New Rare Earth Metal Bis(alkyl)s Bearing an Iminophosphonamido Ligand. Synthesis and Catalysis toward Highly 3,4-Selective Polymerization of Isoprene

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Received September 23, 2007

New rare earth metal bis(alkyl) complexes [(NPN^{Ph})Ln(CH$_2$SiMe$_3$)$_2$(THF)] (NPN^{Ph}: N(Ph)PPh$_2$=NC$_6$H$_2$Me$_3$-2,4,6; Ln = Sc (**3a**), Ln = Y (**3b**), Ln = Lu (**3c**)) and [(NPN^{Py})Sc(CH$_2$SiMe$_3$)$_2$(THF)] (NPN^{Py} = N(Py)PPh$_2$=NC$_6$H$_2$Me$_3$-2,4,6) (**3d**)) have been prepared via protonolysis reaction between rare earth metal tris(alkyl)s and the corresponding iminophosphonamines. Complexes **3a**−**d** are analogous monomers of THF solvate. Each metal ion coordinates to a η^2-chelated NPN ligand and two *cis*-located alkyl groups, adopting tetrahedron geometry. The scandium complex [(NPN^{Ph})Sc(CH$_2$SiMe$_3$)$_2$(THF)] in combination with [PhNHMe$_2$][B(C$_6$F$_5$)$_4$] and Al*i*Bu$_3$ forms the first non-Cp-ligated rare earth metal based catalyst system to provide extremely high activity and 3,4-selectivity for the polymerization of isoprene. The resultant high molecular weight polymer ($M_n = 99 \times 10^4$) with narrow molecular weight distribution (PDI = 1.55) has a 3,4-regularity up to 94.7% (Tp = –40 °C, toluene, 2 h, 100% yield). The complexes **3b** and **3c**, with a larger ionic radius, are less regioselective, and **3d**, with an electron-donating pyridyl moiety, is inert. The probable initiation species and mechanistic scenario are also presented.

Introduction

The past half-century has witnessed the development of the catalysts for the regio- and stereoselective polymerization of conjugated dienes such as butadiene and isoprene, because the resulting polymers find wide applications in the synthetic elastomer industry due to their outstanding performances. The Ziegler–Natta catalyst systems based on transition metals including titanium, cobalt, nickel, and the distinguished lanthanide metal alkoxides and carboxylates under the presence of aluminum alkyls or aluminum alkyls/borate[1] provide high *cis*-1,4 selectivity for the polymerization of diene to afford the most important synthetic rubber.[2] The f- and d-block element metallocenes combined with MAO or AlR$_3$ have also attracted increasing attention due to their tremendously high specific *cis*-1,4 selectivity.[3–5] Recently, non-cyclopentadienyl (non-Cp) ligated lanthanide alkylaluminates[6] and PNP-type rare earth metal cationic units (PNP: bis(phosphinophenyl)amido)[7] have gathered an upsurge in such research interest, which led to controllable polymerization with respect to the molecular weight, polydispersities, and regularity. In the meantime, the interest of *trans*-1,4-regulated polymerization has emerged in the high-performance rubber or tires industry.[8] The Ln(allyl)$_2$Cl(MgCl$_2$)$_2$/AlR$_3$ system has been designed to initiate the 1,4-*trans* polymerization of isoprene,[9] while the neodymium boron hydrido complex Nd(BH$_4$)$_3$(THF)$_3$ with the activator Mg(*n*Bu)$_2$ has also exhibited 1,4-*trans* selectivity, the catalytic performance of which is significantly improved by introducing a Cp ligand into the molecule to generate a half-metallocene Cp*Nd-

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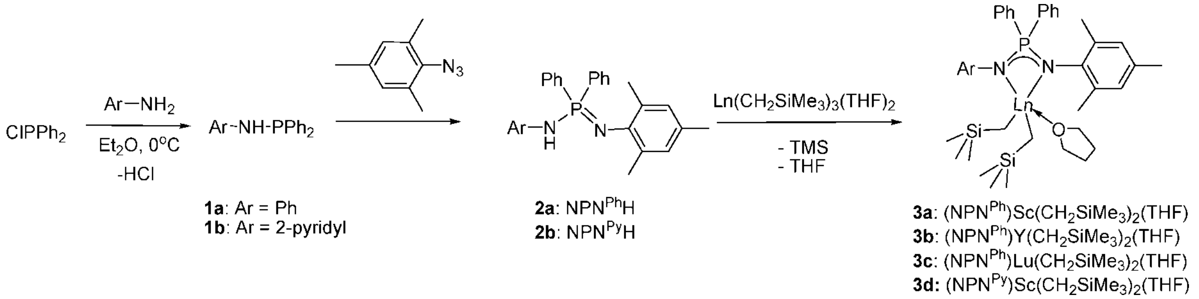
10.1021/om700945r

Scheme 1. Synthesis of Complexes 3a−d



$(BH_4)_2(THF)_2$.[10] In contrast, 3,4-polymerization of isoprene has been explored less, although this polymer is used as an important component of high-performance rubber.[11] Only few catalytic systems can initiate the 3,4-polymerization of isoprene, as isoprene prefers to coordinate to the metal center of many catalytic systems in a *cis*-1,4 mode, generating a thermally stable η^3-π-butenyl species, whereas coordinating in a 3,4-η^2-mode to leave the bulky allylic group dangling,[7] the steric hindrance at the metal center is requisite. To date, efficient 3,4-selective catalyst systems are a transition-metal complex domain, such as $AlEt_3$-$Ti(OR)_4$,[12a,b] $(dmpe)_2CrCl_2$-MAO (dmpe: 1,2-bis(dimethylphosphino)ethane),[12c] and some iron-based complexes containing chelating nitrogen ligands.[13] In a few cases, the 3,4-selectivity is over 90%. Although rare earth metal complexes have played significant roles in *cis*- and *trans*-selective polymerization, they usually do not show 3,4-selectivity except for a very recent breakthrough achieved by Hou's group, who employed a half-metallocene yttrium precursor activated by $[Ph_3C][B(C_6F_5)_4]$ to provide isotactic 3,4-polyisoprene.[14] Therefore, further exploration of new catalyst systems of high 3,4-selectivity based on rare earth metals and other elements is of obvious interest.

Our group has been carrying out the synthesis of non-Cp-ligated rare earth metal bis(alkyl)s that have exhibited high catalytic activity toward polymerizations of polar monomers and olefins.[15] The complexes bearing phosphorus auxiliary ligands have the potential for catalyzing the specific polymerization of conjugated dienes, because the introduction of a "large" and "soft" phosphorus donor is anticipated to increase the steric bulk and to lower the electron density of metal center, which is favored for initiating the polymerization of nonpolar monomers. Although Ti, Zr, Ni, etc., metal complexes[16] with NPN-type ligands have been reported and their chemistry has been studied,[17] the corresponding rare earth metal analogues are unknown, as far as we are aware. Herein, we wish to report the first example of NPN-type rare earth metal bis(alkyl)s, which in combination with $[PhNHMe_2][B(C_6F_5)_4]$ and $AliBu_3$ act as the first non-Cp group 3 metal precursors for the 3,4-selective polymerization of isoprene. The probable active species and the mechanistic scenario will also be discussed.

