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Cationic Scandium Anisyl Species in Styrene Polymerization Using Anisole and *N,N*-Dimethyl-*o*-toluidine as Chain-Transfer Agents

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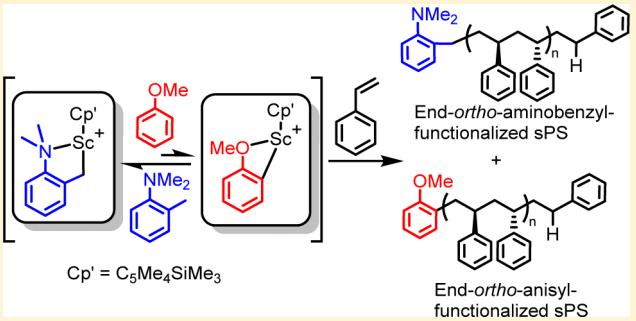
Supporting Information

ABSTRACT: This work aimed to clarify the involvement of a cationic scandium anisyl species in the scandium-catalyzed chain-transfer polymerization of styrene using anisole as a chain-transfer agent (CTA) as well as its behavior in the presence of *N,N*-dimethyl-*o*-toluidine. The reaction of anisole with the catalyst precursor $[(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)][B(C_6F_5)_4]$ (**2**) generated by the reaction of $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**1**) with $[Ph_3C][B(C_6F_5)_4]$ gave the structurally characterizable anisole-coordinated ion-pair complex $[(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)(C_6H_5OMe)][B(C_6F_5)_4]$ (**3**). The aminobenzyl unit in **3** remained intact even in the presence of an excess amount of anisole. The formation of an anisyl species from **3** was not observed by ^{1}H NMR. However, the polymerization of styrene by **3** at either room temperature or 70 °C yielded the anisyl-end-functionalized syndiotactic polystyrene (sPS) as a major product in addition to the dimethylaminobenzyl-end-capped sPS. These results suggest that an equilibrium between the aminobenzyl species **3** and a scandium anisyl species should exist, although the latter was not detected by ^{1}H NMR. The reaction of the half-sandwich scandium bis(anisyl) complex $(C_5Me_4SiMe_3)Sc(C_6H_4OMe\text{-}o)_2$ (**4**) with 1 equiv of $[Ph_3C][B(C_6F_5)_4]$ in THF afforded the THF-coordinated cationic scandium monoanisyl complex $[(C_5Me_4SiMe_3)Sc(C_6H_4OMe\text{-}o)(thf)_2][B(C_6F_5)_4]$ (**5**), which upon reaction with HMPA gave the structurally characterizable HMPA-coordinated analogue $[(C_5Me_4SiMe_3)Sc(C_6H_4OMe\text{-}o)(hmpa)_2][B(C_6F_5)_4]$ (**6**). The **4**/$[Ph_3C][B(C_6F_5)_4]$ combination in toluene showed high activity for styrene polymerization, selectively yielding the anisyl-end-functionalized sPS. In addition to anisole, *N,N*-dimethyl-*o*-toluidine was also found to serve as an efficient CTA for the polymerization of styrene by **1**/$[Ph_3C][B(C_6F_5)_4]$, which selectively afforded the aminobenzyl-functionalized sPS.



INTRODUCTION

Syndiotactic polystyrene (sPS), in which the adjacent phenyl substituents are stereoregularly oriented opposite to each other along the polymer chain, has wide potential applications as an engineering plastic because of its unique properties such as high melting point, high crystallization rate, and excellent chemical/solvent resistance.[1−3] The syndiospecific chain-transfer polymerization of styrene has received much interest, because this protocol can, in principle, offer an efficient route for the catalytic synthesis of end-functionalized sPS with controllable molecular weight. However, studies on the syndiospecific chain-transfer polymerization of styrene are still limited, because few catalyst/chain-transfer agent (CTA) systems were known to show high stereoselectivity and high efficiency for the syndiospecific chain-transfer polymerization of styrene. It has been previously reported that the use of some organosilanes and organoboranes as CTAs in the titanium-catalyzed polymerization of styrene afforded the corresponding end-functionalized silyl-sPS[4] and boryl-sPS,[5] respectively. However, the chain-transfer efficiency of these titanium-based catalysts was generally low and the molecular weight of the resulting polymers was not controllable. The mechanistic aspects of the chain-transfer reactions remained unclarified because of the complexity of the catalyst systems.[6]

