3,4-regulation. A detailed investigation of the catalytic performances of the complexes is in process.

## Conclusion

In summary, we have demonstrated several efficient routes for the preparation of rare earth metal bis(alkyl) complexes bearing indenyl-functionalized NHC ligands via the deprotonation of an indenyl imidazolium bromide by a lithium alkyl followed by deprotonation of the *in situ*-generated intermediate of the neutral indenyl N-heterocyclic carbene by a rare earth metal alkyl species. The complexes represent the first examples of functionalized NHC covalently bonding to rare earth metal alkyl units, which display rare monomeric and solvent-free structures, having potential as homogeneous catalysts.

## Experimental Section

**General Methods.** 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 an MBraun SPS system. Organometallic samples for NMR spectroscopic measurements were prepared in the glovebox by use of NMR tubes sealed with paraffin film.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AV400 (FT, 400 MHz for  $^1\text{H}$ ; 100 MHz for  $^{13}\text{C}$ ) spectrometer. NMR assignments were confirmed by  $^1\text{H}$ - $^1\text{H}$  COSY and  $^1\text{H}$ - $^{13}\text{C}$  HMQC experiments when necessary. IR spectra were recorded on a VERTEX 70 FT-IR. Polymer molecular weight was measured on a TOSOH HLC 8220 GPC with THF as eluent. Elemental analyses were performed at National Analytical Research Centre of Changchun Institute of Applied Chemistry (CIAC). Indene was obtained from Aldrich and purified by distillation before use. Bromoethylidene, mesitylamine, glyoxal, *para*-formaldehyde, etc., were purchased from the National Medicine Company (China) and were used without further purification.

**X-ray Crystallographic Studies.** Crystals for X-ray analysis were obtained as described in the preparations. The crystals were manipulated in a glovebox. Data collections were performed at  $-86.5$  °C on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were 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 calculated positions and were included in the structure calculation without further refinement of the parameters.

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**Synthesis of Indenyl Imidazolium Bromide (IndH-NHC-H)-Br.** At  $-78$  °C, 54 mL (1.60 mol/L) of *n*-butyllithium was dropwise added to the hexane solution (50 mL) of indene (9.960 g, 85.74 mmol), and the mixture was warmed to room temperature slowly and kept stirring overnight. Filtration and washing with hexane afforded white solids of indenyllithium. The ether suspension of indenyllithium was cooled to  $-78$  °C, which was added dropwise to bromoethylidene (32.216 g, 171.49 mmol) within 2 h. Warming to room temperature slowly, reaction for more than 12 h, and removal of volatiles *in vacuo* gave oily residues, which were passed through a silica gel column with hexane as eluent to afford pure bromoethylidene (Ind-EtBr) in 66.1% yield (12.640 g). Treatment of Ind-EtBr (6.330 g, 28.37 mmol) with 1-(mesityl)imidazole<sup>22</sup> (5.285 g, 28.37 mmol) in 1,4-dioxane (60 mL) under refluxing for 5 days gave sticky oils after removal of volatiles. The sticky oils were dissolved in  $\text{CH}_2\text{Cl}_2$  and precipitated with ether. The resulting viscous products were passed through a silica gel column with acetyl acetate as eluent to wash off the movable parts. The silica gel column was washed with methanol to collect the nonmovable part. Driving of methanol gave the anticipated compound (IndH-NHC-H)Br (7.572 g, 65.2%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  1.94 (s, 6H,  $\text{C}_6\text{H}_2\text{Me}_3$ ), 2.31 (s, 3H,  $\text{C}_6\text{H}_2\text{Me}_3$ ), 3.32 (s, 2H, indene), 3.35 (t,  $J_{\text{H-H}} = 6.4$  Hz, 2H,  $\text{CH}_2\text{CH}_2$ ), 5.14 (t,  $J_{\text{H-H}} = 6.4$  Hz, 2H,  $\text{CH}_2\text{CH}_2$ ), 6.47 (s, 1H, indene), 6.95 (s, 2H,  $\text{C}_6\text{H}_2\text{Me}_3$ ), 6.99 (s, 1H, NCH), 7.15–7.46 (multi, 4H, indene), 7.58 (s, 1H, NCH), 10.24 (s, 1H, imidazolium-H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  17.36 (s, 2C,  $\text{C}_6\text{H}_2\text{Me}_3$ ), 21.02 (s, 1C,  $\text{C}_6\text{H}_2\text{Me}_3$ ), 28.65 (s, 1C,  $\text{CH}_2\text{-CH}_2$ ), 38.05 (s, 1C, indene), 49.25 (s, 1C,  $\text{CH}_2\text{CH}_2$ ), 118.78 (s, 1C, indene), 122.53, 123.24 (s, s, 2C, NCH), 124.05, 125.24, 126.45 (multi, s, 3C, indene), 129.60 (s, 1C, *ipso*- $\text{C}_6\text{H}_2\text{Me}_3$ ), 129.76 (s, 2C,  $\text{C}_6\text{H}_2\text{Me}_3$ ), 132.04 (s, 1C, indene), 134.13 (s, 1C, *ipso*-indene), 138.00 (s, 1C,  $\text{C}_{\text{ylidene}}$ ), 138.77 (s, 1C, *ipso*- $\text{C}_6\text{H}_2\text{Me}_3$ ), 141.25 (s, 2C, *ipso*- $\text{C}_6\text{H}_2\text{Me}_3$ ), 143.86, 144.11 (s, s, 2C, *ipso*-indene). IR (KBr pellets):  $\nu$  3426 (w), 3039 (s), 2953 (s), 2921 (s), 1755 (w), 1711 (m), 1608 (m), 1564 (m), 1547 (s), 1486 (m), 1459 (s), 1382 (m), 1330 (w), 1264 (w), 1205 (s), 1162 (m), 1108 (w), 1070 (m), 856 (m), 774 (m)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{23}\text{H}_{25}\text{BrN}_2$  (%): C, 67.48; H, 6.16; N, 6.84. Found: C, 66.89; H, 6.03; N, 7.16.