Results and Discussion

Synthesis and Characterization of NPN-Type Rare Earth Metal Bis(alkyl) Complexes 3a−d. The iminophosphonamines $ArNHP(Ph_2){=}NC_6H_2Me_3$-2,4,6 (**2a** ($NPN^{Ph}H$): Ar = Ph; **2b** ($NPN^{Py}H$): Ar = 2-pyridyl) were prepared via Staudinger reaction between aminodiphenylphosphine $ArNHPPh_2$ (**1a**: Ar = Ph; **1b**: Ar = 2-pyridyl) and 1 equiv of mesityl azide. Protonolysis of the rare earth metal tris(alkyl)s $Ln(CH_2SiMe_3)_3(THF)_2$ with **2a** or **2b** gave the bis(alkyl) complexes $[(NPN^{Ph})Ln(CH_2SiMe_3)_2(THF)]$ (**3a**: Ln = Sc; **3b**: Ln = Y; **3c**: Ln = Lu) or $[(NPN^{Py})Sc(CH_2SiMe_3)_2(THF)]$ (**3d**) in quantitative yield, respectively (Scheme 1). The ^1H NMR spectrum of **3a** displayed an AB spin at δ 0.45 and 0.77 ($J_{H\text{-}H}$ = 12 Hz) assigned to the methylene protons of the metal alkyl Sc-CH_2SiMe$_3$, indicating that the methylene protons were diastereotopic. In contrast, the resonances of the methylene protons of Sc-CH_2SiMe$_3$ in **3d** overlapped with silylmethyl, which might be attributed to the electron-donating pyridyl moiety, while the methylene protons of Y-CH_2SiMe$_3$ in **3b** showed a doublet at δ 0.11 due to coupling with the yttrium ion ($J_{Y\text{-}C\text{-}H}$ = 2.7 Hz) and those of Lu-CH_2SiMe$_3$ in **3c** exhibited a broad resonance around δ −0.07, suggesting that the metal alkyl species in both **3b** and **3c** were fluxional in the solution state. This difference may be attributed to the smaller ionic radius of Sc^{3+} compared to those of Y^{3+} and Lu^{3+}.

The solid-state structures of **3a−d** were confirmed by X-ray diffraction to be isostructural monomers with a coordinated THF molecule (Table 1, Figures 1–4).[18] The coordination geometry around the metal center is best described as a distorted tetrahedron. The two alkyl species are located in *cis*-position.

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(18) The ^1H NMR and ^{13}C NMR spectra of complexes **3a−d**; see Supporting Information.

Table 1. Summary of Crystallographic Data for Complexes 3a−d

	3a	**3b**	**3c**	**3d**
formula	$C_{39}H_{56}N_2OPSi_2Sc$	$C_{39}H_{56}N_2OPSi_2Y$	$C_{39}H_{56}N_2OPSi_2Lu$	$C_{38}H_{55}N_3OPSi_2Sc$
fw	700.97	744.92	830.98	701.96
cryst syst	tetragonal	tetragonal	tetragonal	tetragonal
space group	$I4(1)/a$	$I4(1)/a$	$I4(1)/a$	$I4(1)/a$
a (Å)	20.6332(7)	20.8477(10)	20.7862(19)	20.6088(4)
b (Å)	20.6332(7)	20.8477(10)	20.7862(19)	20.6088(4)
c (Å)	38.833(3)	39.083(3)	39.098(7)	38.8061(15)
α (deg)	90	90	90	90
β (deg)	90	90	90	90
γ (deg)	90	90	90	90
V (Å^3)	16532.3(14)	16986.6(16)	16893(4)	16481.8(8)
Z	16	16	16	16
D_c (g/cm^3)	1.127	1.165	1.307	1.132
μ (mm^{-1})	0.304	1.496	2.461	0.306
no. of reflns collcd	46 392	47 759	47 267	46 255
no. of reflns with $I_o > 2\sigma(I_o)$	8156	8383	8321	8130
no. of variables	424	424	424	424
R_{int}	0.1280	0.1696	0.0294	0.0599
GOF	0.833	0.937	1.049	0.942
R	0.0551	0.0613	0.0286	0.0458
R_w	0.0891	0.1028	0.0689	0.1140
R(all data)	0.1442	0.1703	0.0393	0.0697
R_w(all data)	0.1103	0.1331	0.0751	0.1267

The NPN ligand chelates to the metal ion in a η^2-mode, adopting meridional configuration, leading to the two N-aryl rings perpendicular to each other. This structure is in contrast to related early transition-metal complexes, where the N-aryl rings are almost parallel.[16a,b] The average Ln−N bond length is 2.189(3) Å for **3a**, 2.342(4) Å for **3b**, 2.299(2) Å for **3c**, and 2.190(2) Å for **3d**, while the mean Ln−C bond length is 2.220(3) Å for **3a**, 2.389(4) Å for **3b**, 2.343(3) Å for **3c**, and 2.227(2) Å for **3d**, respectively. Both fall within the normal values.[19] The bond length of N(1)−P (1.606(3) Å) is similar to N(2)−P (1.616(2) Å), suggesting that the electrons delocalize within the N−P−N fragment. The bond angles of C−Ln−C varying from 111.88(9)° (**3d**) to 112.90(16)° (**3b**) are much smaller than in the amidinate yttrium bis(alkyl) complex (NCN^{Ph})Y(CH_2SiMe_3)$_2$THF,[19a] suggesting a more bulky environment of the NPN ligand than the NCN ligand. It is noteworthy that in **3d** the double-bond length of N(3)−C(5) (1.342(3) Å) is similar to the single-bond length of N(2)−C(5) (1.397(3) Å) (Figure 4), indicating an electron delocalization over N(3)−C(5)−N(2). As a result, the electron-donating nitrogen (N(3)) of the pyridyl ring affects the electron negativity of the scandium ion although no direct bond between Sc and N(3) is observed, which has a significant influence on the catalytic performance of **3d** (*vide infra*).

Polymerization of Isoprene. The catalytic performance of NPN-type bis(alkyl) precursors **3** for the polymerization of isoprene (IP) has been investigated. We noted that they showed no activity alone. The binary system of **3a**/AlR_3 also did not induce visible polymerization. Activation of **3a** with the Brønsted acid [$PhNHMe_2$][$B(C_6F_5)_4$] was attempted to generate the ion pair [(NPN^{Ph})Sc(CH_2SiMe_3)(THF)]$^+$[$B(C_6F_5)_4$]$^-$ via alkyl abstraction;[20] however, the resulting cations could not provide polymerization. This suggested that the resulting ion pair might exist as a contact adduct of less activity, consistent with the previously reported systems.[4–6,21] Upon addition of a slight excess of Al*i*Bu$_3$ ([Al]$_0$/[Sc]$_0$ = 10) to [(NPN^{Ph})Sc(CH_2SiMe_3)(THF)]$^+$[$B(C_6F_5)_4$]$^-$, the polymerization took place immediately ([IP]$_0$/[Sc]$_0$ = 1000) to reach a complete conversion in 5 min at 20 °C. For the lutetium and yttrium counterparts, **3b** and **3c**, rapid polymerization was also observed albeit with slightly low activity. This suggested that the Lewis-acidic Sc ion is more favored for the coordination and insertion of nonpolar isoprene. The resultant polyisoprene (PIP) has high molecular weight (M_n = (26.6–48.7) × 10^4) with narrow polydispersity (M_w/M_n = 1.32–1.71), indicating the single-site nature of this catalyst system. Strikingly, a high 3,4-selectivity of 88.5% was achieved in the case of scandium precursor **3a**, which dropped slightly to 80.1% for the lutetium analogue **3c**. However, for the yttrium counterpart **3c**, the selectivity decreased greatly to 43.8% (Table 2, entries 4–6). Obviously, the specific selectivity is strongly dependent on the ionic radius of the central metal ion in a trend of Sc > Lu > Y, reverse of the trend of ionic radius Sc (0.89 Å) < Lu (1.00 Å) < Y (1.04 Å).[22] The smaller the ion radius, the more steric hindrance can be found around the metal center, which leads to the 4,3-insertion of isoprene. This result was in disagreement with the

