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Article

Stereoselective Polymerization of Styrene with Cationic Scandium Precursors Bearing Quinolyl Aniline Ligands

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The novel N-R-quinolinyl-8-amino ligands HL^{1-5} (R = 2,6-$Me_2C_6H_3$ (HL^1), 2,4,6-$Me_3C_6H_2$ (HL^2), 2,6-$Et_2C_6H_3$ (HL^3), 2,6-$^iPr_2C_6H_3$ (HL^4), C_6H_5 (HL^5)) reacted with $Sc(CH_2SiMe_3)_3(THF)_2$ to afford the well-defined complexes $(L^{1-5})Sc(CH_2SiMe_3)_2(THF)$ (**1**−**5**), which were fully characterized by NMR spectral and X-ray diffraction analyses. Complexes **1**−**3** combined with organoborates to establish binary systems that exhibited high activity for the polymerization of styrene, while **4** was less active and **5** was almost inert. The cationic complex $[L^1Sc(CH_2SiMe_3)(DME)_2][B(C_6F_5)_4]$ (**6**) was successfully isolated by treatment of **1** with $[PhMe_2NH][B(C_6F_5)_4]$, and represents probably the structural model of the initiation active species. Remarkably, upon addition of aluminum trialkyls to the binary systems, distinguished improvement in catalytic performances was achieved, among which the ternary system **1**/5Al^{i}Bu$_3$/$[Ph_3C][B(C_6F_5)_4]$ displayed the highest activity (1.56×10^6 g mol^{-1} h^{-1}) and syndioselectivity ($r = 0.94$) via a chain-end control mechanism governed by the concerted steric effect of the ligand and the aluminum alkyls. This represents the first non-cyclopentadienyl stabilized rare-earth metal based catalyst showing both high activity and specific selectivity for the polymerization of styrene, which might shed new light on designing more efficient precursors and further investigation of the mechanism for this polymerization.

Introduction

Polystyrene (PS), one of the most widely used plastics, has atactic, syndiotactic, and isotactic microstructures that are determined by the catalysts applied through radical, anionic, and coordination mechanisms. The stereoregular syndiotactic polystyrene (sPS) has a high melting point, as does the isotactic polystyrene (iPS), and moreover can crystallize faster, having potential applications as engineering plastics.[1] Thus, since the first sPS prepared via coordination polymerization by using the monocyclopentadienyl (Cp) titanium-based catalyst system Cp*$TiCl_3$/MAO reported by Ishihara in 1986,[2] tremendous amounts of titanium compounds bearing such half-sandwich ligands have been investigated.[3] Improved catalytic performances can be achieved by replacing a chloride group from Cp*$TiCl_3$ with an anionic moiety such as aryloxide,[4] amide,[4c] anilide,[4c] ketimide,[5] or bidentate aniline-ethoxy.[6] Introducing more steric and electron-donating indenyl[7a] and fluorenyl[7b] ligands also brings about an increasing activity, stereoselectivity, and thermal stability to the attached titanium metal centers,[7] whereas a too crowded environment around a central metal induces a drop in activity for the related bis(cyclopentadienyl) titanium complexes, which might prohibit bulky monomer styrene (St) from coordinating to the active sites.[3e,8] Regarding the Ziegler−Natta-type catalytic systems with the general formula TiX_4/MAO (X = Cl, Br, OMe, OEt, O^{i}Pr, OBu, Bz)[3e,9]

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and the titanium complexes stabilized by non-Cp ligands such as amidinate,[10] phenoxyimine,[11] and bis(phenolate),[12] medium to high syndiotacticity can be obtained albeit with relatively low activity.

On the other hand, rare-earth metal based systems are usually superior with respect to the activity and the regioselectivity for the polymerization of 1,3-conjugated dienes;[13] however they generally exhibit low activity for the polymerization of styrene until the recent landmark neutral lanthanocenes [(CpCMe$_2$Flu)Ln(allyl)(thf)][14] and cationic half-sandwich scandium complex [Cp′Sc(CH$_2$SiMe$_3$)$_2$(THF)$_2$]/[Ph$_3$C][B(C$_6$F$_5$)$_4$],[15] which provide extremely high syndioselectivity. In contrast, the non-Cp-ligated lanthanide complexes display medium to high activity under high pressure (> 500 MPa) or high temperature (70−100 °C), but give low stereoregular polystyrenes ($r \leq 0.6$).[16] Therefore, exploring non-Cp-ligated complexes attached by lanthanide elements that can initiate highly active and stereoselective polymerization of styrene is an attractive and challenging subject, as the non-Cp metal complexes have garnered an upsurge in research interest in other fields because of their strong metal−ligand bonds and exceptional and tunable steric and electronic features required for compensating coordinative unsaturation of metal centers and catalytic activity toward polymerization.

Recently, we have successfully synthesized a series of non-Cp-ligated rare-earth metal complexes that display versatile catalytic activities and selectivity toward the polymerizations of 1,3-conjugated dienes or lactide,[17] which is achieved by swiftly adjusting the sterics and electronics of ligands. These results compel us to investigate the possibility of designing new non-Cp-ligated rare-earth metal complexes that could provide both high activity and specific selectivity for the polymerization of styrene. To date, the amidinates,[18] guanidinates,[19] β-diketiminates,[20] salicylaldiminates,[21] etc., non-Cp ligand supported rare-earth metal complexes have been extensively examined; however, those bearing quinolinyl ligands remain scarce and are inert for styrene polymerization (*vide infra*).[22] Herein we report the synthesis and characterization of the novel non-Cp quinolinyl aniline ligands and the corresponding scandium complexes. Under activation of organoborates and aluminum alkyls these complexes display high syndioselectivity for the polymerization of styrene with high activity under mild conditions, which represents the first example of the non-Cp-ligated rare-earth metal complexes possessing such distinguished catalytic performances. In addition, the successful isolation and full characterization of a cationic ion pair provided a probable model structure for the true active species in this polymerization process that may facilitate the further investigation of the mechanism.

Results and Discussion

Synthesis and Characterization of Quinolinyl Anilido Scandium Complexes. N-R-Quinoline-8-amino ligands HL$^{1-5}$ (R = 2,6-Me$_2$C$_6$H$_3$ (HL^1), 2,4,6-Me$_3$C$_6$H$_2$ (HL^2), 2,6-Et$_2$C$_6$H$_3$ (HL^3), 2,6-^{i}Pr$_2$C$_6$H$_3$ (HL^4), C$_6$H$_5$ (HL^5)) were prepared by amination of 8-bromoquinoline with relevant anilines.[23] The acid−base reaction between scandium tris(alkyl) complex Sc(CH$_2$SiMe$_3$)$_3$(THF)$_2$ and one equivalent of HL$^{1-5}$ in hexane at room temperature afforded the corresponding complexes **1**−**5** in quantitative yields (Scheme 1). The ^{1}H NMR spectra of complexes **1**−**4** show a similar topology, giving an AB spin (J_{H-H} = 11.3−11.6 Hz) around δ 0.15−0.46 assigned to the methylene protons of the metal alkyl moiety Sc-CH_2SiMe$_3$, indicating that the methylene protons are diastereotopic. In contrast, the methylene protons of Sc-CH_2SiMe$_3$ in **5** are fluxional and exhibit a broad resonance around δ 0.29. X-ray diffraction analyses show

