# **ORGANOMETALLICS**

# Unusual Si—H Bond Activation and Formation of Cationic Scandium Amide Complexes from a Mono(amidinate)-Ligated Scandium Bis(silylamide) Complex and Their Performance in Isoprene Polymerization

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**Supporting Information** 



**ABSTRACT:** Amine elimination of scandium tris(silylamide) complex  $Sc[N(SiHMe_2)_2]_3(THF)$  with 1 equiv of the amidine  $[PhC(N-2,6-Pr_2C_6H_3)_2]H$  in toluene afforded the neutral mono(amidinate) scandium bis(silylamide) complex  $[PhC(N-2,6-Pr_2C_6H_3)_2]Sc[N(SiHMe_2)_2]_2$  (1) in 93% isolated yield. When 1 was activated with 1 equiv of  $[Ph_3C][B(C_6F_5)_4]$  in the presence of THF, the unexpected cationic amidinate scandium amide complex  $[{PhC(N-2,6-Pr_2C_6H_3)_2}ScN{SiHMe_2}_{SiMe_2N}(SiHMe_2)_2](THF)_2][B(C_6F_5)_4]$  (2) was generated. Treatment of 1 with excess AlMe<sub>3</sub> gave the Sc/Al heterometallic methyl complex  $[PhC(N-2,6-Pr_2C_6H_3)_2]Sc[(\mu-Me)_2AlMe_2]_2$  (3). All these complexes were well-characterized by elemental analysis, NMR spectroscopy, and X-ray crystallography. The combination  $1/[Ph_3C][B(C_6F_5)_4]$  in toluene showed activity toward isoprene polymerization. Addition of excess AlMe<sub>3</sub> to the  $1/[Ph_3C][B(C_6F_5)_4]$  catalyst system switched the regioselectivity of isoprene polymerization from 3,4-specific to cis-1,4-selective.

# INTRODUCTION

Cationic rare-earth-metal complexes containing reactive Ln-C  $\sigma$ -bonds have received intense attention in recent years, and these complexes have shown unique reactivity and selectivity in organic transformation and polymerization.<sup>1</sup> However, most of these reported catalyst precursors, for example,  $[LLnR_2]$  (L = monoanionic ancillary ligand, Ln = rare-earth metal, R = alkyl, benzyl, allyl, etc.), are generally difficult to handle and to store due to ligand redistribution and thermal instability. Thus, it is of great interest to explore less sensitive precatalyst candidates. As far as bond disruption enthalpy, structural diversity, and thermal stability are concerned, rare-earth-metal bis(amide) complexes (Ln–N  $\sigma$ -bonded derivatives, LLn(NR'<sub>2</sub>)<sub>2</sub>) are expected to possess reactivity comparable to that of Ln-C  $\sigma$ bonded complexes.<sup>2</sup> Recently, we found that rare-earth-metal bis(amide) complexes are thermally stable and highly effective stereospecific olefin polymerization precatalysts.<sup>3,4</sup> Even though these complexes are highly active species in polymerization, their novel structures have not yet been intensively studied. Only a few cationic rare-earth-metal amide complexes have been fully characterized, in comparison to the many wellknown cationic rare-earth-metal alkyl complexes.<sup>5,6</sup> The

cationic indenyl-ligated rare-earth-metal amide [(2-Me-Ind)-LnN(SiMe<sub>3</sub>)<sub>2</sub>(THF)<sub>x</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (x = 0, 2) is obtained via an unexpected abstraction of one indenyl ligand from the bis(indenyl) rare-earth-metal mono(amide) complex (2-Me-Ind)<sub>2</sub>Ln[N(SiMe<sub>3</sub>)<sub>2</sub>] by organoborate, as reported by Tardif and Kaita.<sup>5</sup> The other is the  $\beta$ -diketiminate-ligated samarium amide complex [{(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)NC(CH<sub>2</sub>)CHC(CH<sub>3</sub>)N-(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)}SmN(SiMe<sub>3</sub>)<sub>2</sub>(THF)<sub>2</sub>][BPh<sub>4</sub>], which is formed from the treatment of the dianionic  $\beta$ -diketiminate samarium mono(amide) complex {(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)NC(CH<sub>2</sub>)CHC(CH<sub>3</sub>)-N(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)}SmN(SiMe<sub>3</sub>)<sub>2</sub>(THF) with [HNEt<sub>3</sub>][BPh<sub>4</sub>], reported by Shen et al. recently.<sup>6</sup> These cationic rare-earthmetal amide species are not obtained from their corresponding rare-earth-metal bis(amide) complexes, and the amide groups are constrained to the sterically hindered  $-N(SiMe_3)_2$  group.