By using a cationic half-sandwich scandium alkyl catalyst such as $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**1**)/$[Ph_3C][B(C_6F_5)_4]$, we have recently achieved for the first time the highly efficient syndiospecific chain-transfer polymerization of styrene using anisoles as CTAs, which gave the end-*o*-anisyl-functionalized sPS with well-controlled molecular weight (Scheme 1).[7] This chain-transfer polymerization is believed to proceed through the *o*-C−H activation (deprotonation) of an anisole unit by a cationic scandium aminobenzyl species followed by styrene insertion into the resulting scandium−anisyl bond (Scheme 1).[8,9] A cationic half-sandwich scandium anisyl species such as **A** was thought to be the true active catalyst species. However, in contrast to the large number of rare-earth alkyl

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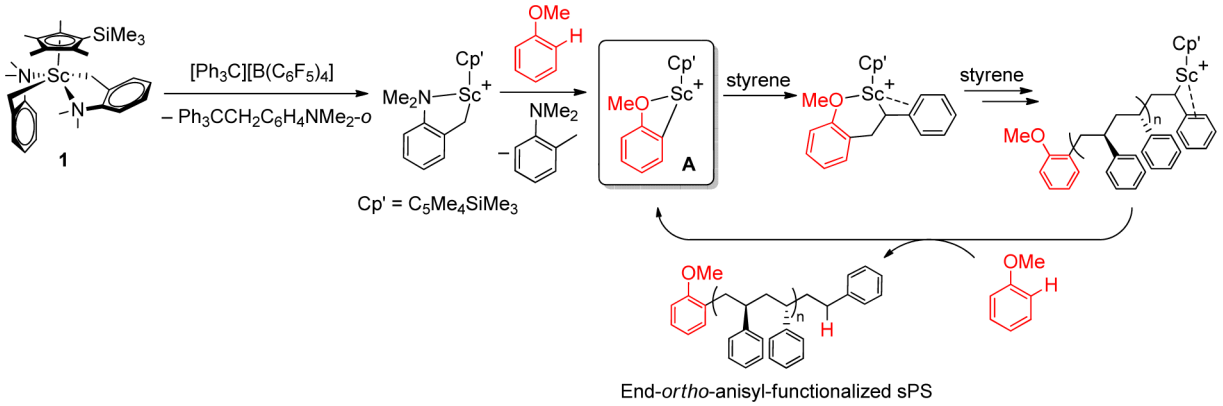
Scheme 1. Scandium-Catalyzed Chain-Transfer Polymerization of Styrene Using Anisole as a Chain Transfer Agent[7]



complexes reported in the literature,[10] well-defined rare-earth anisyl complexes are scarce. In particular, a structurally characterized cationic rare-earth anisyl complex has remained unknown to date, although a few neutral rare-earth anisyl complexes such as $(C_5Me_5)_2Y(2\text{-}C_6H_4OMe)$,[11] $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2SiMe_2NtBu)(2\text{-}C_6H_4OMe)(thf)]$,[12] and $[Sc(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NtBu)(2\text{-}C_6H_4OMe)(thf)]$[9a] have been reported previously.

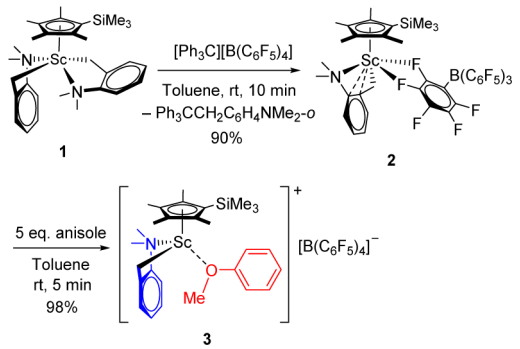
In this paper, we report the synthesis, structural characterization, and styrene polymerization and C–H activation behaviors of the first cationic half-sandwich scandium anisyl complex. We have found that a cationic half-sandwich scandium anisyl species is highly active for the syndiospecific polymerization of styrene as well as for the $C(sp^3)$–H activation of the *o*-methyl group in *N*,*N*-dimethyl-*o*-toluidine, although it was unstable in the absence of a Lewis base. These findings not only have provided unprecedented insights into the mechanistic details of the scandium-catalyzed chain-transfer polymerization of styrene using anisole as a CTA but have also led to the discovery of the validity of *N*,*N*-dimethyl-*o*-toluidine as an efficient CTA for the scandium-catalyzed syndiospecific chain-transfer polymerization of styrene.