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[20] Complex **3a** was treated with 1 equiv of [$PhNHMe_2$][$B(C_6F_5)_4$] in C_6D_6. The resulting solution was transferred to an NMR tube and analyzed by NMR spectroscopy, which showed the absence of resonances for complex **3a** and quantitative formation of $SiMe_4$ and $PhNMe_2$ and signals assigned to the newly formed cationic species [(NPN^{Ph})Sc(CH_2SiMe_3)(THF)][$B(C_6F_5)_4$]. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 0.11 (s, 12H, $SiMe_4$), 0.29 (s, 9H, CH_2SiMe_3), 0.73 (s, 2H, CH_2SiMe_3), 1.38 (s, 6H, *o*-$NC_6H_2Me_2$), 1.40 (br, THF), 2.23 (d, $^4J_{H\text{-}H}$ = 2.4 Hz, 3H, *p*-NC_6H_2Me), 2.63 (s, 6H, $PhNMe_2$), 3.79 (br, THF), 6.74, 6.76 (sd, 4H, NC_6H_2, $PhNMe_2$), 6.81–6.87 (m, 3H, $PhNMe_2$), 6.91 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 1H, *p*-NC_6H_5), 7.05–7.11 (m, 6H, *m,p*-P(C_6H_5)$_2$), 7.19 (t, $^3J_{H\text{-}H}$ = 7.6 Hz, 2H, *m*-NC_6H_5), 7.33–7.37 (dd, 2H, *o*-NC_6H_5), 7.51–7.56 (m, 4H, *o*-P(C_6H_5)$_2$). ^{19}F NMR (282.4 MHz, C_6D_6, 25 °C): δ −56.13 (d, $^3J_{F\text{-}F}$ = 11.3 Hz, *ortho*-F), −86.75 (t, $^3J_{F\text{-}F}$ = 19.8 Hz, *para*-F), −90.71 (t, $^3J_{F\text{-}F}$ = 16.9 Hz, *meta*-F). ^{11}B NMR (96.3 MHz, C_6D_6, 25 °C): δ −16.78.

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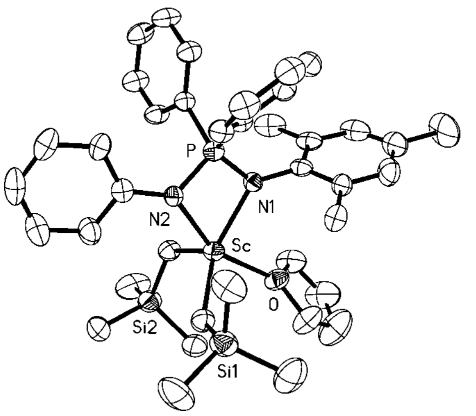

Figure 1. X-ray structure of **3a** with 35% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sc−N(1) = 2.175(2), Sc−N(2) = 2.203(3), Sc−O = 2.197(2), Sc−C(32) = 2.220(3), Sc−C(36) = 2.220(3), Sc−P = 2.874(3), N(1)−P = 1.606(3), N(2)−P = 1.616(2), N(1)−Sc−N(2) = 64.56(9), C(32)−Sc−C(36) = 111.90(12), O−Sc−C(32) = 93.28(11), O−Sc−C(36) = 94.75(11), Sc−C(32)−Si(1) = 132.88(17), Sc−C(36)−Si(2) = 125.30(16).

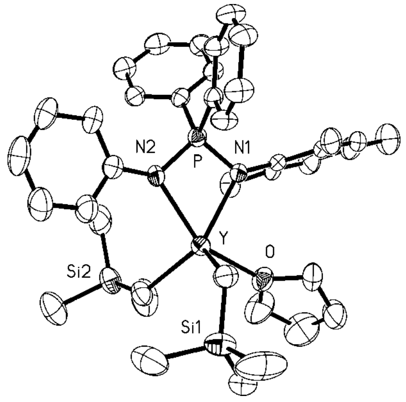

Figure 2. X-ray structure of **3b** with 35% probability thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Y−N(1) = 2.335(3), Y−N(2) = 2.349(4), Y−O = 2.332(3), Y−C(32) = 2.373(4), Y−C(36) = 2.404(4), N(1)−Y−N(2) = 63.37(12), C(32)−Y−C(36) = 112.90(16), O−Y−C(32) = 95.82(15), O−Y−C(36) = 94.47(15), Y−C(32)−Si(1) = 123.1(2), Y−C(36)−Si(2) = 129.0(2).

half-metallocene dimeric systems, where Y shows the highest 3,4-selectivity among the rare earth metals.[14] It is also in contrast to the Ziegler–Natta-type catalysts that the Nd catalysts are the most active and specifically selective (*cis*-1,4) for the diene polymerization.[2c,5c] Surprisingly, **3d** did not exhibit activity with the addition of both activators, which could be attributed to the electrodonating pyridyl fragment in **3d** compared to the phenyl ring in **3a** resulting in an increase of the electron negativity of the Sc metal center (Table 2, entry 7).

Besides the central metal type, the steric bulkiness of the aluminum alkyls is crucial to adjust the activity and selectivity. When $\mathrm{AlMe_3}$ was used as coactivator, the combination of **3a**/$[\mathrm{PhNHMe_2}][\mathrm{B(C_6F_5)_4}]/[\mathrm{AlMe_3}]$ exhibited not only low selectivity (76.5%) but also low activity. This might be attributed to the adduct formation between the sterically less demanding aluminum methyl and the cationic rare earth metal catalyst, resulting in a less active aluminate species.[9,23,24] For the more steric $\mathrm{AlEt_3}$, both the catalytic activity and the selectivity of the corresponding system increased obviously. With the more bulky $\mathrm{Al}i\mathrm{Bu_3}$ as the coactivator, a 3,4-regularity as high as 88.5% could be reached (Table 2, entries 4, 8, 9). It is worth noting that an equimolar amount of $\mathrm{Al}i\mathrm{Bu_3}$ is insufficient to activate the precursors. Rapid polymerization could only be achieved with at least 5 equiv of $\mathrm{Al}i\mathrm{Bu_3}$.[2c,d,4–6,21] The roles of $\mathrm{AlR_3}$ were to coordinate to the inert contact ion pair (*vide supra*) to generate the highly active bimetallic species (*vide infra*).[21d] More importantly, $\mathrm{AlR_3}$ can abstract the THF molecules coordinated to the catalytic precursor and the ammonium borate salt under the formation of $[\mathrm{AlR_3(THF)}x]$,[21b] as the presence of the solvated THF molecule in the living metal center is well-known to compete with the coordination of the nonpolar isoprene monomer, resulting in cleavage of the alkyl-bridged bimetallic active species by generating the inert monomeric THF solvates.[23] High loading of $\mathrm{Al}i\mathrm{Bu_3}$ resulted in high activity;

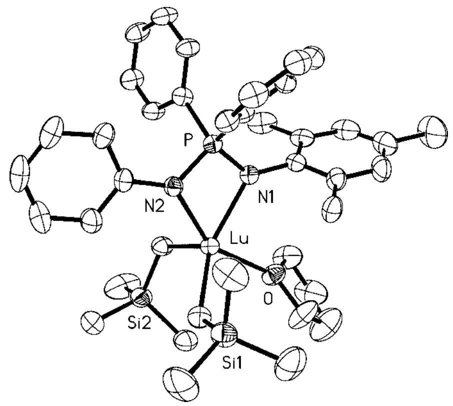

Figure 3. X-ray structure of **3c** with 35% probability thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Lu−N(1) = 2.290(2), Lu−N(2) = 2.308(2), Lu−O = 2.297(2), Lu−C(32) = 2.332(3), Lu−C(36) = 2.354(3), N(1)−Lu−N(2) = 64.74(9), C(32)−Lu−C(36) = 112.51(12), O−Lu−C(32) = 95.61(11), O−Lu−C(36) = 94.54(11), Lu−C(32)−Si(1) = 129.80(19), Lu−C(36)−Si(2) = 123.09(17).