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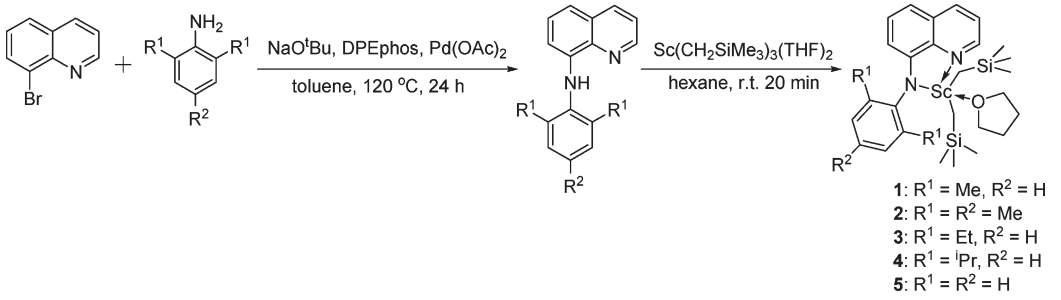
Scheme 1. Synthesis of Complexes 1−5



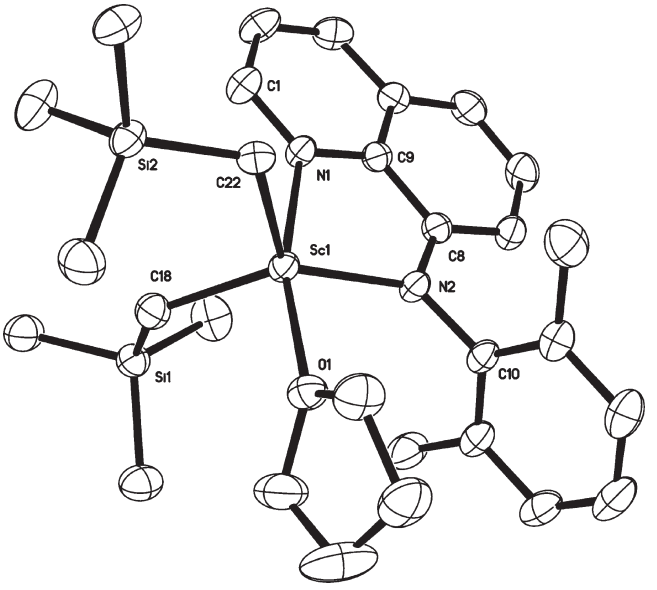


Figure 1. ORTEP drawing of complex **1** with 35% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sc(1)−N(1) 2.284(3), Sc(1)−N(2) 2.145(2), Sc(1)−C(18) 2.211(3), Sc(1)−C(22) 2.242(3), Sc(1)−O(1) 2.179(2), N(1)−C(9) 1.368(4), N(2)−C(8) 1.374(4), N(2)−C(10) 1.439(4), N(2)−Sc(1)−N(1) 73.42(9), C(18)−Sc(1)−C(22) 111.18(12), N(2)−Sc(1)−O(1) 91.84(9), O(1)−Sc(1)−N(1) 164.85(9), N(2)−Sc(1)−C(18) 122.46(11), N(2)−Sc(1)−C(22) 124.09(11).

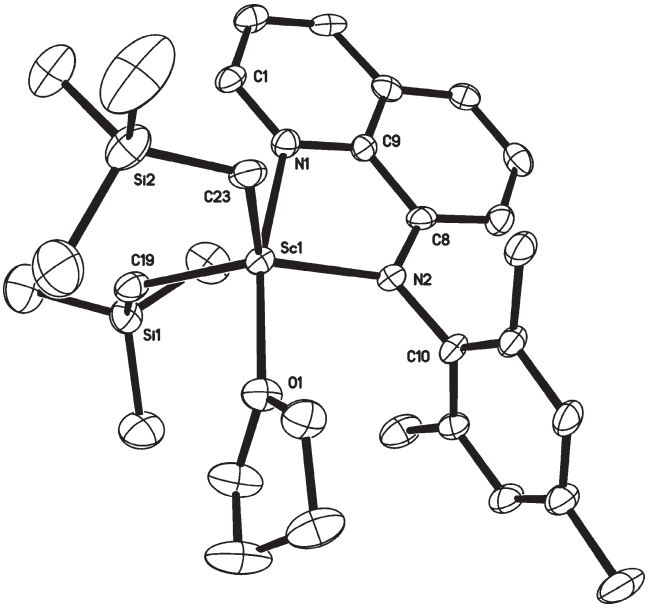


Figure 2. ORTEP drawing of complex **2** with 35% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sc(1)−N(1) 2.292(5), Sc(1)−N(2) 2.121(5), Sc(1)−C(19) 2.233(6), Sc(1)−C(23) 2.236(6), Sc(1)−O(1) 2.184(4), N(1)−C(9) 1.369(7), N(2)−C(8) 1.378(7), N(2)−C(10) 1.442(7), N(2)−Sc(1)−N(1) 73.67(17), C(19)−Sc(1)−C(23) 116.0(2), O(1)−Sc(1) −N(1) 166.49(17).

that complexes **1**, **2**, and **5** are isostructural mononuclear compounds with a coordinating THF molecule, adopting a distorted trigonal-bipyramidal geometry (Figures 1−3). The ligands chelate to the Sc^{3+} ion in a κ^2-N,N bidentate mode, leading to the N-aryl ring and the quinolinyl ring perpendicular to each other. The nitrogen atom N(1) of the quinolinyl ring and the oxygen O(1) of the THF molecule are axial, forming a large angle with Sc(1) (N(1)−Sc(1)−O(1), 165.72°), while the two alkyl carbon atoms and the aniline nitrogen atom N(2) occupy equatorial positions. The average bond lengths of Sc−C and Sc−N(2) fall within the normal values,[17g,22] while the bond angles of C−Sc−C, varying from 109.50(9)° (**5**) to 116.0(2)° (**2**), are comparable to those found in other scandium bis(alkyl) complexes.[17c,d,g,22]

The reaction of **1** with one equivalent of $[PhMe_2NH][B(C_6F_5)_4]$ performed in DME at room temperature allowed the successful isolation of its cationic counterpart $[L^1Sc(CH_2SiMe_3)(DME)_2][B(C_6F_5)_4]$ (**6**) (Scheme 2). An X-ray diffraction study establishes that **6** is a separated ion pair where the $[L^1Sc(CH_2SiMe_3)(DME)_2]^+$ cation adopts a distorted octahedral geometry different from its neutral precursor **1** (Figure 4). The Sc−C bond distance in **6** (2.193(4) Å) is shorter than that in **1** (av 2.227 Å), and so are the Sc−N bond lengths (Sc−N(1): 2.263(3) Å (**6**) vs 2.284(3) Å (**1**); Sc−N(2): 2.105(3) Å (**6**) vs 2.145(2) Å (**1**)). This might be attributed to the more electron-deficient metal center in **6** that leads to much stronger bond lengths.