**Synthesis of Complex (Ind-NHC)Y( $\text{CH}_2\text{SiMe}_3$ )<sub>2</sub> (**1**).** (a) In a glovebox, (IndH-NHC-H)Br (0.150 g, 0.366 mmol) and  $\text{Y}(\text{CH}_2\text{-SiMe}_3)_4\text{Li}(\text{THF})_4$  (0.269 g, 0.366 mmol) were added to a 25 mL flask, and the reaction took place immediately upon the addition of toluene (15 mL). The reaction mixture turned from a suspension to clear solution gradually and the color changed to deep red. The solution was maintained for 40 min and then concentrated until it became cloudy. The precipitated LiBr was removed by filtration. The filtrate was concentrated under reduced pressure and then cooled to  $-30$  °C. Colorless crystalline complex **1** was isolated within several days (0.082 g, 37.9%). (b) To a flask were added (IndH-NHC-H)Br (0.150 g, 0.366 mmol),  $\text{LiCH}_2\text{SiMe}_3$  (0.035 g, 0.366 mmol), and 10 mL of toluene. After reacting for 20 min under vigorous stirring, the reaction mixture was added to a toluene solution (10 mL) of  $\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$  (0.181 g, 0.366 mmol), which was maintained for another 20 min. The phenomena and the process of workup were similar to that described previously in procedure (a). A high yield of complex **1** was isolated (0.135 g, 62.4%).  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$   $-2.09$ ,  $-1.81$  (ABX, dd,  $^2J_{\text{H-H}} = 10.8$  Hz,  $^2J_{\text{Y-H}} = 2.8$  Hz, 2H, Y- $\text{CH}_2\text{SiMe}_3$ ),  $-0.86$ ,  $-0.57$  (ABX, dd,  $^2J_{\text{H-H}} = 10.8$  Hz,  $^2J_{\text{Y-H}} = 2.8$  Hz, 2H, Y- $\text{CH}_2\text{-SiMe}_3$ ), 0.28 (s, 9H, Y- $\text{CH}_2\text{SiMe}_3$ ), 0.44 (s, 9H, Y- $\text{CH}_2\text{SiMe}_3$ ), 1.79 (s, 3H,  $\text{C}_6\text{H}_2\text{Me}_3$ ), 1.92 (s, 3H,  $\text{C}_6\text{H}_2\text{Me}_3$ ), 2.21 (s, 3H,  $\text{C}_6\text{H}_2\text{Me}_3$ ), 2.72–2.77 (multi, 1H,  $\text{CH}_2\text{CH}_2$ ), 2.81–2.87 (multi, 1H,  $\text{CH}_2\text{CH}_2$ ), 3.57–3.62 (multi, 1H,  $\text{CH}_2\text{CH}_2$ ), 3.81–3.87 (multi, 1H,  $\text{CH}_2\text{CH}_2$ ), 5.88 (d,  $^3J_{\text{H-H}} = 1.2$  Hz, 1H, NCH), 6.07 (d,  $^3J_{\text{H-H}} = 1.2$  Hz, 1H, NCH), 6.70 (s, 1H,  $\text{C}_6\text{H}_2\text{Me}_3$ ), 6.77, 6.81 (AB,  $^3J_{\text{HH}} = 3.2$  Hz, 2H,