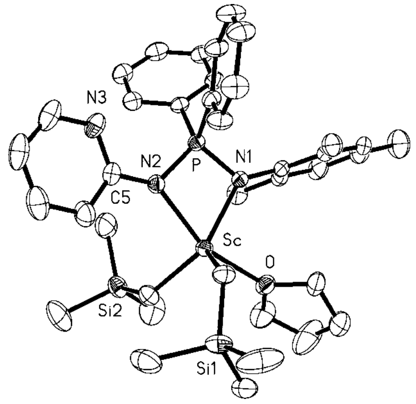

Figure 4. X-ray structure of **3d** with 35% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sc−N(1) = 2.1780(17), Sc−N(2) = 2.2021(18), Sc−O = 2.1974(16), Sc−C(32) = 2.222(2), Sc−C(36) = 2.232(2), Sc−P = 2.8942(7), N(1)−P = 1.6164(18), N(2)−P = 1.6246(18), N(3)−C(5) = 1.342(3), N(2)−C(5) = 1.397(3), N(1)−Sc−N(2) = 67.37(6), C(31)−Sc−C(35) = 111.88(9), O−Sc−C(31) = 95.05(8), O−Sc−C(35) = 94.11(8), Sc−C(31)−Si(1) = 124.79(12), Sc−C(35)−Si(2) = 131.76(13).

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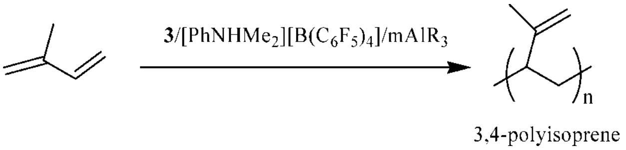
(23) (a) Arndt, S.; Spaniol, T. P.; Okuda, J. *Angew. Chem., Int. Ed.* **2003**, *42*, 5075–5079. (b) Zimmermann, M.; Törnroos, K.; Anwander, R. *Angew. Chem., Int. Ed.* **2007**, *46*, 3126–3130.

(24) Bochmann, M.; Lancaster, S. *Angew. Chem. Int. Ed.* **1994**, *33*, 1634–1637.

Table 2. Polymerization of Isoprene by Using Various Catalyst Systems[a]



							microstructure [b]			
entry	cat.	AlR_3	[Al]/[Ln]	temp, °C	time, min	yield, %	3,4 (%)	1,4 (%)	M_n[c] × 10^{-4}	M_w/M_n
1	B	Al^iBu_3	0	20	720	trace				
2	**3**+B	0	0	20	720	trace				
3	3	Al^iBu_3	50	20	720	trace				
4	**3a**+B	Al^iBu_3	10	20	5	100	88.5	11.5	13.9	1.54
5	**3b**+B	Al^iBu_3	10	20	10	95	43.8	56.2	6.8	1.32
6	**3c**+B	Al^iBu_3	10	20	10	95	80.1	19.9	12.2	1.71
7	**3d**+B	Al^iBu_3	10	20	10					
8	**3a**+B	$AlMe_3$	10	20	20	67	76.5	23.5	12.0	1.80
9	**3a**+B	$AlEt_3$	10	20	20	100	81.5	18.5	9.6	1.62
10	**3a**+B	Al^iBu_3	2	20	20	38	86.0	14.0	15.4	1.65
11	**3a**+B	Al^iBu_3	5	20	20	91	86.1	15.5	15.2	1.61
12	**3a**+B	Al^iBu_3	20	20	5	100	87.8	12.2	9.6	1.52
13	**3a**+B	Al^iBu_3	40	20	5	100	87.2	12.8	7.6	1.73
14	**3a**+B	Al^iBu_3	50	20	5	100	88.0	12.0	6.0	2.06
15	**3a**+B	Al^iBu_3	70	20	5	100	87.5	12.5	6.3	2.52
16	**3a**+B	Al^iBu_3	10	50	20	100	71.1	28.9	9.8	1.61
17	**3a**+B	Al^iBu_3	10	0	20	100	90.6	9.4	54.3	1.58
18	**3a**+B	Al^iBu_3	10	−20	120	94	92.7	7.3	70.2	1.57
19	**3a**+B	Al^iBu_3	20	−40	120	97	94.7	5.3	99.0	1.55
20	**3a**+B	Al^iBu_3	50	−60	720	52	95.0 [d]	5.0	150.7	1.59

[a] Toluene, 5 mL; B: $[PhNHMe_2][B(C_6F_5)_4]$; $[IP]_0:[Ln]_0 = 1000$; [B]:[Ln] = 1 (mol/mol). [b] On the basis of ^1H NMR and ^{13}C NMR integration in $CDCl_3$. [c] Determined by means of GPC against polystyrene standards. [d] 3,4-:*cis*-1,4:*trans*-1,4 = 95:4.13:0.87.

however chain transfer leads to a decrease in the experimental M_n of the resultant PIP and a broadening of the molecular weight distribution as well (Table 2, entries 10–16).

Since the activity of the Sc system is very high, we examined its low-temperature behavior. As expected, the high activity remained even at −40 °C such that a complete conversion could be achieved in 2 h, whereas at a much lower temperature of −60 °C, the reaction became sluggish (52%) even with a high loading of $Al\textit{i}Bu_3$ ([Al]/[Ln] = 50) and prolonged reaction time (12 h). Strikingly, with a decrease of temperature, an obvious increase of 3,4-regularity from 88.5% at 20 °C to 92.5% at −20 °C was observed. A much higher value of 94.7% was achieved when the temperature was lowered to −40 °C and reached 95% at −60 °C. In the meantime, the molecular weight of the resulting PIP increased greatly varying from 9.8×10^4 to 150×10^4 with the decrease of the temperature, while the molecular weight distribution kept a narrow range, possibly as a result of a decrease in chain transfer, etc., side reactions (Table 2, entries 4, 17–20). On the contrary, when the polymerization was performed at a high temperature of 50 °C, the selectivity dropped drastically to 71.1% accompanied by lower molecular weight and broadened polydispersity albeit at the same level of activity (Table 2, entry 16).

The Active Species. To investigate the active species, isolation of single crystals deduced from the ternary system **3a**/$[PhNHMe_2][B(C_6F_5)_4]/Al\textit{i}Bu_3$, was attempted but failed. Fortunately, monitoring the reaction mixture by ^1H NMR spectroscopy provided information about the reaction species, which shed some lights on the probable mechanistic aspect of the polymerization. As shown in Scheme 2, first, complex **3a** was dealkylated by the Brønsted acid $[PhNHMe_2][B(C_6F_5)_4]$ to generate the ion pair $[(NPN^{Ph})Sc(CH_2SiMe_3)(THF)]^+[B(C_6F_5)_4]^-$ (**A**),[20] accompanied by the release of $SiMe_4$ ($\delta = 0$ ppm in the ^{13}C NMR spectrum) and $PhMe_2N$ ($\delta = 2.39$ ppm). No signals of **3a** were observed. The newly formed **A** showed a singlet at δ 0.73 assigned to the methylene protons of $Sc\text{-}CH_2SiMe_3$ differentiated from the AB spin in **3a**. Addition of excess isoprene to **A** exhibited no new signals beyond isoprene and **A**, suggesting that **A**, a contact ion pair bearing a solvated THF molecule, could not initiate the polymerization. However, upon addition of excess $Al\textit{i}Bu_3$, **A** transferred into **B**, the scandium-alkyl-aluminate ion pair $[(NPN^{Ph})Sc(\mu\text{-}CH_2SiMe_3)Al\textit{i}Bu_2(\mu\text{-}CH_2CH(CH_3)_2]^+[B(C_6F_5)_4]^-$.[24–26] A doublet at δ −0.73 was assigned to Sc and Al units of $Sc(\mu\text{-}CH_2SiMe_3)Al$.[2c,21c,27] Meanwhile the methylene protons of the isopropyl group bridging the Sc and Al units, $Sc(\mu\text{-}C\textit{H}_2CH(CH_3)_2)Al$, gave a doublet at δ 0.28, while those from the terminal $Al\text{-}C\textit{H}_2CH(CH_3)_2$ showed a doublet at δ 0.31. Both were different from the methylene protons of free $Al\textit{i}Bu_3$ (δ0.23), suggesting that the alkyl-exchange reaction among the bridged, terminal, and free alkyl fragments were slow on the NMR time scale for this system. THF resonances shifted from δ 3.79 in **A** to δ 3.48,