Polymerization of Styrene. The catalytic performances of complexes **1**−**5** for the polymerization of styrene (St) have been investigated. The representative polymerization data are summarized in Table 1 and show that neither the single components **1**−**5** nor the binary systems (**1**−**5**)/Al^{i}Bu$_3$ could initiate the polymerization of styrene. To our delight, upon activation of $[Ph_3C][B(C_6F_5)_4]$ or $[PhMe_2NH][B(C_6F_5)_4]$, the resultant cationic systems based on complexes **1**−**3** showed high activity at room temperature to reach a completeness within half an hour. The resultant polystyrene had a relatively narrow polydispersity (M_w/M_n = 1.59−1.75), indicative of the single-site nature of these systems. Under the same conditions complex **4**, bearing *o*-isopropyl groups of the

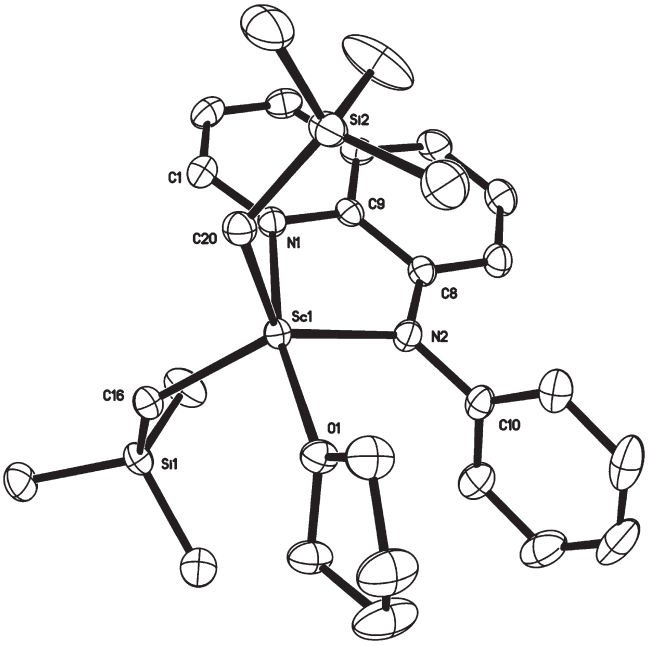
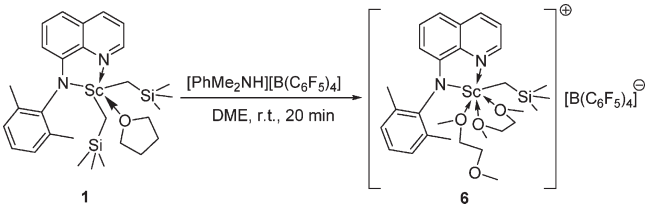


Figure 3. ORTEP drawing of complex **5** with 35% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sc(1)−N(1) 2.293(2), Sc(1)−N(2) 2.1335(19), Sc(1)−C(16) 2.230(2), Sc(1)−C(20) 2.230(2), Sc(1)−O(1) 2.1714(17), N(1)−C(9) 1.367(3), N(2)−C(8) 1.377(3), N(2)−C(10) 1.429(3), N(2)−Sc(1)−N(1) 73.50(7), C(20)−Sc(1)−C(16) 109.50(9), O(1)−Sc(1)−N(1) 165.83(7).

Scheme 2. Synthesis of Cationic Scandium Complex 6 Bearing a Quinoline Ligand



N-aryl ring of the ligand, was relatively less active, owing to the more steric environment around the central metal (entries 1−5). However complex **5** was almost inert (entry 6). NMR spectrum monitoring revealed that **5** was unstable even at room temperature, as the signals of the methylene protons disappeared completely within 4 h and the resonances of unknown products appeared, suggesting that the ligand in **5** was not bulky enough to stabilize the scandium bis(alkyl) species and was prone to redistribution.

Remarkably, addition of only one equivalent of Al^iBu_3, usually as an impurity scavenger,[24,25] to **1**/$[Ph_3C][B(C_6F_5)_4]$ brought about an obvious improvement in the activity for the resultant ternary system. The catalytic activity increased stepwise with the amount of Al^iBu_3, reaching a peak value when 5 equiv of Al^iBu_3 was loaded (entries 7−9). The type of aluminum alkyls played a significant role in adjusting the activity. The system **1**/$AlMe_3$/$[Ph_3C][B(C_6F_5)_4]$ exhibited

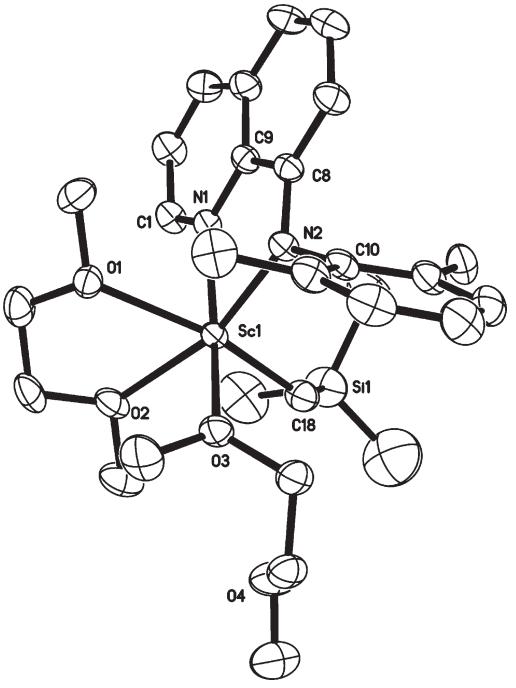


Figure 4. ORTEP drawing of the cationic part of **6** with 35% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sc(1)−N(1) 2.263(3), Sc(1)−N(2) 2.105(3), Sc(1)−C(18) 2.193(4), Sc(1)−O(1) 2.311(3), Sc(1)−O(2) 2.260(3), Sc(1)−O(3) 2.200(3), N(1)−C(9) 1.368(5), N(2)−C(8) 1.390(4), N(2)−C(10) 1.437(4), N(2)−Sc(1)−N(1) 75.46(11), C(18)−Sc(1)−O(1) 159.92(14), C(18)−Sc(1)−O(2) 92.30(14), N(2)−Sc(1)−O(3) 94.60(11), O(3)−Sc(1)−N(1) 166.70(11), N(2)−Sc(1)−C(18) 104.88(14).

low activity, consistent with those based on rare-earth metal[25] or titanium[26] reported previously, which might be attributed to the adduct formation between the sterically less demanding aluminum methyl and the central metal to result in the less active aluminate species. When switching to $AlEt_3$, the activity of the corresponding system increased obviously, and the highest activity was obtained when Al^iBu_3 was used (entries 9, 13, 14). The catalytic activity was also significantly influenced by fluorinated borate/borane in the order $[Ph_3C][B(C_6F_5)_4]$ > $[PhMe_2NH][B(C_6F_5)_4]$ > $B(C_6F_5)_3$ (entries 9, 15, 16). Moreover, with the catalytic system **1**/Al^iBu_3/$[Ph_3C][B(C_6F_5)_4]$, the increase of monomer-to-initiator molar ratio from 500 to 3000 caused the molecular weight of the resultant PS to increase correspondingly from 4.1×10^4 g/mol to 26.5×10^4 g/mol but not linearly, indicating that the polymerization proceeded in a controllable manner rather than in a living mode (entries 18−21). It was noteworthy that the *ortho*-substituent of the N-aryl ring of the ligand affected the catalytic activity drastically. The highest activity of 1.56×10^6 g mol^{-1} h^{-1} was achieved for complex **1**, bearing *ortho*-methyl substituent, which halved for complex **3**, containing *ortho*-ethyl, and almost is lost for complex **4**, having a bulky *ortho*-isopropyl, as the spatial steric ligands might block styrene coordination to the active sites (entries 11, 12). This could be proved further by the catalytic performance of the tridentate quinolinyl anilido-iminato scandium bis(alkyl) complex **7** reported recently by our

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(26) Kawabe, M.; Murata, M. *J. Polym. Sci. A: Polym. Chem.* **2001**, *39*, 3692.