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indene), 6.80 (s, 1H, C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>), 7.08–7.19 (multi, 3H, indene), 7.94 (d, <sup>3</sup>J<sub>H-H</sub> = 8.4 Hz, 1H, indene). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 4.82 (s, 3C, Y-CH<sub>2</sub>SiMe<sub>3</sub>), 5.03 (s, 3C, Y-CH<sub>2</sub>SiMe<sub>3</sub>), 18.15 (s, 1C, C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>), 18.38 (s, 1C, C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>), 21.39 (s, 1C, C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>), 28.95 (s, 1C, CH<sub>2</sub>CH<sub>2</sub>), 39.52 (d, 1C, J<sub>Y-C</sub> = 39.7 Hz, Y-CH<sub>2</sub>SiMe<sub>3</sub>), 42.77 (d, 1C, J<sub>Y-C</sub> = 37.9 Hz, Y-CH<sub>2</sub>SiMe<sub>3</sub>), 54.03 (s, 1C, CH<sub>2</sub>CH<sub>2</sub>), 98.28 (s, 1C, indene), 109.24 (s, 2C, *ipso*-indene), 118.85 (s, 1C, indene), 119.40 (s, 1C, indene), 120.89 (s, 1C, NCH), 121.58 (s, 1C, indene), 121.83 (s, 1C, NCH), 122.04 (s, 1C, indene), 124.97 (s, 1C, indene), 130.06, 130.27 (s,s, 2C, C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>), 135.25 (s, 1C, *ipso*-indene), 135.54 (s, 1C, *ipso*-C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>), 135.86 (s, 2C, *ipso*-C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>), 140.23 (s, 1C, *ipso*-C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>), 191.23 ppm (d, J<sub>Y-C</sub> = 46.0 Hz, 1C, Y-C<sub>ylidene</sub>). IR (KBr pellets): ν 3159 (w), 3133 (m), 2947 (s), 1678 (w), 1608 (w), 1555 (w), 1487 (m), 1458 (m), 1403 (m), 1381 (w), 1350 (m), 1333 (m), 1247 (s), 1234 (s), 1209 (w), 1159 (w), 1106 (m), 1030 (w), 862 (s), 753 (s), 740 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>31</sub>H<sub>45</sub>YN<sub>2</sub>Si<sub>2</sub> (%): C, 63.02; H, 7.68; N, 4.74. Found: C, 62.91; H, 7.56; N, 4.69.