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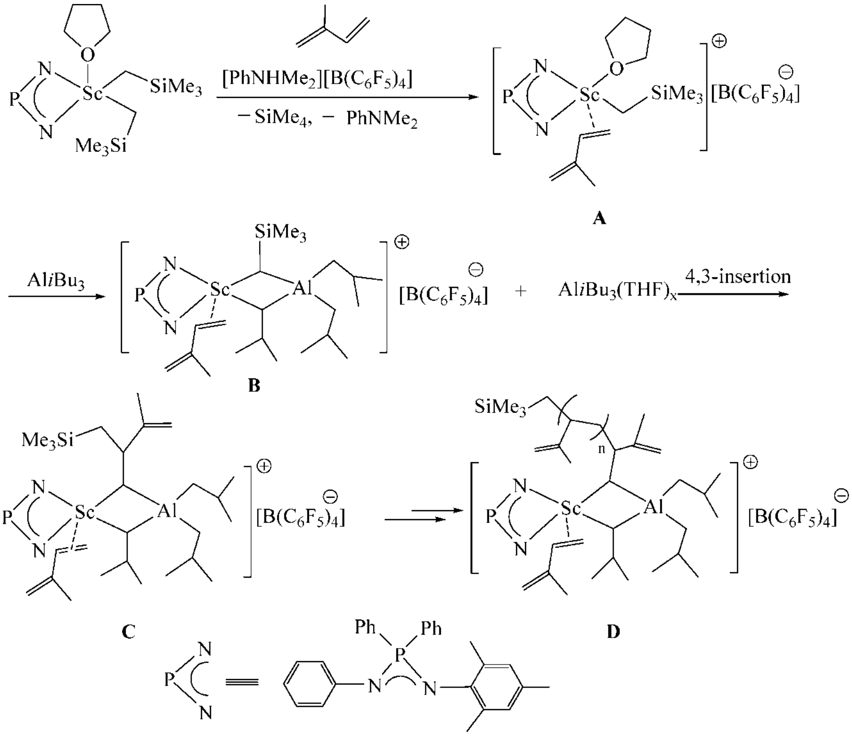
(25) Treatment of complex **3a** by $[PhNHMe_2][B(C_6F_5)_4]$ in C_6D_6 at room temperature for several minutes afforded cationic units $[(NPN^{Ph})Sc(CH_2SiMe_3)(THF)][B(C_6F_5)_4]$, which upon addition of 10 equiv of $Al\textit{i}Bu_3$ generated cationic scandium-aluminute $[(NPN^{Ph})Sc(\mu\text{-}CH_2SiMe_3)Al\textit{i}Bu_2(\mu\text{-}CH_2CH(CH_3)][B(C_6F_5)_4]$. ^1H NMR (400 MHz, C_6D_6, 25 °C): δ −0.72, −0.74 (AB, $^2J_{H\text{-}H} = 8$ Hz, 2H, $C\textit{H}_2SiMe_3$), 0.12 (s, 12H, $SiMe_4$), 0.23 (d, $^3J_{H\text{-}H} = 6.4$ Hz, 12H, $Al(C\textit{H}_2CH(CH_3)_2)_3$), 0.28 (d, $^3J_{H\text{-}H} = 6$ Hz, 2H, $\mu\text{-}C\textit{H}_2CH(CH_3)_2Al\textit{i}Bu_2$), 0.31 (d, $^3J_{H\text{-}H} = 7.2$ Hz, 4H, $\mu\text{-}\textit{i}BuAl(C\textit{H}_2CH(CH_3)_2)_2$), 0.39 (s, 9H, $CH_2Si\textit{Me}_3$), 1.10 (br, THF), 1.30 (d, $^3J_{H\text{-}H} = 6$ Hz, 36H, $Al(CH_2CH(C\textit{H}_3)_2)_3$), 1.33 (s, 6H, $\textit{o}\text{-}NC_6H_2\textit{Me}_2$), 1.36 (d, $^3J_{H\text{-}H} = 6.8$ Hz, 18 H, $Al(CH_2CH(C\textit{H}_3)_2)_3$), 2.08 (s, 6H, $Al(CH_2C\textit{H}(CH_3)_2)_3$), 2.21–2.27 (m, 6H, $(\mu\text{-}CH_2C\textit{H}(CH_3)_2)Al(CH_2C\textit{H}(CH_3)_2)_2$, $\textit{p}\text{-}NC_6H_2\textit{Me}$), 2.39 (s, 6H, $PhN\textit{Me}_2$), 3.48 (br, THF), 6.74 (s, 2H, NC_6H_2), 6.78–6.87 (m, 3H, $\textit{Ph}NMe_2$), 6.94–7.02 (m, 3H, $\textit{o,p}\text{-}NC_6H_5$), 7.08–7.18 (m, 8H, $\textit{m,p}\text{-}P(C_6H_5)_2$, $PhNMe_2$, $\textit{m}\text{-}NC_6H_5$), 7.45–7.60 (m, 4H, $\textit{o}\text{-}P(C_6H_5)_2$). ^{19}F NMR (282.4 MHz, C_6D_6, 25 °C): δ −56.12 (s, *o*-F), −86.65 (t, $^3J_{F\text{-}F} = 19.8$ Hz, *p*-F), −90.59 (br, *m*-F). ^{11}B NMR (96.3 MHz, C_6D_6, 25 °C): δ −16.78. The ^1H NMR spectrum and $^1H{-}^1H$ COSY of adduct **3a**/$[PhNHMe_2][B(C_6F_5)_4]/Al\textit{i}Bu_3$, see Supporting Information.

(26) (a) Petros, R. A.; Norton, J. R. *Organometallics* **2004**, *23*, 5105–5107. (b) Bolton, P. D.; Clot, E.; Cowley, A. R.; Mountford, P. *Chem. Commun.* **2005**, 3313–3315.

(27) (a) Dietrich, H. M.; Raudaschl-Sieber, G.; Anwander, R. *Angew. Chem., Int. Ed.* **2005**, *44*, 5303–5306. (b) Fischbach, A.; Perdih, F.; Herdtweck, E.; Anwander, R. *Organometallics* **2006**, *25*, 1626–1642.

Scheme 2. Proposed Active Species and Mechanistic Scenario



indicating that THF is abstracted from **A** by Al*i*Bu$_3$ to generate Al*i*Bu$_3$(THF)$_x$. Thus, **B** should be the true active species that prefers to coordinate to isoprene in an η^2-mode owing to the geometry (or sterics) of the NPN ancillary ligand as well as the steric demand of the aluminum alkyl. The bimetallic structure is thought to remain intact during the polymerization and seems crucial for the regiospecificity of these catalyst systems.

Conclusions

A new type of non-Cp-ligated rare earth metal bis(alkyl) complexes bearing the NPN (iminophosphonamido) ancillary ligand, (NPN)Ln(CH$_2$SiMe$_3$)$_2$(THF), have been synthesized and well-defined. These complexes in combination with an ammonium borate salt and AlR$_3$ provide high activity and 3,4-selectivity for the polymerization of isoprene. The catalyst performances are influenced significantly by the kind of center metal ion, the electron negativity of the ligand, the steric bulk of the aluminum alkyl, and the polymerization conditions. High activity and up to 95% 3,4-selectivity could be achieved with the optimum ternary system composed of the more Lewis acidic scandium complex [(NPN^{Ph})Sc(CH$_2$SiMe$_3$)$_2$(THF)] and [PhNHMe$_2$][B(C$_6$F$_5$)$_4$] and the bulky Al*i*Bu$_3$ at low temperature.