Table 1. Polymerization of Styrene by Complexes 1−7/AlR_3/Borate[a]

entry	cat.	[Al]/[Ln]	time/min	yield/g	activity[b]	M_n[c] × 10^{-4}	M_w/M_n[c]	r[d]
1	**1/A**		30	0.52	104	3.8	1.75	0.72
2	**1/B**		30	0.35	70	2.9	1.70	0.71
3	**2/A**		30	0.45	90	3.5	1.68	0.70
4	**3/A**		30	0.40	80	3.0	1.59	0.68
5	**4/A**		30	0.23	46	2.3	1.61	0.56
6	**5/A**		180	trace				
7	**1/A**	1	10	0.52	302	5.1	2.20	
8	**1/A**	3	5	0.52	624	4.0	2.01	
9	**1/A**	5	2	0.52	1560	2.3	1.87	0.94
10	**2/A**	5	5	0.52	624	2.0	2.06	0.93
11	**3/A**	5	5	0.52	624	1.5	1.96	0.93
12	**4/A**	5	30	0.52	104	2.8	1.56	0.61
13[e]	**1/A**	5	5	0.52	624	2.0	1.58	0.94
14[f]	**1/A**	5	240	0.37	9	2.7	1.63	0.66
15	**1/B**	5	5	0.52	624	2.8	1.93	0.93
16	**1/C**	5	30	0.52	104	4.0	1.82	0.93
17	**6**	10	120	0.21	11	1.7	1.96	0.93
18[g]	**1/A**	5	60	0.52	52	4.1	1.72	0.94
19[h]	**1/A**	5	120	1.01	50	7.4	1.86	0.94
20[i]	**1/A**	5	240	1.89	47	17.9	2.29	0.94
21[j]	**1/A**	5	360	2.56	43	26.5	2.20	0.94
22	**7/A**	5	60	0				

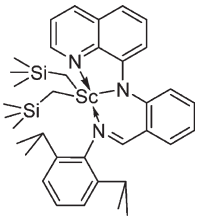
[a] General conditions: 10^{-5} mol of Sc complex; in chlorobenzene; monomer/solvent = 5:2 (v/v); [Al] = Al^{i}Bu$_3$; T_p: 25 °C; [St]/[Ln] = 500; [Ln]/[activator] = 1:1 (activator = [Ph_3C][$B(C_6F_5)_4$] (**A**), [$PhMe_2NH$]-[$B(C_6F_5)_4$] (**B**), $B(C_6F_5)_3$ (**C**)). [b] Given in kg of PS/(mol Sc·h). [c] Determined by GPC in THF at 40 °C against polystyrene standard. [d] Determined by ^{13}C NMR. [e] [Al] = $AlEt_3$. [f] [Al] = $AlMe_3$. [g] Monomer/solvent = 1:3 (v/v); [St]/[Ln] = 500. [h] Monomer/solvent = 1:3 (v/v); [St]/[Ln] = 1000. [i] Monomer/solvent = 1:3 (v/v); [St]/[Ln] = 2000. [j] Monomer/solvent = 1:3 (v/v); [St]/[Ln] = 3000.

group (Chart 1),[22] which was employed as a precursor to initiate the polymerization of styrene but is inert. The space-filling drawings of the molecular structures displayed clearly a too crowded environment around the Sc^{3+} ion in **7** as compared with **1** (Figure 5). Noteworthy was that the cationic complex **6** activated by Al^{i}Bu$_3$ to extrude the coordinated DME molecules could catalyze the polymerization of styrene with moderate activity, suggesting that **6** to some degree represented a reaction intermediate in this process (entry 17).

The microstructure of the isolated PS was determined by ^{13}C NMR spectroscopic analysis according to the resonance integrals of the methylene carbon, which was strongly dependent on the catalyst system applied.[27] PS obtained by using the binary systems was moderately stereoregular, with the *r*-diad value varying from 0.56 to 0.72. Strikingly, the ternary systems exhibited high stereoselectivity to afford sPS with *r* diad up to 0.94 in high yield. This represented the first example of rare-earth metal based precursors bearing non-Cp ligands displaying both high specific selectivity and activity. This result suggested the presence of the coordination of aluminum alkyls to the active metal center and the concerted spatial bulkiness of aluminum alkyls and the ligands orienting styrene insertion into the active sites in certain directions, causing an increase in selectivity. Thus the less steric aluminum tris(methyl)s did not facilitate the formation of a highly syndioselective ternary system but provided only low syndiotactic PS (r = 0.66). This could be proved further by the behavior of the organoborate, which showed negligent influence on the selectivity because it existed as a discrete counterion of the cationic active species without bonding to the active center (see the molecular structure of complex **6** *vide supra*; ^{19}F NMR spectra of **6** and **1**/[Ph_3C][$B(C_6F_5)_4$]/Al^{i}Bu$_3$ are almost the same; see SFigures 9, 17, 18). It should be noted that the too crowded environment could also bring about a drop in selectivity, as the case of using precursor **4**, bearing much bulkier isopropyl groups (entry 12). We presumed that the geometry of **4** arising from the bulky ligand did not facilitate the syndiotactic configuration resulting from the phenyl−phenyl repulsive interaction.[28] These results were consistent with the microstructure analysis of the obtained sPs samples.

The ^{13}C NMR spectrum of the phenyl *ipso*-carbon region of polystyrene samples is shown in Figure 6,[29] where the main signal is assigned to the *rrrr* pentad, while the other four arise from the probable single-*m* pentads *rmrr* and *mrrr* and the double-*m* pentads *rmmr* and *mmrr*, respectively. Because [*rmrr*] = [*mrrr*], a chain-end control mechanism arising from steric control was assumed to operate for the formation of sPS with this catalyst system; as for a site-control mechanism, the integrals of the pentads should abide by the rule of 2[*rmmr*] = [*mmrr*] = [*mrrr*].[30]

Chart 1. Molecular Structure of Complex 7



7

Conclusion

We have demonstrated that the non-Cp quinolinyl-anilino-ligated scandium bis(alkyl) complexes activated by [Ph_3C][$B(C_6F_5)_4$] generated a single-site cationic system possessing a high activity with moderate selectivity for the polymerization of styrene, while the ternary system composed of these complexes and AlR_3 and organoborates/borane displayed both high activity and high specific selectivity to afford syndiotactic polystyrene via a chain-end control mechanism governed by the concerted steric effects of the ligands and the coactivator aluminum alkyls. The

(27) In the ^{13}C NMR spectra in tetrachloroethane-d_2 at 100 °C, the four distinct signals of the methylene carbon of polystyrene obtained by **1**/Al^{i}Bu$_3$/[Ph_3C][$B(C_6F_5)_4$] correspond best with those reported by Harder et al (SFigure 13a). Thus they can be assigned to the *rrmrr* (45.95 ppm), *mrrrr* (45.06 ppm), *rrrr* (44.44 ppm), and the *rmrrr* hexads (43.34 ppm), and the intensity of the *rrmrr*, *mrrrr*, and *rmrrr* hexads complies with an approximate 1:2:2 ratio. The signal assignments of the methylene carbon in tetrachloroethane-d_2 and chloroform-*d* are similar (sFigure 13b), as is the tacticity of our polymers measured by ^{13}C NMR spectroscopic analysis in chloroform-*d*. See: (a) Feil, F.; Harder, S. *Macromolecules* **2003**, *36*, 3446. (b) Kawamura, T.; Toshima, N.; Matsuzaki, K. *Macromol. Rapid Commun.* **1994**, *15*, 479. (c) Harder, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2714. (d) Harder, S.; Feil, F.; Knoll, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 4261.

(28) Longo, P.; Proto, A.; Zambelli, A. *Macromol. Chem. Phys.* **1995**, *196*, 3015.