**Synthesis of Complex (Ind-NHC)Lu(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> (2).** Following procedure (b) described above, (IndH-NHC-H)Br (0.150 g, 0.366 mmol) was first reacted with LiCH<sub>2</sub>SiMe<sub>3</sub> (0.035 g, 0.366 mmol) for 20 min in a 25 mL sample tube, and then a toluene solution (10 mL) of Lu(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> (0.213 g, 0.366 mmol) was added *in situ*. The mixture was kept stirring for another 2 h. The phenomena and the process of workup were similar to those described previously. Complex **2** was isolated in a 68.9% yield (0.171 g). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ -2.44, -2.09 (AB, <sup>2</sup>J<sub>H-H</sub> = 10.8 Hz, 2H, Lu-CH<sub>2</sub>SiMe<sub>3</sub>), -1.08, -0.78 (AB, <sup>2</sup>J<sub>H-H</sub> = 10.8 Hz, 2H, Lu-CH<sub>2</sub>SiMe<sub>3</sub>), 0.30 (s, 9H, Lu-CH<sub>2</sub>SiMe<sub>3</sub>), 0.45 (s, 9H, Lu-CH<sub>2</sub>SiMe<sub>3</sub>), 1.77 (s, 3H, C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>), 1.92 (s, 3H, C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>), 2.21 (s, 3H, C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>), 2.70–2.76 (multi, 1H, CH<sub>2</sub>CH<sub>2</sub>), 2.79–2.86 (multi, 1H, CH<sub>2</sub>CH<sub>2</sub>), 3.54–3.59 (multi, 1H, CH<sub>2</sub>CH<sub>2</sub>), 3.83–3.90 (multi, 1H, CH<sub>2</sub>CH<sub>2</sub>), 5.87 (d, <sup>3</sup>J<sub>H-H</sub> = 1.6 Hz, 1H, NCH), 6.06 (d, <sup>3</sup>J<sub>H-H</sub> = 1.6 Hz, 1H, NCH), 6.69 (s, 1H, C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>), 6.75, 6.76 (AB, <sup>3</sup>J = 3.2 Hz, 2H, indene), 6.79 (s, 1H, C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>), 7.10 (s, 1H, indene), 7.11 (s, 1H, indene), 7.16–7.21 (multi, 1H, indene), 7.94 (d, <sup>3</sup>J<sub>H-H</sub> = 8.4 Hz, 1H, indene). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 4.99 (s, 3C, Lu-CH<sub>2</sub>SiMe<sub>3</sub>), 5.18 (s, 3C, Lu-CH<sub>2</sub>SiMe<sub>3</sub>), 18.16 (s, 1C, C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>), 18.41 (s, 1C, C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>), 21.38 (s, 1C, C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>), 28.74 (s, 1C, CH<sub>2</sub>CH<sub>2</sub>), 44.98 (s, 1C, Lu-CH<sub>2</sub>SiMe<sub>3</sub>), 49.61 (s, 1C, Lu-CH<sub>2</sub>SiMe<sub>3</sub>), 54.31 (s, 1C, CH<sub>2</sub>CH<sub>2</sub>), 97.99 (s, 1C, indene), 108.44 (s, 2C, *ipso*-indene), 118.62 (s, 1C, indene), 119.48 (s, 1C, indene), 121.11 (s, 1C, NCH), 121.50 (s, 1C, indene), 121.89 (s, 1C, NCH), 122.11 (s, 1C, indene), 125.44 (s, 1C, indene), 129.93, 130.15 (s,s, 2C, C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>), 135.29 (s, 1C, *ipso*-indene), 135.61 (s, 1C, *ipso*-C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>), 135.95 (s, 2C, *ipso*-C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>), 140.16 (s, 1C, *ipso*-C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>), 199.92 ppm (s, 1C, Lu-C<sub>ylidene</sub>). IR (KBr pellets): ν 3160 (w), 3134 (w), 3060 (w), 3028 (w), 2947 (s), 2892 (m), 2841 (w), 2804 (w), 1679 (w), 1608 (w), 1556 (w), 1487 (m), 1458 (m), 1404 (m), 1381(w), 1351 (m), 1334 (m), 1248 (s), 1236 (s), 1209 (w), 1159 (w), 1108 (m), 1030 (m), 857 (s), 816 (m), 753 (s), 740 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>31</sub>H<sub>45</sub>-LuN<sub>2</sub>Si<sub>2</sub> (%): C, 55.01; H, 6.70; N, 4.14. Found: C, 54.49; H, 6.11; N, 3.97.

**Synthesis of Complex (Ind-NHC)Sc(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> (3).** Following the procedure (b) described above, (IndH-NHC-H)Br (0.150 g, 0.366 mmol) was first reacted with LiCH<sub>2</sub>SiMe<sub>3</sub> (0.035 g, 0.366 mmol) for 20 min in a 25 mL flask and then added *in situ* to a 10 mL toluene solution of Sc(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> (0.165 g, 0.366