Experimental Section

General Considerations. All manipulations were performed under a dry and oxygen-free argon atmosphere using standard high-vacuum Schlenk techniques or in a glovebox. All solvents were purified from an MBraun SPS system. ClPPh$_2$, AlMe$_3$, AlEt$_3$, Al*i*Bu$_3$, LnCl$_3$, and LiCH$_2$SiMe$_3$ were purchased from Aldrich. Mesityl azide, 2-pyridyl-NHPPh$_2$, PhNHPPh$_2$, [PhNHMe$_2$][B(C$_6$F$_5$)$_4$], and Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (Ln = Sc, Y, Lu) were prepared according to published procedures.[28] Isoprene (99%, Acros) was dried over CaH$_2$ under stirring for 48 h and distilled before use. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV400 (FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C) or AV300 (FT, 300 MHz for ^{1}H; 75 MHz for ^{13}C). NMR assignments were confirmed by ^{1}H−^{1}H (COSY) and ^{1}H−^{13}C (HMQC) experiments when necessary. ^{11}B NMR spectra were referenced to an external standard of BF$_3$·Et$_2$O (0.0 ppm) in C$_6$D$_6$. ^{19}F NMR spectra are referenced to CF$_3$COOH using an external standard in C$_6$D$_6$. IR spectra were recorded on a VERTEX 70 FT-IR. Elemental analyses were performed at National Analytical Research Centre of Changchun Institute of Applied Chemistry (CIAC). The molecular weights (M_n) were measured by TOSOH HLC-8220 GPC at 40 °C using THF as eluent (the flow rate is 0.35 mL/min) against polystyrene standards.

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 Kα radiation (λ= 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 the calculated positions and were included in the structure calculation without further refinement of the parameters.

Synthesis of PhNHPPh$_2$=NC$_6$H$_2$-2,4,6-Me$_3$ (2a, NPN^{Ph}H). In a 100 mL Schlenk flask, a THF solution (15 mL) of mesityl azide (6.1 mmol, 0.97 g) was added dropwise to a THF solution (30 mL) of phenylaminodiphenylphosphine (**1a**) (6.0 mmol, 1.66 g) at 0 °C

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under nitrogen atmosphere. The reaction mixture was stirred for 12 h at room temperature. Removal of volatiles gave white solids that were further purified by washing with diethyl ether/hexane to afford pure white solids of NPN^{Ph}H (**2a**) (1.80 g, 73%). ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ 2.06 (s, 6H, *o*-NC$_6$H$_2$*Me*$_3$), 2.19 (s, 3H, *p*-NC$_6$H$_2$ *Me*$_3$), 5.28 (br, 1H, NH), 6.71 (s, 2H, NC$_6$H$_2$), 6.84 (t, $^{3}J_{\text{H-H}}$ = 7.5 Hz, 1H, *p*-NC$_6$H$_5$), 6.95 (d, $^{3}J_{\text{H-H}}$ = 7.8 Hz, 2H, *o*-NC$_6$H$_5$), 7.12 (t, $^{3}J_{\text{H-H}}$ = 7.8 Hz, 2H, *m*-NC$_6$H$_5$), 7.37–7.43 (m, 4H, *m*-PC$_6$H$_5$), 7.47–7.53 (m, 2H, *p*-PC$_6$H$_5$), 7.73–7.80 (m, 4H, *o*-PC$_6$H$_5$). ^{13}C NMR (75.5 MHz, CDCl$_3$, 25 °C): δ 20.35 (s, 2C, *o*-NC$_6$H$_2$*Me*$_3$), 20.65 (s, 1C, *p*-NC$_6$H$_2$*Me*$_3$), 118.35 (d, $^{3}J_{\text{p-c}}$ = 6.0 Hz, 2C, *o*-NC$_6$H$_5$), 120.72 (s, 1C, *p*-NC$_6$H$_5$), 128.58 (s, 2C, *m*-NC$_6$H$_2$), 128.74 (d, $^{3}J_{\text{p-c}}$ = 13.0 Hz, 4C, *m*-PC$_6$H$_5$), 129.04 (s, 2C, *m*-NC$_6$H$_5$), 129.120 (d, $^{1}J_{\text{p-c}}$ = 27.9 Hz, 2C, *ipso*-PC$_6$H$_5$), 131.10(s, 1C, *ipso*-NC$_6$H$_2$), 131.70 (s, 2C, *p*-PC$_6$H$_5$), 132.07 (d, $^{2}J_{\text{p-c}}$ = 9.4 Hz, 4C, *o*-PC$_6$H$_5$), 132.83 (s, 2C, *ipso*-NC$_6$H$_2$), 142.07 (s, 1C, *ipso*-NC$_6$H$_5$), 142.65 (s, 1C, *ipso*-NC$_6$H$_2$). IR (KBr pellets): v 3326 (s), 3057 (m), 2909 (m), 2851 (w), 1605 (s), 1501 (s), 1478 (s), 1435 (s), 1390 (w), 1340 (s), 1283 (s), 1230 (s), 1185 (w), 1173 (w), 1160 (w), 1120 (s),1075 (w), 1060 (s), 1029 (m), 1000 (m), 929 (w), 888 (s), 862 (s), 790 (m), 755 (s), 723 (m), 713 (m), 695 (s). Anal. Calcd (%) for C$_{27}$H$_{27}$N$_2$P (410.49): C, 79.00; H, 6.63; N, 6.82. Found: C, 78.86; H, 6.53; N, 6.76.

Synthesis of 2-Pyridyl-NHPPh$_2$=NC$_6$H$_2$-2,4,6-Me$_3$ (2b, NPN^{Py}H). Following the similar procedure, treatment of mesityl azide (6.1 mmol, 0.97 g, in 30 mL THF) with 2-pyridylaminodiphenylphosphane (**1b**) (6.0 mmol, 1.64 g in 30 mL THF) yielded NPN^{Py}H (**2b**) (1.70 g, 69%). ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ 2.07 (s, 6H, *o*-NC$_6$H$_2$*Me*$_3$), 2.15 (s, 3H, *p*-NC$_6$H$_2$*Me*$_3$), 6.47 (br, 1H, 4-Py), 6.64 (s, 2H, NC$_6$H$_2$), 6.86 (d, $^{3}J_{\text{P-H}}$ = 8.1 Hz,1H, 6-Py), 7.30–7.39 (m, 1H, 5-Py, 4H, *m*-PC$_6$H$_5$), 7.45 (t, $^{1}J_{\text{H-H}}$ = 7.8 Hz, 2H, *p*-PC$_6$H$_5$), 7.73–7.79 (m, 4H, *o*-PC$_6$H$_5$), 7.84 (br, 1H, 3-Py). ^{13}C NMR (75.5 MHz, CDCl$_3$, 25 °C): δ 20.06 (s, 2C, *o*-NC$_6$H$_2$*Me*$_3$), 21.06 (s, 1C, *p*-NC$_6$H$_2$*Me*$_3$), 112.86 (br, 1C, 6-Py), 117.34 (br, 1C, 4-Py), 128.50 (d, $^{2}J_{\text{p-c}}$ = 12.8 Hz, 4C, *o*-PC$_6$H$_5$), 129.26 (s, 2C, *m*-NC$_6$H$_2$), 129.82 (br, 2C, *ipso*-NC$_6$H$_2$), 131.52 (s, 1C, *ipso*-NC$_6$H$_2$), 132.00 (d, $^{4}J_{\text{P-C}}$ = 1.6 Hz, *p*-PC$_6$H$_5$), 133.13 (d, $^{3}J_{\text{P-C}}$ = 9.3 Hz, *m*-PC$_6$H$_5$), 136.54 (s, 1C, *ipso*-NC$_6$H$_5$), 137.50 (s, 1C, 5-Py), 147.34 (s, 1C, 3-Py). IR (KBr pellets): v 3305(s), 2962(w), 2914(w), 1590(s), 1546(s), 1481(s), 1460(s), 1428(s), 1364(m), 1334(s), 1281(s), 1221(s), 1179(m), 1158(m), 1140(w), 1120(s), 1107(s), 1071(m), 1048(s), 1025(s), 1000(m), 982(s), 911(s), 861(s), 801(s), 774(s), 749(m), 742(m), 719(s), 706(s), 694(s). Anal. Calcd (%) for C$_{26}$H$_{26}$N$_3$P: C, 75.89; H, 6.37; N, 10.21. Found: C, 75.84; H, 6.36; N, 10.13.