During our study on the essential role of rare-earth-metal bis(amide) complexes as catalyst precursors in polymerization, it was found that the Si–H  $\sigma$  bond in the mono(amidinate)-ligated scandium bis(silylamide) complex [PhC(N-

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2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>]Sc[N(SiHMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub> (1) could be activated by [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] to generate the unexpected cationic amidinate scandium amide complex [{PhC(N-2,6<sup>-</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>}-ScN{SiHMe<sub>2</sub>}{SiMe<sub>2</sub>N(SiHMe<sub>2</sub>)<sub>2</sub>(THF)<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (2). Remarkably, addition of AlMe<sub>3</sub> to the 1/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] catalyst system not only increased the polymerization activity but also switched the regioselectivity of the polymerization from 3,4-specific to cis-1,4-selective. Moreover, the reaction of 1 with excess AlMe<sub>3</sub> afforded the amidinate Sc/Al heterometallic methyl complex [PhC(N-2,6<sup>-i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>]Sc[( $\mu$ -Me)<sub>2</sub>AlMe<sub>2</sub>]<sub>2</sub> (3) via amide–alkyl exchange. This demonstrated that the active species in the binary catalyst system 1/ [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] and in the ternary catalyst system 1/ [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]/AlMe<sub>3</sub> are strikingly different. Here we wish to report these results.

# RESULTS AND DISCUSSION

Amine elimination of the scandium tris(silylamide) complex  $Sc[N(SiHMe_2)_2]_3$ (THF) with 1 equiv of the amidine [PhC(N-2,6-'Pr\_2C\_6H\_3)\_2]H in toluene at 100 °C for 3 h, after workup, afforded the mono(amidinate) scandium bis(silylamide) complex [PhC(N-2,6-'Pr\_2C\_6H\_3)\_2]Sc[N(SiHMe\_2)\_2]\_2 (1) in 93% isolated yield (Scheme 1). Elemental analysis, NMR

Scheme 1. Synthesis of Mono(amidinate)-Ligated Scandium Bis(silylamide) Complex 1



spectroscopy, and X-ray crystallography confirmed the composition of 1 and showed that it is a neutral, mononuclear, and solvent-free species. The FT-IR spectrum contains wellresolved  $\nu$ (SiH) bands around 2109 and 2070 cm<sup>-1</sup>, showing an asymmetrical coordination of silylamide groups to the center metal.<sup>3,7</sup> Room-temperature <sup>1</sup>H NMR spectra of 1 in  $C_6D_6$ showed that the resonances of the isopropyl groups on the aryl rings were two doublets, indicating a restricted rotation of N-Carvl bonds. Complex 1 is thermally stable at ambient temperature in the glovebox and soluble in THF, toluene, and diethyl ether but sparingly soluble in aliphatic solvents such as hexane and pentane. Single crystals of 1 suitable for X-ray diffraction were grown from a mixture of hexane and toluene at -30 °C. The molecular structure is shown in Figure 1. The metal center is coordinated to a bidentate amidinate ligand through two nitrogen atoms and two nitrogen atoms from two silylamide groups to form a distorted-tetrahedral geometry. The planes of the three phenyl groups on the amidinate backbone are not coplanar with the plane formed by C1N1Sc1N2, which reduces the delocalization of  $\pi$  electrons among these moieties. The Sc-N(amidinate) bond distances in 1 (average 2.159 Å) are shorter than those in [PhC(N-2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>]Sc-(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(THF) (average 2.207 Å)<sup>8</sup> and in [TolC(N- $2,6-{}^{i}Pr_{2}C_{6}H_{3})_{2}]Y[N(SiHMe_{2})_{2}]_{2}(THF)$  (average 2.382 Å).<sup>9</sup> Both Sc-N(SiHMe<sub>2</sub>)<sub>2</sub> bond distances in 1 are 2.065(3) Å, which are comparable with those in  $Sc[N(SiHMe_2)_2]_3(THF)$ (average 2.069 Å)<sup>10</sup> and mono(aminopyridinate)Sc[N-(SiHMe\_2)\_2]\_2 (average 2.049 Å).<sup>11</sup>



Figure 1. Molecular structure of 1. Hydrogen atoms (except those on SiH) are omitted for clarity. Selected bond lengths (Å) and angles (deg): N1-C1 = 1.336(5), C1-N2 = 1.347(5), Sc1-N1 = 2.158(3), Sc1-N2 = 2.160(3), Sc1-N3 = 2.065(3), Sc1-N4 = 2.065(3); N1-Sc1-N2 = 62.15(11), N3-Sc1-N4 = 120.42(13), N1-C1-N2 = 112.3(3).