mmol). The mixture was kept stirring for another 2 h. The phenomena and the process of workup were similar to those described previously, and a high yield of complex **3** was isolated (0.130 g, 64.9%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ -1.82, -1.58 (AB, <sup>2</sup>J<sub>H-H</sub> = 10.8 Hz, 2H, Sc-CH<sub>2</sub>SiMe<sub>3</sub>), -0.29, -0.09 (AB, <sup>2</sup>J<sub>H-H</sub> = 10.8 Hz, 2H, Sc-CH<sub>2</sub>SiMe<sub>3</sub>), 0.25 (s, 9H, Sc-CH<sub>2</sub>-SiMe<sub>3</sub>), 0.40 (s, 9H, Sc-CH<sub>2</sub>SiMe<sub>3</sub>), 1.76 (s, 3H, C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>), 1.97 (s, 3H, C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>), 2.20 (s, 3H, C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>), 2.76–2.79 (multi, 2H, CH<sub>2</sub>CH<sub>2</sub>), 3.51–3.57 (multi, 1H, CH<sub>2</sub>CH<sub>2</sub>), 3.89–3.95 (multi, 1H, CH<sub>2</sub>CH<sub>2</sub>), 5.90 (d, <sup>3</sup>J<sub>H-H</sub> = 1.6 Hz, 1H, NCH), 6.09 (d, <sup>3</sup>J<sub>H-H</sub> = 1.6 Hz, 1H, NCH), 6.67 (s, 1H, C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>), 6.80 (s, 1H, C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>), 6.85, 6.89 (AB, <sup>3</sup>J<sub>HH</sub> = 3.2 Hz, 2H, indene), 7.05–7.10 (multi, 2H, indene), 7.12–7.18 (multi, 1H, indene), 7.96 (d, J<sub>H-H</sub> = 8.4 Hz, 1H, indene). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 4.48 (s, 3C, Sc-CH<sub>2</sub>SiMe<sub>3</sub>), 4.62 (s, 3C, Sc-CH<sub>2</sub>SiMe<sub>3</sub>), 18.27 (s, 1C, C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>), 18.51 (s, 1C, C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>), 21.38 (s, 1C, C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>), 28.44 (s, 1C, CH<sub>2</sub>CH<sub>2</sub>), 46.13 (br, 1C, Sc-CH<sub>2</sub>SiMe<sub>3</sub>), 50.48 (br, 1C, Sc-CH<sub>2</sub>SiMe<sub>3</sub>), 53.48 (s, 1C, CH<sub>2</sub>CH<sub>2</sub>), 100.95 (s, 1C, indene), 110.15- (s, 2C, *ipso*-indene), 118.52 (s, 1C, indene), 120.15 (s, 1C, indene), 120.60 (s, 1C, NCH), 121.57 (s, 1C, indene), 121.72 (s, 1C, NCH), 122.28 (s, 1C, indene), 126.29 (s, 1C, indene), 129.75, 129.90 (s,s, 2C, C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>), 135.48 (s, 1C, *ipso*-indene), 135.80 (s, 1C, *ipso*-C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>), 136.54 (s, 2C, *ipso*-C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>), 139.85 (s, 1C, *ipso*-C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>), 188.01 ppm (br, 1C, Sc-C<sub>ylidene</sub>). IR (KBr pellets): ν 3160 (m), 3133 (m), 3007 (w), 2948 (s), 2892 (m), 2845 (m), 2809 (m), 1679 (w), 1609 (w), 1557 (m), 1488 (m), 1458 (s), 1404 (m), 1381 (w), 1353 (m), 1336 (m), 1248 (s), 1237 (s), 1208 (w), 1160 (w), 1109 (m), 1031 (m), 862 (s), 817 (s), 751 (s), 742 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>31</sub>H<sub>45</sub>ScN<sub>2</sub>Si<sub>2</sub> (%): C, 68.09; H, 8.29; N, 5.12. Found: C, 68.02; H, 8.13; N, 5.20.

**Isoprene Polymerization.** In a glovebox, isoprene (1.0 mL, 10 mmol) was added into a 25 mL flask. Then 10 μmol of complex **2** and 1 equiv of AlEt<sub>3</sub> (0.01 mmol) and 1 equiv of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (9.6 mg, 0.01 mmol) were added to initiate the polymerization. After stirring for 12 h, methanol was injected into the system to terminate the polymerization. The reaction mixture was poured into a large quantity of methanol to precipitate the white solid of polyisoprene, which was filtered and dried under vacuum at ambient temperature to constant weight, yielding 0.544 g of polymer.

**Acknowledgment.** We are thankful for financial support from National Natural Science Foundation of China for Project Nos. 20571072 and 20674081; The Ministry of Science and Technology of China for Project No. 2005CB623802; and “Hundred Talent Program” of CAS. We are indebted to Prof J. G. Zhang for discussions on NMR analysis.

**Supporting Information Available:** Experimental details and <sup>1</sup>H NMR data for rare earth metal tetra(alkyl) lithium, <sup>1</sup>H, <sup>13</sup>C, and <sup>1</sup>H–<sup>13</sup>C HMQC NMR spectra for (IndH-NHC-H)Br, <sup>13</sup>C NMR spectrum for complex **1**, <sup>1</sup>H and <sup>13</sup>C NMR spectra for complexes **2** and **3**, <sup>1</sup>H–<sup>13</sup>C HMQC NMR spectrum for complex **2**, <sup>1</sup>H NMR spectrum for polyisoprene, ORTEP drawings of molecular structures for complexes **2** and **3**, and CIF files and crystallographic data for complexes **1**–**3**, including atomic coordinates, full bond distances, and bond angles as well as anisotropic thermal parameters, are available free of charge via the Internet at <http://pubs.acs.org>.

OM0700922