Synthesis of (NPN^{Ph})Sc(CH$_2$SiMe$_3$)$_2$(THF) (3a). To a hexane solution (3.0 mL) of Sc(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (0.180 g, 0.4 mmol) was dropwise added 1 equiv of **2a** (0.164 g, 0.4 mmol in 4 mL THF) at room temperature. The mixture remained stirring for 3 h at room temperature and then was concentrated to about 1 mL. Addition of 3 mL of hexane and cooling to −30 °C for 12 h afforded crystalline solids, which were washed with a small amount of hexane to remove impurities and dried *in vacuo* to give white powders of **3a** (0.17 g, 61%). Single crystals grew from the mixture of THF/hexane (1:5 v/v) at −30 °C within 12 h. ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ 0.44, 0.47 (AB, $^{2}J_{\text{H-H}}$ = 11.6 Hz, 2H, C*H*$_2$SiMe$_3$), 0.57 (s, 18H, SiMe$_3$), 0.76, 0.79 (AB, $^{2}J_{\text{H-H}}$ = 11.2 Hz, 2H, C*H*$_2$SiMe$_3$), 1.02 (br, 4H, THF), 1.73 (s, 6H, *o*-NC$_6$H$_2$*Me*$_3$), 2.21 (s, 3H, *p*-NC$_6$H$_2$*Me*$_3$), 3.85 (br, 4H, THF), 6.71 (s, 2H, NC$_6$H$_2$), 6.88 (t, $^{3}J_{\text{H-H}}$ = 7.2 Hz, 1H, *p*-NC$_6$H$_5$), 7.01–7.05 (m, 4H, *m*-PC$_6$H$_5$), 7.08–7.09 (m, 2H, *p*-PC$_6$H$_5$), 7.27 (t, $^{3}J_{\text{H-H}}$ = 7.6 Hz, 2H, *m*-NC$_6$H$_5$), 7.48 (d, $^{3}J_{\text{H-H}}$ = 8 Hz, 2H, *o*-NC$_6$H$_5$), 7.78–7.83 (m, 4H, *o*-PC$_6$H$_5$). ^{13}C NMR (100 MHz, C$_6$D$_6$, 25 °C): δ 4.70 (s, 6C, SiMe$_3$), 20.91 (s, 2C, *o*-NC$_6$H$_2$*Me*$_3$), 21.19 (s, 1C, *p*-NC$_6$H$_2$*Me*$_3$), 25.02 (s, 2C, THF), 42.56 (br, 2C, *C*H$_2$SiMe$_3$), 71.72 (s, 2C, THF), 120.33 (s, 1C, *p*-NC$_6$H$_5$), 122.46 (d, $^{3}J_{\text{p-c}}$ = 15 Hz, 2C, *o*-NC$_6$H$_5$), 129.06 (d, $^{3}J_{\text{p-c}}$ = 11 Hz, 4C, *m*-PC$_6$H$_5$), 129.50 (s, 2C, *m*-NC$_6$H$_5$), 129.81 (s, 2C, *m*-NC$_6$H$_2$), 131.18 (s, 1C, *ipso*-NC$_6$H$_2$), 131.92,132.34 (s, 2C, *ipso*-NC$_6$H$_2$), 132.15 (s, 2C, *p*-PC$_6$H$_5$) 133.20 (d, $^{2}J_{\text{p-c}}$ = 10 Hz, 4C, *o*-PC$_6$H$_5$), 135.30 (d, $^{1}J_{\text{p-c}}$ = 5 Hz, 2C, *ipso*-PC$_6$H$_5$), 141.75 (s, 1C, *ipso*-NC$_6$H$_2$), 148.80 (s, 1C, *ipso*-NC$_6$H$_5$). IR (KBr pellets): v 3644 (w), 3056 (w), 2947 (s), 2858 (w), 1595 (s), 1570 (w), 1495 (m), 1478 (s), 1437 (s), 1374 (w), 1300 (s), 1248 (s), 1182 (w), 1163 (m), 1117 (s), 1079 (w), 1035 (m), 1003 (s), 981 (m), 948 (w), 863 (s), 804 (s), 752 (s), 719 (s), 692 (s), 679 (m). Anal. Calcd (%) for C$_{39}$H$_{56}$N$_2$OPSi$_2$Sc: C, 66.82; H, 8.05; N, 4.00. Found: C, 66.79; H, 7.96; N, 3.87.

Synthesis of (NPN^{Ph})Y(CH$_2$SiMe$_3$)$_2$(THF) (3b). Following a similar procedure described for the preparation of **3a**, complex **3b** was isolated from the reaction of Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (0.198 g, 0.4 mmol in 3.0 mL hexane) with 1 equiv of **2a** (0.164 g, 0.4 mmol in 4 mL THF) in a 57% yield (0.17 g). Single crystals grew from the mixture of THF/hexane (1:5 v/v) at −30 °C within 12 h. ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ 0.12 (s, 4H, C*H*$_2$SiMe$_3$), 0.59 (s, 18H, SiMe$_3$), 1.05 (br, 4H, THF), 1.77 (s, 6H, *o*-NC$_6$H$_2$*Me*$_3$), 2.20 (s, 3H, *p*-NC$_6$H$_2$*Me*$_3$), 3.66 (br, 4H, THF), 6.70 (s, 2H, NC$_6$H$_2$), 6.84 (t, $^{3}J_{\text{H-H}}$ = 7.2 Hz, 1H, *p*-NC$_6$H$_5$), 7.01–7.13 (m, 6H, *p,m*-PC$_6$H$_5$), 7.22 (t, $^{3}J_{\text{H-H}}$ = 7.6 Hz, 2H, *m*-NC$_6$H$_5$), 7.34 (d, $^{3}J_{\text{H-H}}$ = 8 Hz, 2H, *o*-NC$_6$H$_5$), 7.80–7.83 (m, 4 H, *o*-PC$_6$H$_5$). ^{13}C NMR (100 MHz, C$_6$D$_6$, 25 °C): δ 5.05 (s, 6C, SiMe$_3$), 20.90 (s, 2C, *o*-NC$_6$H$_2$*Me*$_3$), 21.17 (s, 1C, *p*-NC$_6$H$_2$*Me*$_3$), 25.54 (s, 2C, THF), 37.71 (d, $^{1}J_{\text{Y-C}}$ = 39.9 Hz, 2C, *C*H$_2$SiMe$_3$), 70.09 (br, 2C, THF), 120.33 (s, 1C, *p*-NC$_6$H$_5$), 122.41 (d, $^{3}J_{\text{p-c}}$ = 15 Hz, 2C, *o*-NC$_6$H$_5$), 129.06 (d, $^{3}J_{\text{p-c}}$ = 11 Hz, 4C, *m*-PC$_6$H$_5$), 129.69 (s, 2C, *m*-NC$_6$H$_5$), 129.81 (s, 2C, *m*-NC$_6$H$_2$), 131.54 (s, 1C, *ipso*-NC$_6$H$_2$), 131.67,132.59 (s, 2C, *ipso*-NC$_6$H$_2$), 132.00 (s, 2C, *p*-PC$_6$H$_5$), 132.94 (d, $^{2}J_{\text{p-c}}$ = 9 Hz, 4C, *o*-PC$_6$H$_5$), 135.14 (d, $^{1}J_{\text{p-c}}$ = 6 Hz, 2C, *ipso*-PC$_6$H$_5$), 142.03 (s, 1C, *ipso*-NC$_6$H$_2$), 148.85 (s, 1C, *ipso*-NC$_6$H$_5$). IR (KBr pellets): v 3654 (w), 3055 (w), 2947 (s), 2856 (w), 1595 (s), 1568 (w), 1494 (m), 1477 (s), 1437 (s), 1372 (w), 1300 (s), 1284 (s), 1182 (w), 1162 (m), 1117 (s), 1079 (w), 1036 (m), 1003 (s), 978 (m), 947 (w), 860 (s), 798 (s), 752 (s), 719 (m), 693 (s). Anal. Calcd (%) for C$_{39}$H$_{56}$N$_2$OPSi$_2$Y: C, 62.88; H, 7.58; N, 3.76. Found: C, 62.81; H, 7.60; N, 3.69.