The neutral amidinate scandium bis(silylamide) complex 1 alone showed no activity toward isoprene polymerization.<sup>12</sup> However, upon activation with 1 equiv of  $[Ph_3C][B(C_6F_5)_4]$  in toluene at room temperature, 1 became active for the polymerization of isoprene in a 3,4-selective fashion, and the conversion reached 100% in 45 min at the initial feed ratio [M]/[Sc] = 500 (Table 1, run 2). This finding is surprising, since isoprene polymerization catalyzed by  $[RC(N-2,6-Me_2C_6H_3)_2]Y[N(SiMe_3)_2]_2/[Ph_3C][B(C_6F_5)_4]$  (R = Ph, Cy) showed no activity at all.<sup>4</sup>

To understand the true active species with this binary catalyst system, a stoichiometric reaction of 1 with  $[Ph_2C][B(C_4F_5)_4]$ was carried out. The <sup>1</sup>H NMR monitoring technique showed that addition of 1 equiv of  $[Ph_3C][B(C_6F_5)_4]$  to 1 in  $C_6D_5Cl$  at room temperature instantly produced a cationic scandium amide species, with the release of Ph<sub>3</sub>CH in a 1:1 molar ratio (not the release of  $Ph_3C-N(SiHMe_2)_2$ ). The formation of Ph<sub>3</sub>CH during the reaction indicated that the cationic species generated was not the anticipated product [{PhC(N-2,6-<sup>*i*</sup> $Pr_2C_6H_3)_2$ Sc-N(SiHMe\_2)\_2][B(C\_6F\_5)\_4]. On a preparation scale, reaction of 1 with  $[Ph_3C][B(C_6F_5)_4]$  in a 1:1 molar ratio in toluene at room temperature, after the volatiles were removed and the residue washed with hexane, gave a cationic scandium amide species whose component was identical with that obtained from NMR-scale experiments. Unfortunately, attempts to obtain single crystals suitable for X-ray analysis were unsuccessful. However, addition of a small amount of THF into a toluene solution of the cationic scandium amide complex, after workup, afforded the THF-coordinated cationic amidinate scandium amide complex  $[{PhC(N-2,6^{-i}Pr_2C_6H_3)_2}]$ - $ScN{SiHMe_2}{SiMe_2N(SiHMe_2)_2}(THF)_2[B(C_6F_5)_4]$  (2) as colorless microcrystals in 65% isolated yield (Scheme 2). Complex 2 is thermally stable at ambient temperature for weeks

#### Table 1. Isoprene Polymerization by Amidinate-Ligated Scandium Catalysts<sup>a</sup>

|                                |            | 3,4-polyisopre | 1 /[Ph <sub>3</sub> C][B( | $\frac{C_6F_5)_{4}}{n} \qquad \frac{1}{(Ph_3C)[B(C)]}$                     |                 | C <sub>6</sub> F <sub>5)4</sub> ]/AIMe <sub>3</sub> |                             |   |
|--------------------------------|------------|----------------|---------------------------|--|-----------------|---|-----------------------------|---|
| run                            | complex    | [M]/[Sc]       | Sc/Al/B                   | t (min)  | yield (%)       | $M_{n}^{b}$ (×10 <sup>4</sup> )                     | $M_{\rm w}/M_{\rm n}^{\ b}$ | 3,4/cis-1,4/trans-1,4 <sup>c</sup>      |
| 1                              | 1          | 500            | 1/0/1                     | 15   | 58              | 10.54   | 1.76                        | 86/13/1                                 |
| 2                              | 1          | 500            | 1/0/1                     | 45   | 100             | 14.71   | 1.61                        | 89/9/2                                  |
| 3                              | 2          | 500            | 1/0/0                     | 30   | 0               |   |                             |   |
| 4                              | 2a         | 500            | 1/0/0                     | 15   | 56              | 9.87  | 1.68                        | 88/11/1                                 |
| 5                              | 1          | 500            | 1/5/1                     | 2  | 100             | 3.53  | 1.51                        | 6/93/1                                  |
| 6                              | 1          | 1000           | 1/5/1                     | 2  | 100             | 4.95  | 1.79                        | 2/94/4                                  |
| 7                              | 3          | 500            | 1/0/0                     | 30   | 0               |   |                             |   |
| 8                              | 3          | 500            | 1/0/1                     | 2  | 98              | 8.03  | 1.56                        | 5/94/1                                  |
| <i>a a b b b b b b b b b b</i> | <i>c</i> 1 |                | 1 5 51                    | $\alpha$ $\left[ \left( n \right) \right] \left[ \left( n \right) \right]$ | 7 - / - / / ) - | / 1   | a ha                        | 11 000 0 000000000000000000000000000000 |