(29) For assignments of major peaks of phenyl *ipso*-carbon, see: (a) Michiue, K.; Onda, M.; Tanaka, H.; Makio, H.; Mitani, M.; Fujita, T. *Macromolecules* **2008**, *41*, 6289. (b) Sato, H.; Tanaka, Y. *J. Polym. Sci., Part B: Polym. Phys.* **1983**, *21*, 1667. (c) Zambelli, A.; Longo, P.; Pellecchia, C.; Grassi, A. *Macromolecules* **1987**, *20*, 2035. (d) Longo, P.; Proto, A.; Zambelli, A. *Macromol. Chem. Phys.* **1995**, *196*, 3015.

(30) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355.

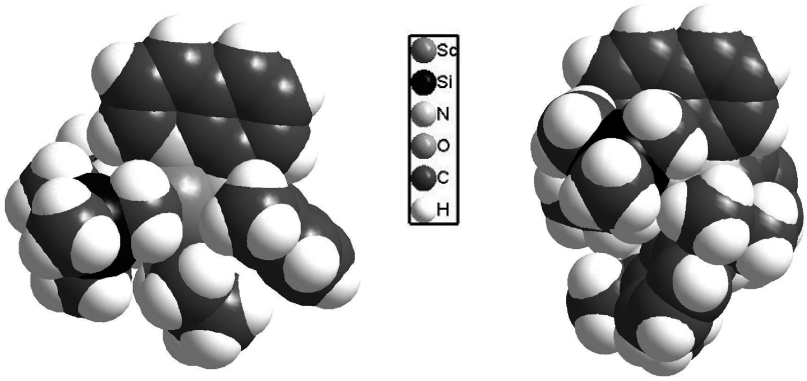


Figure 5. Space-filling drawings of the molecular structures viewed from above the plane of the quinolinyl ring. Complex **1** (left) and complex **7** (right).

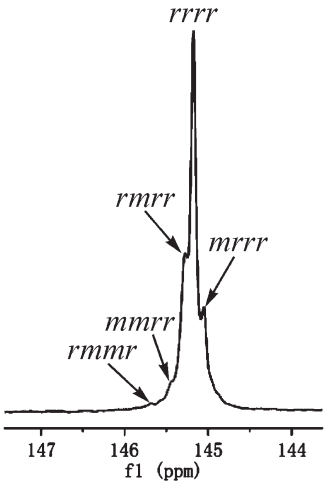


Figure 6. ^{13}C NMR spectrum ($CDCl_3$, 25 °C) of the phenyl *ipso*-carbon region of polystyrene obtained with **1**/Al^{i}Bu$_3$/[Ph_3C][$B(C_6F_5)_4$] (Table 1, entry 9).

isolation and full characterization of the cationic scandium complex from a binary system represented to some degree the true active species in the styrene polymerization process, which could also explain why orgnoborates in the present catalyst systems influenced more significantly the activity than the selectivity, as they exist as a discrete counterion of the cationic active species without interaction with the active sites. To our knowledge, this is the first example of rare-earth metal based precursors attached to the non-Cp ligands showing high syndioselectivity for polymerization of styrene with high activity simultaneously, which might provide clues for designing new efficient catalysts.

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 via a SPS system. Anilines, NaO^{t}Bu, bis[2-(diphenylphosphino)phenyl] ether, 8-bromoquinoline, $Pd(OAc)_2$, $B(C_6F_5)_3$, and aluminum alkyls were purchased from Aldrich and used without further purification. [Ph_3C][$B(C_6F_5)_4$] and [$PhMe_2NH$][$B(C_6F_5)_4$] were prepared according to the published procedures.[31] Styrene (99%, Acros) was dried over CaH_2 under stirring for 48 h and distilled before use. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV400 (FT, 400 MHz for ^1H; 100 MHz for ^{13}C), AV300 (FT, 300 MHz for ^1H; 75 MHz for ^{13}C), or AV600 (FT, 600 MHz for ^1H; 150 MHz for ^{13}C). ^{19}F NMR spectra (282 MHz) are referenced to external C_6H_5F. The molecular weight (M_n) was measured by TOSOH HLC-8220 GPC at 40 °C using THF as eluent (the flow rate is 0.35 mL/min) against polystyrene standards. Elemental analyses were performed at National Analytical Research Centre of Changchun Institute of Applied Chemistry. X-ray analysis was 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 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.

Preparation of the Ligands. ***N*-(2,6-Dimethylphenyl)quinolin-8-amine (HL^1).** 2,6-Dimethylaniline (1.45 g, 12 mmol), $Pd(OAc)_2$ (22 mg, 0.10 mmol), Na^{t}OBu (1.44 g,15 mmol), 8-bromoquinoline (2.08 g, 10 mmol), bis[2-(diphenylphosphino)phenyl] ether (DPEphos, 80.80 mg, 0.15 mmol), and anhydrous degassed toluene (20 mL) were added to a flask. The solution was stirred at 120 °C overnight, and then water (40 mL) was added. The organic phase was extracted with toluene (90 mL) and dried over anhydrous $MgSO_4$. Purification by column chromatography on silica gel eluting with ethyl acetate and petroleum ether (v/v, 10:1) afforded HL^1 (1.15 g, 46%). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 2.21 (s, 6H, *o*-$NC_6H_3Me_2$), 6.22 (d, $^3J_{H-H}$ = 7.5 Hz, 1H, quinoline), 7.05−7.15 (m, 5H, $NC_6H_3Me_2$, quinoline), 7.21 (t, $^3J_{H-H}$ = 3.9 Hz, 1H, quinoline), 7.39 (q, $^3J_{H-H}$ = 4.2 Hz, 1H, quinoline), 7.52 (br s, 1H, NH), 8.08 (d, $^3J_{H-H}$ = 8.1 Hz, 1H, quinoline), 8.77 (dd, $^3J_{H-H}$ = 4.2 Hz, $^4J_{H-H}$ = 1.5 Hz, 1H, quinoline). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 18.23 (2C, *o*-$NC_6H_3Me_2$), 106.01, 114.74, 121.31 (3C, quinoline), 126.10 (1C, $NC_6H_3Me_2$), 127.58 (1C, quinoline), 128.43 (2C, $NC_6H_3Me_2$), 128.81, 135.99 (2C, quinoline), 136.60 (2C, $NC_6H_3Me_2$), 137.96 (1C, $NC_6H_3Me_2$), 138.14, 142.73, 147.08 (3C, quinoline).

***N*-Mesitylquinolin-8-amine (HL^2).** Following the same procedure described for the formation of HL^1, treatment of 2,4,6-trimethylaniline (1.62 g, 12 mmol), $Pd(OAc)_2$ (22 mg, 0.10 mmol), Na^{t}OBu (1.44 g,15 mmol), 8-bromoquinoline (2.08 g, 10 mmol), and bis[2-(diphenylphosphino)phenyl] ether (DPEphos, 80.8 mg, 0.15 mmol) gave HL^2 (1.26 g, 48%). ^1HNMR (300 MHz, $CDCl_3$, 25 °C): δ 2.21 (s, 6H, *o*-NC_6H_2-Me_2), 2.33 (s, 3H, *p*-NC_6H_2Me), 6.26 (d, $^3J_{H-H}$ = 7.5 Hz, 1H, quinoline), 6.99 (s, 2H, $NC_6H_2Me_3$), 7.09 (dd, $^3J_{H-H}$ = 8.1 Hz, $^4J_{H-H}$ = 0.9 Hz, 1H, quinoline), 7.26 (t, $^3J_{H-H}$ = 7.8 Hz, 1H, quinoline), 7.42 (q, $^3J_{H-H}$ = 4.2 Hz, 1H, quinoline), 7.49 (br s, 1H, NH), 8.12 (d, $^3J_{H-H}$ = 8.1 Hz, 1H, quinoline), 8.80 (dd, $^3J_{H-H}$ = 4.2 Hz, $^4J_{H-H}$ = 1.5 Hz, 1H, quinoline). ^{13}C NMR

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(75 MHz, $CDCl_3$, 25 °C): δ 18.12 (2C, *o*-$NC_6H_2Me_3$), 20.92 (1C, *p*-$NC_6H_2Me_3$), 105.89, 114.50, 121.28, 127.63, 128.81 (5C, quinoline), 129.13 (2C, $NC_6H_2Me_3$), 135.44 (1C, quinoline), 135.62 (1C, $NC_6H_2Me_3$), 135.97 (1C, quinoline), 136.43 (2C, $NC_6H_2Me_3$), 137.96 (1C, $NC_6H_2Me_3$), 143.08, 147.01 (2C, quinoline).