Synthesis of (NPN^{Ph})Lu(CH$_2$SiMe$_3$)$_2$(THF) (3c). Following a similar procedure described previously, treatment of Lu(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (0.232 g, 0.4 mmol in 3.0 mL toluene) with 1 equiv of **2a** (0.164 g, 0.4 mmol in 4 mL of THF) afforded complex **3c** (0.22 g, 68%). Single crystals grew from the mixture of THF/hexane (1:5 v/v) at −30 °C within 12 h. ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ 0.07 (br, 4H, C*H*$_2$SiMe$_3$), 0.58 (s, 18H, SiMe$_3$), 1.05 (br, 4H, THF), 1.78 (s, 6H, *o*-NC$_6$H$_2$*Me*$_3$), 2.22 (s, 3H, *p*-NC$_6$H$_2$*Me*$_3$), 3.68 (br, 4H, THF), 6.71 (s, 2H, NC$_6$H$_2$), 6.84 (t, $^{3}J_{\text{H-H}}$ = 7.2 Hz, 1H, *p*-NC$_6$H$_5$), 7.05–7.11 (m, 6H, *m,p*-PC$_6$H$_5$), 7.22 (t, $^{3}J_{\text{H-H}}$ = 7.6 Hz, 2H, *m*-NC$_6$H$_5$), 7.34 (d, $^{3}J_{\text{H-H}}$ = 8 Hz, 2H, *o*-NC$_6$H$_5$), 7.78–7.82 (m, 4H, *o*-PC$_6$H$_5$). ^{13}C NMR (100 MHz, C$_6$D$_6$, 25 °C): δ 5.22 (s, 6C, SiMe$_3$), 20.81 (s, 2C, *o*-NC$_6$H$_2$*Me*$_3$), 21.13 (s, 1C, *p*-NC$_6$H$_2$*Me*$_3$), 25.19 (s, 2C, THF), 44.44 (s, 2C, *C*H$_2$SiMe$_3$), 70.67 (br, 2C, THF), 120.25 (s, 1C, *p*-NC$_6$H$_5$), 122.40 (d, $^{3}J_{\text{p-c}}$ = 15 Hz, 2C, *o*-NC$_6$H$_5$), 129.06 (d, $^{3}J_{\text{p-c}}$ = 12 Hz, 4C, *m*-PC$_6$H$_5$), 129.55 (s, 2C, *m*-NC$_6$H$_5$), 129.75 (s, 2C, *m*-NC$_6$H$_2$), 131.71,132.63 (s, 2C, *ipso*-NC$_6$H$_2$), 132.06 (s, 2C, *p*-PC$_6$H$_5$), 132.98 (d, $^{2}J_{\text{p-c}}$ = 9 Hz, 4C, *o*-PC$_6$H$_5$), 135.36 (d, $^{1}J_{\text{p-c}}$ = 6 Hz, 2C, *ipso*-PC$_6$H$_5$), 141.90 (s, 1C, *ipso*-NC$_6$H$_2$), 148.72 (s, 1C, *ipso*-NC$_6$H$_5$). IR (KBr pellets): v 3655 (w), 3056 (w), 2946 (s), 2855 (w), 1595 (s), 1569 (w), 1494 (m), 1478 (s), 1437 (s), 1372 (w), 1300 (s), 1248 (s), 1182 (w), 1163 (m), 1118 (s), 1109 (m), 1079 (w), 1036 (m), 1003 (s), 994 (w), 979 (m), 947 (w), 861 (s), 801 (s), 752 (s), 714 (s), 691 (s). Anal. Calcd (%) for C$_{39}$H$_{56}$N$_2$OPSi$_2$Lu: C, 56.37; H, 6.79; N, 3.37. Found: C, 56.30; H, 6.73; N, 3.31.

Synthesis of (NPN^{Py})Sc(CH$_2$SiMe$_3$)$_2$(THF) (3d). According to the same workup procedure as that of **3a**, **2b** (0.164 g, 0.4 mmol in 4 mL of toluene) was used instead of **2a** to react with Sc(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (0.180 g, 0.4 mmol) to generate complex

3d in a high yield (0.18 g, 69%). Single crystals were isolated from a mixture of toluene/hexane (1:5 v/v) at −30 °C within 12 h. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 0.55–0.61 (m, 22H, C*H*$_2$Si*Me*$_3$), 1.07 (br, 4H, THF), 1.78 (s, 6H, *o*-NC_6H_2*Me*$_2$), 2.20 (s, 3H, *p*-NC_6H_2*Me*$_3$), 3.85 (br, 4H, THF), 6.39 (t, 1H, 4-Py), 7.06 (s, 2H, NC_6H_2), 7.06–7.12(m, 6H, *m,p*-PC_6H_5), 7.40 (t, 1H, 5-Py), 7.86–7.93(m, 2H, 3,6-Py; 4H, *m*-PC_6H_5). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 4.66 (s, 6C, $SiMe_3$), 21.09 (s, 2C, *o*-NC_6H_2*Me*$_3$), 21.16 (s, 1C, *p*-NC_6H_2*Me*$_3$), 25.31 (s, 2C, THF), 42.51 (br, 2C, *C*H_2SiMe_3), 70.88 (s, 2C, THF), 115.33(s, 1C, 4-Py), 116.67(d, $^3J_{\text{p-c}} = 17$ Hz, 1C, 6-Py), 129.79(s, 1C, *m*-NC_6H_2), 131.59(s, 2C, *p*-PC_6H_5), 131.90(s,1C, *ipso*-NC_6H_2), 132.21,132.86(s, 2C, *ipso*-NC_6H_2), 133.27(d, $^2J_{\text{p-c}} = 10$ Hz, 4C, *o*-PC_6H_5), 135.36(d, $^1J_{\text{p-c}} = 5$ Hz, 2C, *ipso*-PC_6H_5), 137.65(s, 1C, 5-Py), 142.26(s, 1C, *ipso*-NC_6H_2), 147.94(s, 1C, 3-Py), 161.23(s, 1C, *ipso*-Py). IR (KBr pellets): υ 3653(w), 3057(w), 2947(s), 2858(w), 1589(s), 1555(m), 1465(s), 1427(s), 1335(s), 1304(s), 1288(w), 1251(s), 1186(w), 1163(m), 1147(m), 1118(s), 1046(m), 1017(w), 999(s), 980(w), 947(w), 862(s), 779(s), 744(s), 719(s), 693(s), 682(m). Anal. Calcd (%) for $C_{38}H_{55}N_3OPSi_2Sc$ (701.96): C, 65.02; H, 7.90; N, 5.99. Found: C, 64.95; H, 7.84; N, 5.94.

Isoprene Polymerization. To a 50 mL flask were added **3a** (7.0 mg, 0.010 mmol), toluene (2 mL), and a toluene solution (3 mL) of $[PhMe_2NH][B(C_6F_5)_4]$ (8.0 mg, 0.010 mmol) and isoprene (0.68 g, 10.0 mmol). The reaction apparatus was placed in a bath at the designated temperature. The polymerization took place immediately upon addition of 1.0 mL of a toluene solution (0.5 M) of Al*i*Bu$_3$. After stirring for 5 min, the viscous mixture was poured into ethanol (ca. 30 mL) containing a small amount of hydrochloric acid to terminate the polymerization. The precipitated polymer was isolated by filtration, washed with ethanol, and then dried under vacuum at 40 °C to a constant weight (0.68 g, 100%).

Acknowledgment. The authors are grateful for financial support from The National Natural Science Foundation of China for Projects Nos. 20571072 and 20674081; The Ministry of Science and Technology of China for Project No. 2005CB623802; and the “Hundred Talent Scientist Program” of Chinese Academy of Sciences.

Supporting Information Available: The ^{1}H NMR spectrum of polyisoprene, the details of the preparation and ^{1}H NMR and ^{1}H−^{1}H COSY spectra of complexes **3a**−**d**, and the crystallographic information file (CIF) for complexes **3a**−**d**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM700945R