<sup>*a*</sup>Conditions: performed in toluene; Sc 20  $\mu$ mol; B = [Ph<sub>3</sub>C][[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]; 1/3 (v/v) isoprene/toluene; 25 °C. <sup>*b*</sup>Determined by GPC in THF at 40 °C against a polystyrene standard. <sup>*c*</sup>Determined by <sup>1</sup>H NMR in CDCl<sub>3</sub>.





in the glovebox and soluble in THF and chlorobenzene but insoluble in toluene and hexane. X-ray diffraction revealed unambiguously that 2 consists of a separated [{PhC(N- $2_{6}$ <sup>i</sup> $Pr_{2}C_{6}H_{3}$ )<sub>2</sub> $ScN{SiHMe_{2}}{SiMe_{2}N(SiHMe_{2})_{2}}(THF)_{2}$ <sup>+</sup> cation and  $[B(C_6F_5)_4]^-$  anion (Figure 2). The metal center is five-coordinated to a bidentate amidinate ligand, an amide group, and two THF molecules to adopt a distorted-trigonalbipyramidal geometry. The amide group occupies an axial position relative to the N1C1Sc1N2 plane. The Sc-N(amidinate) (2.208(3) and 2.173(3) Å) and Sc-N(amide) (2.043(3) Å) bond distances in 2 are close to those in the neutral complex 1 (Sc1-N1 = 2.158(3), Sc1-N2 = 2.160(3), and Sc1-N3 = 2.065(3) Å). The formation of 2 from treatment of 1 with  $[Ph_3C][B(C_6F_5)_4]$  in the presence of THF instead of simple silylamide  $(-N(SiHMe_2)_2)$  abstraction was unexpected. A possible mechanism for the transformation of 1 to 2 may involve concerted Si-H  $\sigma$ -bond activation by

[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], accompanied by silylamide migration (Scheme 2). This is the first example of such an unusual Si– H  $\sigma$ -bond activation in rare-earth-metal complexes to our knowledge.<sup>13</sup> It also proves indirectly that 1 could be converted into a cationic amide species, albeit not in an expected manner. Although the isolated THF-coordinated 2 was not active for isoprene polymerization (Table 1, run 3), 2a showed activity comparable with that of  $1/[Ph_3C][B(C_6F_5)_4]$  in toluene (Table 1, run 4). Thus, the true active species with the binary catalyst system of  $1/[Ph_3C][B(C_6F_5)_4]$  in toluene is suggested mostly to be a THF-free cationic amide intermediate such as [{PhC(N-2,6-Pr\_2C\_6H\_3)\_2}ScN{SiHMe\_2}{SiMe\_2N(SiHMe\_2)\_2}]-[B(C\_6F\_5)\_4] (2a), as envisioned in the proposed polymerization mechanism (Scheme 3).

Remarkably, addition of AlMe<sub>3</sub> to the  $1/[Ph_3C][B(C_6F_5)_4]$  catalyst system increased the polymerization activity and also switched the regioselectivity of the polymerization from 3,4-

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**Figure 2.** Molecular structure of **2.** Hydrogen atoms (except those on SiH) and the  $[B(C_6F_5)_4]^-$  anion are omitted for clarity. Selected bond lengths (Å) and angles (deg): N1-C1 = 1.344(4), C1-N2 = 1.343(4), Sc1-N1 = 2.208(3), Sc1-N2 = 2.173(3), Sc1-N3 = 2.043(3); N1-Sc1-N2 = 61.27(10), N1-C1-N2 = 112.4(3).