***N*-(2,6-Diethylphenyl)quinolin-8-amine (HL^3).** Following the same procedure described for the formation of HL^1, treatment of 2,6-diethylaniline (1.79 g, 12 mmol), $Pd(OAc)_2$ (22 mg, 0.10 mmol), Na^{t}OBu (1.44 g,15 mmol), 8-bromoquinoline (2.08 g, 10 mmol), and bis[2-(diphenylphosphino)phenyl] ether (DPEphos, 80.8 mg, 0.15 mmol) gave HL^3 (1.36 g, 49%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 1.15 (t, $^3J_{H-H}$ = 7.5 Hz, 6H, CH_2CH_3), 2.62 (br s, 4H, CH_2CH_3), 6.25 (dd, $^3J_{H-H}$ = 7.5 Hz, $^4J_{H-H}$ = 1.2 Hz, 1H, quinoline), 7.08 (dd, $^3J_{H-H}$ = 8.1 Hz, $^4J_{H-H}$ = 1.2 Hz, 1H, quinoline), 7.21−7.27 (m, 4H, $NC_6H_3Et_2$, quinoline), 7.42 (q, $^3J_{H-H}$ = 4.2 Hz, 1H, quinoline), 7.58 (br s, 1H, NH), 8.11 (dd, $^3J_{H-H}$ = 8.1 Hz, $^4J_{H-H}$ = 1.5 Hz, 1H, quinoline), 8.81 (dd, $^3J_{H-H}$ = 4.2 Hz, $^4J_{H-H}$ = 1.8 Hz, 1H, quinoline). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 14.88 (2C, CH_2CH_3), 24.73 (2C, CH_2CH_3), 106.00, 114.51, 121.32 (3C, quinoline), 126.63 (2C, $NC_6H_3Et_2$), 126.79 (1C, $NC_6H_3Et_2$), 127.58, 128.75, 135.97, 136.92 (4C, quinoline), 137.81 (1C, $NC_6H_3Et_2$), 142.88 (2C, $NC_6H_3Et_2$), 143.79, 147.06 (2C, quinoline).

***N*-(2,6-Diisopropylphenyl)quinolin-8-amine (HL^4).** Following the same procedure described for the formation of HL^1, treatment of 2,6-diisopropylaniline (2.13 g, 12 mmol), $Pd(OAc)_2$ (22 mg, 0.10 mmol), Na^{t}OBu (1.44 g,15 mmol), 8-bromoquinoline (2.08 g, 10 mmol), and bis[2-(diphenylphosphino)phenyl] ether (DPEphos, 80.8 mg, 0.15 mmol) gave HL^4 (1.62 g, 53%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 1.14 (d, $^3J_{H-H}$ = 10.8 Hz, 12H, $CH(CH_3)_2$), 3.22 (m, 2H, $CH(CH_3)_2$), 6.25 (d, $^3J_{H-H}$ = 7.8 Hz, 1H, quinoline), 7.05 (t, $^3J_{H-H}$ = 8.1 Hz, 1H, quinoline), 7.21−7.34 (m, 4H, $NC_6H_3{}^iPr_2$, quinoline), 7.43 (q, $^3J_{H-H}$ = 4.2 Hz, 1H, quinoline), 7.53 (br s, 1H, NH), 8.11 (d, $^3J_{H-H}$ = 8.1 Hz, 1H, quinoline), 8.82 (dd, $^3J_{H-H}$ = 4.2 Hz, $^4J_{H-H}$ = 1.2 Hz,1H, quinoline). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 23.19 (2C, $CH(CH_3)_2$), 24.73 (2C, $CH(CH_3)_2$), 28.33 (2C, $CH(CH_3)_2$), 106.11, 114.35, 121.36 (3C, quinoline), 123.81 (2C, $NC_6H_3{}^iPr_2$), 127.37 (1C, $NC_6H_3{}^iPr_2$), 127.60, 128.75, 135.26, 135.98 (4C, quinoline), 137.66 (1C, $NC_6H_3{}^iPr_2$), 144.67, 147.06 (2C, quinoline), 147.85 (2C, $NC_6H_3{}^iPr_2$).

***N*-Phenylquinolin-8-amine (HL^5).** Following the same procedure described for the formation of HL^1, treatment of aniline (1.12 g, 12 mmol), $Pd(OAc)_2$ (22 mg, 0.10 mmol), Na^{t}OBu (1.44 g,15 mmol), 8-bromoquinoline (2.08 g, 10 mmol), and bis[2-(diphenylphosphino)phenyl] ether (DPEphos, 80.8 mg, 0.15 mmol) gave HL^5 (1.60 g, 73%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.05 (s, 1H, $^3J_{H-H}$ = 6.3 Hz, NC_6H_5), 7.22 (d, $^3J_{H-H}$ = 8.1 Hz, 1H, quinoline), 7.35−7.45 (m, 6H, NC_6H_5, quinoline), 7.45 (d, $^3J_{H-H}$ = 7.7 Hz, 1H, quinoline), 8.13 (d, $^3J_{H-H}$ = 8.4 Hz, 1H, quinoline), 8.30 (br s, 1H, NH), 8.79 (d, $^3J_{H-H}$ = 3.6 Hz, 1H, quinoline). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 107.76, 116.45 (2C, quinoline), 119.99 (2C, NC_6H_5), 121.48 (1C, NC_6H_5), 122.04, 127.23, 128.81 (3C, quinoline), 129.27 (2C, NC_6H_5), 136.08 (1C, quinoline), 138.50 (1C, NC_6H_5), 140.21, 141.82, 147.20 (3C, quinoline).