RESULTS AND DISCUSSION

Anisole-Coordinated Cationic Scandium Aminobenzyl Complex. In attempts to isolate a cationic half-sandwich scandium anisyl complex, we first carried out the reaction of anisole with the cationic scandium aminobenzyl complex $[(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)][B(C_6F_5)_4]$ (**2**),[13] generated by the reaction of $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**1**) with $[Ph_3C][B(C_6F_5)_4]$. The reaction of **2** with 5 equiv of anisole in toluene at room temperature took place rapidly, affording the corresponding anisole-coordinated scandium aminobenzyl ion-pair complex $[(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)(C_6H_5OMe)][B(C_6F_5)_4]$ (**3**) in 98% yield (Scheme 2). The two benzyl protons in **3** showed two doublets at 1.40 ppm (d, $J_{H,H}$ = 12.3 Hz) and 1.76 ppm (d, $J_{H,H}$ = 12.3 Hz), respectively, in the ^{1}H NMR spectrum in chlorobenzene-d_5 at room temperature, while the four methyl groups on the cyclopentadienyl ring gave four singlet peaks at 1.96, 2.00, 2.08, and 2.26 ppm, respectively, suggesting that the overall structure of **3** is highly rigid in solution.[14] The chemical shift (3.44 ppm) of the methyl protons of the anisole unit in **3** was shifted upfield in comparison with that (3.62 ppm) of free anisole.

An X-ray crystallographic study revealed that **3** adopts a three-legged piano-stool structure, in which the scandium atom

Scheme 2. Isolation of an Anisole-Coordinated Cationic Scandium Aminobenzyl Complex



is bonded to one cyclopentadienyl ligand, one bidentate *N*,*N*-dimethylaminobenzyl ligand, and the oxygen atom of a neutral anisole ligand (Figure 1). The Sc–cyclopentadienyl (Sc(1)–Cp(av) 2.461(2) Å), Sc–benzyl (Sc(1)–C(1) 2.195(3) Å), and Sc–amino group bond distances (Sc(1)–N(1) 2.287(2) Å) in **3** are comparable with those in **2** (Sc–Cp(av) 2.434(3) Å, Sc–C 2.195(3) Å, and Sc–N 2.300(3) Å).[13] The Sc–anisole

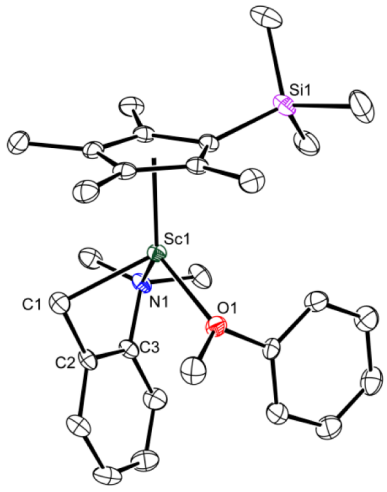


Figure 1. ORTEP drawing of the cationic part of complex **3** with thermal ellipsoids set at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sc(1)–O(1) 2.1729(18), Sc(1)–N(1) 2.287(2), Sc(1)–C(1) 2.195(3), Sc(1)–C(2) 2.662(3), Sc(1)–C(3) 2.724(2), Sc(1)–Cp(av) 2.461(2); Sc(1)–C(1)–C(2) 90.79(16).

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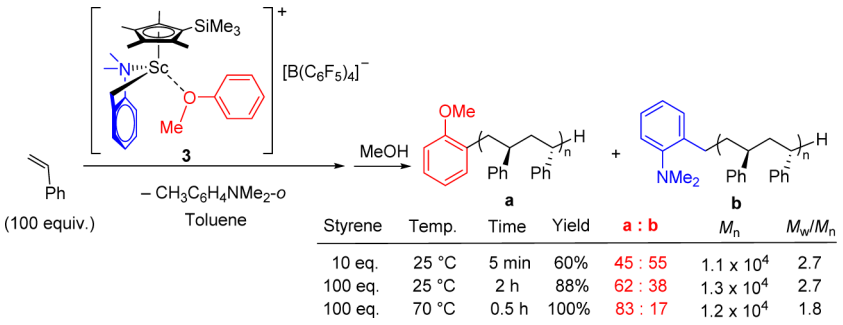
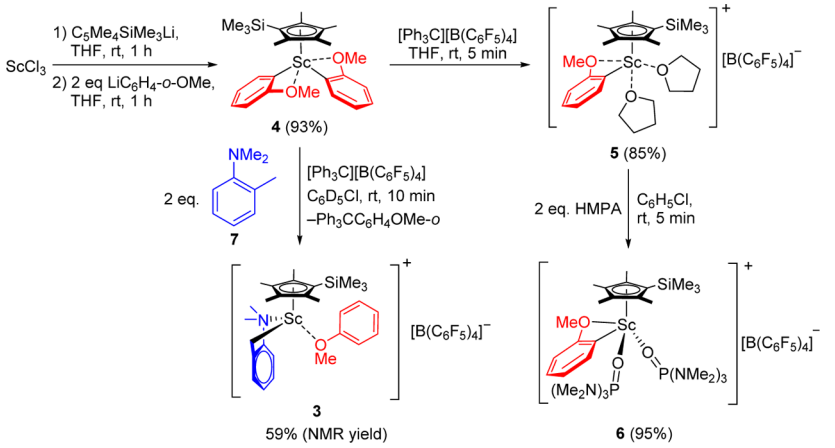
Scheme 3. Styrene Polymerization by an Anisole-Coordinated Cationic Scandium Aminobenzyl Complex