specific to cis-1,4-selective (Table 1, runs 5 and 6). GPC curves indicated that the polyisoprene samples produced by this ternary catalyst system were unimodal, indicative of single-site polymerization behavior. To get some information on the effect of AlMe<sub>3</sub> on the polymerization, the reaction of 1 with excess AlMe<sub>3</sub> in toluene at room temperature was performed, which gave the Sc/Al heterometallic methyl complex [PhC(N-2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>]Sc[( $\mu$ -Me)<sub>2</sub>AlMe<sub>2</sub>]<sub>2</sub> (3) (Figure 3), a product formed via an amide–alkyl exchange (Scheme 4).<sup>7,14</sup> Since the crystal structure of **3** is isomorphous with that of [PhC(N-2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>]Y( $\mu$ -Me)<sub>2</sub>AlMe<sub>2</sub>]<sub>2</sub> from the reaction of [PhC-(N-2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>]Y( $\sigma$ -CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>)<sub>2</sub> with AlMe<sub>3</sub>,<sup>15</sup> the active species in this polymerization should therefore also be a cationic Sc/Al heterobimetallic complex,<sup>16</sup> as postulated by Hou<sup>15</sup> and Kempe.<sup>11,17</sup>



Figure 3. Molecular structure of 3. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): N1-C1 = 1.338(4), Sc1-N1 = 2.171(3), Sc1-C18 = 2.371(5), Sc1-C19 = 2.437(4), Al1-C18 = 2.030(5), Al1-C19 = 2.070(5), Al1-C20 = 1.959(6), Al1-C21 = 1.954(5); N1-C1-N1A = 111.2(5), N1-Sc1-N1A = 61.12(16), C18-Sc1-C19 = 86.87(18), C18-Al1-C19 = 107.44(19), C20-Al1-C21 = 117.5(3).

### CONCLUSION

In summary, on treatment with  $[Ph_3C][B(C_6F_5)_4]$ , an unusual Si-H  $\sigma$ -bond activation and silylamide migration took place in a thermally stable mono(amidinate)-ligated scandium bis-(silylamide) complex (1) and generated an unexpected cationic amidinate scandium amide species, which showed good performance in the 3,4-selective polymerization of isoprene. In addition, introduction of AlMe<sub>3</sub> into the binary catalyst system  $1/[Ph_3C][B(C_6F_5)_4]$  changed the active species from a cationic amide complex to a cationic heterometallic amidinate Sc/Al complex, which showed high activity toward cis-1,4-selective polymerization of isoprene. To the best of our

Scheme 3. Possible Mechanism for 3,4-Selective Polymerization of Isoprene by 1/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]







knowledge, this is the first example of unusual Si–H  $\sigma$ -bond activation in rare-earth-metal complexes and formation of a stable cationic rare-earth-metal mono(amide) complex from a neutral rare-earth-metal bis(amide) complex. We are currently in the process of developing an efficient synthetic strategy for cationic rare-earth-metal mono(amide) derivatives and exploring their reactivity.

## EXPERIMENTAL SECTION

**Materials and Procedures.** All manipulations were performed under pure argon with rigorous exclusion of air and moisture using standard Schlenk techniques and an argon-filled glovebox. Solvents (toluene, hexane, and THF) were distilled from sodium/benzophenone ketyl, degassed by the freeze–pump–thaw method, and dried over fresh Na chips in the glovebox. Anhydrous ScCl<sub>3</sub> and  $[Ph_3C][B(C_6F_5)_4]$  were purchased from Strem. AlMe<sub>3</sub> (1.0 M in hexane solution) was purchased from Acros and used as received. HN(SiHMe<sub>2</sub>)<sub>2</sub> was purchased from Fluoro Chem and used as received. Isoprene was purchased from Acros, dried by stirring with CaH<sub>2</sub>, and distilled before polymerization. Deuterated solvents (CDCl<sub>3</sub>,  $C_6D_6$ , THF- $d_8$ ,  $C_6D_5$ Cl) were obtained from Aldrich. Sc[N(SiHMe<sub>2</sub>)<sub>2</sub>]<sub>3</sub>(THF)<sup>10</sup> and [PhC(N-2,6-iPr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>]H<sup>18</sup> were prepared according to the literature.