Preparation of the Complexes. L^{1}Sc(CH$_2$SiMe$_3$)$_2$(THF) (1). To a hexane solution (3.0 mL) of $Sc(CH_2SiMe_3)_3(THF)_2$ (0.18 g, 0.4 mmol) was dropwise added an equivalent of HL^1 (0.10 g, 0.4 mmol in 4 mL of hexane) at room temperature. The resulting red solution was stirred for 20 min at room temperature and then was concentrated to about 2 mL and cooled to −30 °C for 12 h to afford red crystalline solids, which were washed carefully with a small amount of hexane (0.5 mL) to remove impurities and dried *in vacuo* to give red powders of complex **1** (0.17 g, 81%). Red crystals for X-ray analysis grew from a solution of hexane at −30 °C within 24 h. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 0.16, 0.42 (AB, $^2J_{H-H}$ = 11.3 Hz, 4H, CH_2SiMe_3), 0.27 (s, 18H, $SiMe_3$), 1.08 (br, 4H, THF), 2.33 (s, 6H, *o*-$NC_6H_3Me_2$), 3.69 (br, 4H, THF), 6.14 (d, $^3J_{H-H}$ = 7.8 Hz, 1H, quinoline), 6.79 (d, $^3J_{H-H}$ = 7.8 Hz, 1H, quinoline), 6.95 (q, $^3J_{H-H}$ = 4.8 Hz, 1H, quinoline), 7.06 (t, 1H, $^3J_{H-H}$ = 7.8 Hz, $NC_6H_3Me_2$), 7.17 (d, $^3J_{H-H}$ = 7.5 Hz, 2H, $NC_6H_3Me_2$), 7.24 (t, 1H, $^3J_{H-H}$ = 8.1 Hz, quinoline), 7.71 (d, $^3J_{H-H}$ = 8.1 Hz, 1H, quinoline), 9.13 (d, $^3J_{H-H}$ = 3.0 Hz, 1H, quinoline). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 4.27 (6C, $SiMe_3$), 19.43 (2C, *o*-$NC_6H_3Me_2$), 25.02 (2C, THF), 41.65 (br, 2C, CH_2SiMe_3), 71.81 (2C, THF), 107.18, 111.51, 121.04 (3C, quinoline), 124.54 (1C, $NC_6H_3Me_2$), 129.27 (2C, $NC_6H_3Me_2$), 131.06, 131.16 (2C, quinoline), 135.31 (2C, $NC_6H_3Me_2$), 140.15 (1C, quinoline), 141.41 (1C, $NC_6H_3Me_2$), 146.23, 149.12, 153.00 (3C, quinoline). Anal. Calcd for $C_{29}H_{45}ScN_2Si_2$ (%): C, 64.64; H, 8.42; N, 5.20. Found: C, 63.51; H, 8.19; N, 5.03.

L^{2}Sc(CH$_2$SiMe$_3$)$_2$(THF) (2). Following a similar procedure to that described for the preparation of **1**, the reaction of $Sc(CH_2SiMe_3)_3(THF)_2$ (0.18 g, 0.4 mmol in 3 mL of hexane) with equimolar HL^2 (0.12 g, 0.4 mmol in 4 mL of hexane) gave **2** (0.18 g, 82%). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 0.15, 0.40 (AB, $^2J_{H-H}$ = 11.4 Hz, 4H, CH_2SiMe_3), 0.26 (s, 18H, $SiMe_3$), 1.13 (br, 4H, THF), 2.31 (s, 6H, *o*-$NC_6H_2Me_3$), 2.34 (s, 3H, *p*-$NC_6H_2Me_3$), 3.73 (br, 4H, THF), 6.16 (dd, $^3J_{H-H}$ = 7.8 Hz, $^4J_{H-H}$ = 0.9 Hz, 1H, quinoline), 6.79 (dd, $^3J_{H-H}$ = 8.1 Hz, $^4J_{H-H}$ = 0.9 Hz, 1H, quinoline), 6.95−6.99 (m, 3H, *m*-$NC_6H_2Me_3$, quinoline), 7.22 (t, $^3J_{H-H}$ = 7.8 Hz, 1H, quinoline), 7.74 (dd, $^3J_{H-H}$ = 8.4 Hz, $^4J_{H-H}$ = 1.5 Hz, 1H, quinoline), 9.12 (dd, $^3J_{H-H}$ = 4.8 Hz, $^4J_{H-H}$ = 1.5 Hz, 1H, quinoline). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 4.26 (6C, $SiMe_3$), 19.37 (2C, *o*-$NC_6H_2Me_3$), 21.40 (1C, *p*-$NC_6H_2Me_3$), 25.10 (2C, THF), 41.44 (br, 2C, CH_2SiMe_3), 71.82 (2C, THF), 107.20, 111.38, 121.01 (3C, quinoline), 129.98 (2C, $NC_6H_2Me_3$), 131.07, 131.18 (2C, quinoline), 133.32 (1C, $NC_6H_2Me_3$), 134.91 (2C, $NC_6H_2Me_3$), 140.12 (1C, quinoline), 141.49 (1C, $NC_6H_2Me_3$), 146.19, 146.31, 153.33 (3C, quinoline). Anal. Calcd for $C_{30}H_{47}ScN_2Si_2$ (%): C, 65.18; H, 8.57; N, 5.07. Found: C, 64.39; H, 8.41; N, 4.87.

L^{3}Sc(CH$_2$SiMe$_3$)$_2$(THF) (3). Following a similar procedure to that described for the preparation of **1**, the reaction of $Sc(CH_2SiMe_3)_3(THF)_2$ (0.18 g, 0.4 mmol in 3 mL of hexane) with equimolar HL^3 (0.11 g, 0.4 mmol in 4 mL of hexane) gave **3** (0.19 g, 83%). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 0.20, 0.45 (AB, $^2J_{H-H}$ = 11.6 Hz, 4H, CH_2SiMe_3), 0.28 (s, 18H, $SiMe_3$), 1.13 (br, 4H, THF), 1.22 (t, $^3J_{H-H}$ = 7.5 Hz, 6H, CH_2CH_3), 2.72 (m, 2H, CH_2CH_3), 2.95 (m, 2H,CH_2CH_3), 3.72 (br, 4H, THF), 6.17 (d, $^3J_{H-H}$ = 7.8 Hz, 1H, quinoline), 6.79 (d, $^3J_{H-H}$ = 7.8 Hz, 1H, quinoline), 6.97 (q, $^3J_{H-H}$ = 4.8 Hz, 1H, quinoline), 7.19−7.29 (m, 3H, $NC_6H_3Et_2$, quinoline), 7.74 (d, $^3J_{H-H}$ = 8.1 Hz, 1H, quinoline), 9.15 (d, $^3J_{H-H}$ = 4.8 Hz, 1H, quinoline). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 4.19 (6C, $SiMe_3$), 15.36 (2C, CH_2CH_3), 25.32 (2C, CH_2CH_3), 25.11 (2C, THF), 41.51 (br, 2C, CH_2SiMe_3), 71.85 (2C, THF), 108.23, 111.40, 121.03 (3C, quinoline), 125.00 (1C, $NC_6H_3Et_2$), 126.75 (2C, $NC_6H_3Et_2$), 130.75, 131.09, 140.16 (3C, quinoline), 140.72 (2C, $NC_6H_3Et_2$), 141.30 (1C, $NC_6H_3Et_2$), 146.21, 148.00, 154.21 (3C, quinoline). Anal. Calcd for $C_{31}H_{49}ScN_2Si_2$ (%): C, 65.68; H, 8.71; N, 4.94. Found: C, 64.72; H, 8.39; N, 4.71.

L^{4}Sc(CH$_2$SiMe$_3$)$_2$(THF) (4). Following a similar procedure to that described for the preparation of **1**, the reaction of $Sc(CH_2SiMe_3)_3(THF)_2$ (0.18 g, 0.4 mmol in 3 mL of hexane) with equimolar HL^4 (0.12 g, 0.4 mmol in 4 mL of hexane) gave **4** (0.18 g, 76%). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 0.16, 0.36 (AB, $^2J_{H-H}$ = 11.6 Hz, 4H, CH_2SiMe_3), 0.22 (s, 18H, $SiMe_3$), 1.17 (br, 4H, THF), 1.14 (d, 6H, $CH(CH_3)_2$), 1.28 (d, 6H, $CH(CH_3)_2$), 3.52 (m, 2H, $CH(CH_3)_2$), 3.70 (br, 4H, THF), 6.12 (d, $^3J_{H-H}$ = 7.8 Hz, 1H, quinoline), 6.73 (d, $^3J_{H-H}$ = 7.8 Hz, 1H, quinoline), 6.91 (q, $^3J_{H-H}$ = 4.8 Hz, 1H, quinoline), 7.11−7.30 (m, 4H, $NC_6H_3{}^iPr_2$, quinoline), 7.71 (dd, $^3J_{H-H}$ = 7.4 Hz, $^4J_{H-H}$ = 1.5 Hz, 1H, quinoline), 9.16 (dd, $^3J_{H-H}$ = 4.8 Hz, $^4J_{H-H}$ = 1.5 Hz, 1H, quinoline). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 4.22 (6C, $SiMe_3$), 24.70 (2C, $CH(CH_3)_2$), 25.39