Samples of scandium complexes for NMR spectroscopic measurements were prepared in the glovebox using J. Young valve NMR tubes. NMR ( $^{1}$ H,  $^{13}$ C) spectra were recorded on a Bruker AVANCE III spectrometer at 25 °C and referenced internally to residual solvent resonances unless otherwise stated. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion on a Carlo-Erba EA-1110 instrument; quoted data are the average of at least two independent determinations. FT-IR spectra were recorded on a Bruker TENSOR 27 spectrometer. Molecular weights and molecular weight distributions of the polymers were measured by a PL GPC 50 instrument with two Mixed-B columns at 40 °C using THF as eluent against polystyrene standards: flow rate, 1 mL/min; sample concentration, 1 mg/mL.

[PhC(N-2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>]Sc[N(SiHMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub> (1). A toluene (10 mL) solution of [PhC(N-2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>]H (0.441 g, 1.0 mmol) was added dropwise to a toluene solution (5 mL) of  $Sc[N(SiHMe_2)_2]_3(THF)$ (0.514 g, 1.0 mmol) at room temperature. The reaction mixture was stirred at 100 °C for 3 h to give a clear pale yellow solution. Removal of the volatiles under vacuum afforded a pale yellow powder, which was extracted by hexane  $(2 \times 10 \text{ mL})$ . After hexane was removed, the crude product 1 was obtained as a white powder (0.69 g, 93%). Recrystallization from hexane solution at -30 °C gave 1 as colorless block crystals (0.54 g, 72%). <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ ):  $\delta$  0.17 (d, J = 2.8 Hz, 24H, SiHMe<sub>2</sub>), 0.95 (d, J = 6.8 Hz, 12H, CHMe<sub>2</sub>), 1.43 (d, J= 6.8 Hz, 12H, CHMe<sub>2</sub>), 3.58 (sept, 4H, CHMe<sub>2</sub>), 5.23 (sept, 4H, SiHMe2), 6.59-6.64 (m, 3H, Ar-H), 7.07 (s, 6H, Ar-H), 7.25-7.27 (m, 2H, Ar-H). <sup>13</sup>C NMR (100 MHz,  $C_6D_6$ ):  $\delta$  2.5 (SiHMe<sub>2</sub>), 23.7, 25.2 (CHMe<sub>2</sub>), 29.0 (CHMe<sub>2</sub>), 124.4, 125.1, 127.6, 130.4, 130.7, 131.3, 141.5, 142.8 (Ar-C), 176.4 (NCN). FT-IR (KBr, cm<sup>-1</sup>): 2962 (s), 2868 (m), 2109 (m), 2070 (m), 1624 (s), 1576 (m), 1459 (s),

1357 (m), 1251 (s), 1011 (m), 899 (s), 769 (s), 697 (s). Anal. Calcd for  $C_{39}H_{67}N_4ScSi_4$ : C, 62.51; H, 9.03; N, 7.48. Found: C, 62.65; H, 8.98; N, 7.36.

 $[{PhC(N-2,6-Pr_2C_6H_3)_2}ScN{SiHMe_2}{SiMe_2N(SiHMe_2)_2}][B (C_6F_5)_4$ ] (2a). A toluene solution (20 mL) of  $[Ph_3C][B(C_6F_5)_4]$  (62 mg, 70  $\mu$ mol) was added dropwise into a toluene (15 mL) solution of 1 (50 mg, 70  $\mu$ mmol) at room temperature. The reaction mixture was stirred for 2 h at room temperature to give a clear solution. Removal of the volatiles under vacuum produced a pale yellow powder. The crude product was washed with hexane  $(3 \times 10 \text{ mL})$  to remove Ph<sub>3</sub>CH and dried (70 mg, 71%). <sup>1</sup>H NMR (400 MHz,  $C_6D_5Cl/C_6D_6$ ):  $\delta$  –0.02 (d, J = 2.8 Hz, 6H, NSiHMe<sub>2</sub>), 0.00 (s, 6H, SiMe<sub>2</sub>), 0.01 (s, 12H,  $N(SiHMe_2)_2)$ , 0.84 (d, J = 6.8 Hz, 12H, CHM $e_2$ ), 1.06 (d, J = 6.8 Hz, 12H, CHMe<sub>2</sub>), 3.02 (sept, 4H, CHMe<sub>2</sub>), 4.57 (sept, 2H, SiHMe<sub>2</sub>), 5.36 (sept, 1H, SiHMe<sub>2</sub>), 6.51 (t, J = 7.6 Hz, 2H, Ar-H), 6.55-6.57 (m, 1H, Ar-*H*), 6.87 (d, *J* = 7.6 Hz, 4H, Ar-*H*), 6.91 (d, *J* = 7.6 Hz, 2H, Ar-H), 6.96 (d, J = 7.6 Hz, 2H, Ar-H). Anal. Calcd for C68H73BF20N4ScSi4: C, 57.18; H, 5.12; N, 3.92. Found: C, 57.24; H, 5.31; N, 3.88.

 $[{PhC(N-2,6-^{i}Pr_{2}C_{6}H_{3})_{2}}ScN{SiHMe_{2}}{SiMe_{2}N(SiHMe_{2})_{2}} (THF)_2[B(C_6F_5)_4]$  (2). A toluene solution (15 mL) of  $[Ph_3C][B (C_6F_5)_4$ ] (0.462 g, 0.5 mmol) was added dropwise into a toluene (10 mL) solution of 1 (0.375 g, 0.5 mmol) at room temperature. The reaction mixture was stirred at room temperature to give a clear brown solution. After the reaction mixture was kept at room temperature for 1 h, THF (0.2 g, 3 mmol) was introduced via a pipet to give a clear pale yellow solution. Removal of the volatiles under vacuum produced a pale yellow powder. The crude product was washed by hexane  $(3 \times$ 10 mL) to get rid of Ph<sub>3</sub>CH. The resulting pale yellow powder was dissolved in about 2 mL of a hexane/THF (3/1, v/v) mixture and was kept at room temperature overnight to give 2 as colorless crystals (0.43 g, 65%). <sup>1</sup>H NMR (400 MHz, THF- $d_8/C_6D_6$ ):  $\delta$  0.10 (s, 6H, SiHMe<sub>2</sub>), 0.18 (d, J = 3.6 Hz, 12H, SiHMe<sub>2</sub>), 0.28 (s, 6H, SiMe<sub>2</sub>), 0.72 (br s, 12H, CHMe<sub>2</sub>), 1.15 (d, J = 5.6 Hz, 12H, CHMe<sub>2</sub>), 1.44–1.47 (m, 8H, THF-β-H), 3.03 (br s, 4H, CHMe<sub>2</sub>), 3.55-3.58 (m, 8H, THF-α-H), 4.57 (sept, 2H, SiHMe<sub>2</sub>), 5.13 (sept, 1H, SiHMe<sub>2</sub>), 6.57 (t, J = 7.2 Hz, 2H, Ar-H), 6.65 (t, J = 7.6 Hz, 1H, Ar-H), 6.86 (d, J = 7.2 Hz, 2H, Ar-*H*), 6.97 (d, J = 7.2 Hz, 4H, Ar-*H*), 7.06 (t, J = 7.6 Hz, 2H, Ar-*H*). <sup>13</sup>C NMR (100 MHz, THF- $d_8/C_6D_6$ ):  $\delta$  1.8 (SiHMe<sub>2</sub>), 6.6 (SiMe<sub>2</sub>), 23.7, 25.5 (CHMe<sub>2</sub>), 25.8 (THF-β-C), 28.6 (CHMe<sub>2</sub>), 67.9 (THF-α-C), 125.1, 125.7, 126.7, 127.7, 128.5, 129.3, 129.4, 131.3 (Ar-C), 135.8, 137.7, 138.2, 140.1 (C<sub>6</sub>F<sub>5</sub>), 141.7, 142.3 (Ar-C), 147.9, 150.3 (C<sub>6</sub>F<sub>5</sub>), 180.5 (NCN). Anal. Calcd for C<sub>74</sub>H<sub>89</sub>BF<sub>20</sub>N<sub>4</sub>O<sub>2</sub>ScSi<sub>4</sub>: C, 55.04; H, 5.57; N, 3.47. Found: C, 54.86; H, 5.61; N, 3.59.