(2C, THF), 26.53 (2C, $CH(CH_3)_2$), 28.87 (2C, $CH(CH_3)_2$), 41.42 (br, 2C, CH_2SiMe_3), 72.30 (2C, THF), 110.37, 111.58, 120.99 (3C, quinoline), 124.88 (2C, $NC_6H_3{}^i Pr_2$), 125.67 (1C, $NC_6H_3{}^i Pr_2$), 130.30, 131.06, 140.22 (3C, quinoline), 141.16 (1C, $NC_6H_3{}^i Pr_2$), 145.90 (1C, $NC_6H_3{}^i Pr_2$), 146.45, 146.56, 155.22 (3C, quinoline). Anal. Calcd for $C_{33}H_{53}ScN_2Si_2$ (%): C, 66.62; H, 8.98; N, 4.71. Found: C, 65.81; H, 8.73; N, 4.49.

$L^5Sc(CH_2SiMe_3)_2(THF)$ (5). Following a similar procedure to that described for the preparation of **1**, the reaction of $Sc(CH_2SiMe_3)_3(THF)_2$ (0.18 g, 0.4 mmol in 3 mL of hexane) with equimolar HL^5 (0.09 g, 0.4 mmol in 4 mL of hexane) gave **5** (0.13 g, 61%). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 0.18 (s, 18H, $SiMe_3$), 0.32 (br, 4H, CH_2SiMe_3), 1.06 (br, 4H, THF), 3.73 (br, 4H, THF), 6.55 (d, $^3J_{H-H}$ = 7.8 Hz, 1H, quinoline), 6.80 (d, $^3J_{H-H}$ = 8.1 Hz, 1H, quinoline), 6.96 (q, $^3J_{H-H}$ = 4.8 Hz, 1H, quinoline), 7.07 (m, 1H, NC_6H_5), 7.21−7.32 (m, 5H, NC_6H_5, quinoline), 7.73 (dd, $^3J_{H-H}$ = 8.4 Hz, $^4J_{H-H}$ = 1.5 Hz, 1H, quinoline), 8.99 (dd, $^3J_{H-H}$ = 4.5 Hz, $^4J_{H-H}$ = 1.5 Hz, 1H, quinoline). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 4.23 (6C, $SiMe_3$), 25.08 (2C, THF), 40.10 (br, 2C, CH_2SiMe_3), 71.52 (2C, THF), 108.62, 111.84, 121.07 (3C, quinoline), 124.14 (1C, NC_6H_5), 128.39 (2C, NC_6H_5), 130.33 (2C, NC_6H_5), 130.81, 130.91, 140.05 (3C, quinoline), 141.21 (1C, NC_6H_5), 146.45, 152.43, 155.51 (3C, quinoline). Anal. Calcd for $C_{27}H_{41}ScN_2Si_2$ (%): C, 63.49; H, 8.09; N, 5.48. Found: C, 62.83; H, 7.91; N, 5.29.

$L^1Sc(CH_2SiMe_3)(THF)_2][B(C_6F_5)_4]$ (6). A DME solution (2 mL) of $[PhMe_2NH][B(C_6F_5)_4]$ (60 mg, 0.07 mmol) was slowly added to a DME solution (4 mL) of $L^1Sc(CH_2SiMe_3)_2(THF)]$ (**1**) (39 mg, 0.07 mmol) in 10 min with vigorous stirring and kept stirring for 20 min. Removal of the volatiles gave residues, which were washed with cold hexane and dried under reduced pressure for 2 h to generate **6** (55 mg, 61%). Red single crystals for X-ray diffraction analysis were obtained by recrystallization in chlorobenzene/hexane at −30 °C for several days. ^{1}H NMR (600 MHz, 25 °C, $C_6D_4Cl_2$): δ −0.39 (s, 9H, CH_2SiMe_3), 0.20 (s, 2H, CH_2SiMe_3), 2.12 (s, 6H, o-$NC_6H_3Me_2$), 3.21 (br, $CH_3OCH_2CH_2OCH_3$), 3.51 (br, $CH_3OCH_2CH_2OCH_3$), 5.99 (d, $^3J_{H-H}$ = 7.8 Hz, 1H, quinoline), 6.87 (d, $^3J_{H-H}$ = 7.8 Hz, 1H, quinoline),7.04 (t, $^3J_{H-H}$ = 7.8 Hz, 1H, $NC_6H_3Me_2$), 7.11 (d, $^3J_{H-H}$ = 7.8 Hz, 2H, $NC_6H_3Me_2$), 7.16 (t, $^3J_{H-H}$ = 7.8 Hz, 1H, quinoline),7.47 (q, $^3J_{H-H}$ = 4.8 Hz, 1H, quinoline), 8.20 (d, $^3J_{H-H}$ = 7.8 Hz, 1H, quinoline), 8.50 (br, 1H, quinoline). ^{13}C NMR (150 MHz, 25 °C, $C_6D_4Cl_2$): δ 3.73 (3C, $SiMe_3$), 20.45 (2C, o-$NC_6H_3Me_2$), 51.59 (br, 2C, CH_2SiMe_3), 61.54 (br, 4C $CH_3OCH_2CH_2OCH_3$), 72.29 (4C $CH_3OCH_2CH_2OCH_3$), 110.46, 114.69, 121.81 (3C, quinoline), 126.66 (1C, $NC_6H_3Me_2$), 130.72 (2C, $NC_6H_3Me_2$), 132.25, 142.74, 144.29 (3C, quinoline), 149.02 (Ar), 150.62 (Ar), 151.55 (Ar). ^{19}F NMR (282 MHz, C_6D_6, 25 °C): δ −18.7 (d, o-F), −49.2 (t, p-F), −53.1 (t, m-F). Anal. Calcd for $C_{53}H_{46}BF_{20}ScN_2Si$ (%): C, 51.39; H, 3.74; N, 2.26. Found: C, 50.82; H, 3.39; N, 2.03.

Polymerization of Styrene. A typical procedure for the polymerization was as follows (Table 1, run 9): A solution of **1** (0.01 mmol, 5.40 mg, in 0.1 mL of C_6H_5Cl), 0.10 mmol of Al^iBu_3, and 0.1 mL of C_6H_5Cl solution of $[PhC_3][B(C_6F_5)_4]$ (0.01 mmol, 9.20 mg) were added into a 10 mL reactor. The mixture was stirred at room temperature for 10 min, and 0.52 g (5.0 mmol) of styrene was added under vigorous stirring. After 2 min, methanol was injected into the system to quench the polymerization, and the reaction mixture was poured into a large quantity of methanol containing a small amount of hydrochloric acid to precipitate the white solids. The precipitated polymer was collected by filtration, washed with methanol, and dried under vacuum at 60 °C to a constant weight to afford 0.52 g (100% yield) of polystyrene.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of complexes **1**, **2**, **3**, and **5**; ^{19}F NMR spectra of **6** and **1**/$[Ph_3C][B(C_6F_5)_4]$/Al^iBu_3; crystallographic information files (CIFs) and a table of the summary of crystallographic data and refinements for complexes **1**, **2**, **5**, and **6**; ^{1}H and ^{13}C NMR spectra of selected polystyrene samples; and GPC diagrams for selected polystyrene samples. This material is available free of charge via the Internet at http://pubs.acs.org.