[PhC(N-2,6-<sup>*i*</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>]Sc[( $\mu$ -Me)<sub>2</sub>AlMe<sub>2</sub>]<sub>2</sub> (3). A toluene (10 mL) solution of 1 (0.749 g, 1.0 mmol) was added dropwise to a heptane solution (6 mL) of AlMe<sub>3</sub> (6 mmol, 1.0 M) at room temperature. The reaction mixture was stirred at room temperature for 2 h to give a clear pale yellow solution. Removal of the volatiles under vacuum produced a pale yellow oily residue, which was extracted by toluene (2 × 10 mL). After the side product of Me<sub>2</sub>Al[( $\mu$ -N(SiHMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub>AlMe<sub>2</sub> was separated from the extract solution by fractional recrystallization, the residual mother solution was dried under vacuum. The resulting pale yellow powder was dissolved in

hexane, and the solution was filtered. Concentrating and cooling the filtrate gave 3 as a white powder (0.43 g, 65%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  –0.01 (br s, 24H, [AlMe<sub>4</sub>]<sup>-</sup>), 0.96 (d, *J* = 6.8 Hz, 12H, CHMe<sub>2</sub>), 1.28 (d, *J* = 6.8 Hz, 12H, CHMe<sub>2</sub>), 3.51 (sept, 4H, CHMe<sub>2</sub>), 6.60–6.61 (m, 3H, Ar-H), 6.98–7.03 (m, 6H, Ar-H), 7.09–7.12 (m, 2H, Ar-H). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  23.4 (CHMe<sub>2</sub>), 25.9 (CHMe<sub>2</sub>), 28.8 (CHMe<sub>2</sub>), 124.4, 126.2, 127.4, 130.3, 130.4, 141.4, 142.7 (Ar-C), 177.5 (NCN), the signal for [AlMe<sub>4</sub>]<sup>-</sup> was not observed. Anal. Calcd for C<sub>39</sub>H<sub>63</sub>Al<sub>2</sub>N<sub>2</sub>Sc: C, 71.09; H, 9.66; N, 4.25. Found: C, 70.85; H, 9.47; N, 4.18.

**Typical Procedure for Isoprene Polymerization.** The procedures for isoprene polymerization catalyzed by these scandium complexes were similar, and a typical polymerization procedure is given below. A 50 mL Schlenk flask equipped with a magnetic stirring bar was charged in sequence with the desired amount of the scandium complex, toluene, borate (or borate and methylaluminum) and isoprene. The mixture was stirred vigorously at room temperature for the desired time, during which an increase of viscosity was observed. The reaction mixture was quenched by the addition of ethanol and then poured into a large amount of ethanol to precipitate the polymer, which was dried under vacuum at 60 °C and weighed.

**X-ray Crystallographic Study.** Suitable single crystals of complexes were sealed in a thin-walled glass capillary for determining the single-crystal structure. Intensity data were collected with a Rigaku Mercury CCD area detector in  $\omega$  scan mode using Mo K $\alpha$  radiation ( $\lambda = 0.710$  70 Å). The diffracted intensities were corrected for Lorentz–polarization effects and empirical absorption corrections. The structures were solved by direct methods and refined by full-matrix least-squares procedures based on  $|F|^2$ . All the non-hydrogen atoms were refined anisotropically. The structures were solved and refined using the SHELXL-97 program. CCDC 866532–866534 contain supplementary crystallographic data for complexes 1–3. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

#### ASSOCIATED CONTENT

# **Supporting Information**

Figures giving NMR spectra of complexes 1-3 and CIF files giving full crystallographic data for complexes 1-3. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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(16) In the ternary catalyst system  $1/[Ph_3C][B(C_6F_5)_4]/AlMe_3$ , the addition sequence of  $[Ph_3C][B(C_6F_5)_4]$  or AlMe<sub>3</sub> first to 1 had little effect on either the polymerization activity or the selectivity. However, the isolation of a cationic species from either the treatment of 3 with  $[Ph_3C][B(C_6F_5)_4]$  or the reaction of 2a with AlMe<sub>3</sub> was unsuccessful.

(17) NMR spectroscopic studies showed that reaction of mono(aminopyridinate)Sc[N(SiHMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub> with AlMe<sub>3</sub> gave a mono(-aminopyridinate)Sc[ $(\mu$ -Me)<sub>2</sub>AlMe<sub>2</sub>]<sub>2</sub> species; however, the isolation of this species was not successful.<sup>11</sup> In contrast, mono(aminopyridinate)Ln[N(SiHMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub> (Ln = La, Y) reacted with AlMe<sub>3</sub> by transfer of aminopyrdinate ligand from the rare-earth metal to the aluminum atom; see: Doring, C.; Kempe, R. *Eur. J. Inorg. Chem.* 2009, 412.

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