Styrene	Temp.	Time	Yield	a : b	M_n	M_w/M_n
10 eq.	25 °C	5 min	60%	45 : 55	1.1 x 10^4	2.7
100 eq.	25 °C	2 h	88%	62 : 38	1.3 x 10^4	2.7
100 eq.	70 °C	0.5 h	100%	83 : 17	1.2 x 10^4	1.8

Scheme 4. Synthesis of a Half-Sandwich Scandium Dianisyl Complex and Its Transformation to Cationic Scandium Anisyl and Aminobenzyl Complexes



oxygen bond distance (Sc(1)−O(1) 2.1729(18) Å) is slightly shorter than that of the Sc−O bond (2.208(1) Å) in $(C_5Me_4C_6H_4OMe\text{-}o)Sc(CH_2SiMe_3)_2$,[15] probably due to the more electropositive nature of the Sc atom in **3**. The distances between the Sc atom and the ipso and ortho carbon atoms of the benzyl group in **3** (Sc(1)···C(2) 2.662(3) and Sc(1)···C(3) 2.724(2) Å) are significantly longer than those found in **2** (Sc−C2 2.570(3) Å, Sc−C3 2.643(3) Å),[13] suggesting that the interactions between the aromatic carbons in the aminobenzyl unit and the Sc atom in **3** are weaker as a result of the coordination of an anisole ligand. Consistent with this, the Sc−C1−phenyl (C2) angle in **3** (90.79(16)°) is slightly larger than that in **2** (86.5(2)°).

In view of the high efficiency of anisole as a CTA in the polymerization of styrene catalyzed by **2** or **1**/$[Ph_3C][B(C_6F_5)_4]$,[7] we expected facile formation of an anisyl species (such as **A**) from **3** through *o*-C−H activation (deprotonation) of the anisole ligand by the benzyl unit with release of *N*,*N*-dimethyl-*o*-toluidine (cf. Scheme 1). However, complex **3** was quite stable and no reaction was observed even in the presence of an excess amount of anisole at room temperature. Heating **3** at 70 °C (with or without anisole) led to decomposition to a complicated mixture, while formation of an anisyl species was not observed as monitored by ^{1}H NMR in C_6D_5Cl. However, the polymerization of 10 equiv of styrene by **3** in toluene at room temperature yielded the *o*-anisyl-end-functionalized sPS (**a**) in 45% in addition to the dimethylaminobenzyl-end-capped sPS (**b**) (55%) (Scheme 3).[16] The polymerization of 100 equiv of styrene by **3** in toluene at room temperature gave the *o*-anisyl-end-functionalized sPS (**a**) as a major product (62%), and its yield became even higher (83%) at 70 °C. Atactic polystyrene was not observed in either of the above reactions. These results strongly suggest that an anisyl scandium species should be generated from **3** and may exist in an equilibrium with **3**, although it was not detectable by ^{1}H NMR at either room temperature or 70 °C.[17]

Isolation and Reactivity of Cationic Scandium Anisyl Complexes. In order to obtain a characterizable cationic half-sandwich scandium anisyl complex, we then sought other synthetic routes. The salt metathesis reaction of $ScCl_3$ with 1 equiv of $LiC_5Me_4SiMe_3$ followed by reaction with 2 equiv of (2-methoxyphenyl)lithium in THF at room temperature afforded the half-sandwich scandium bis(anisyl) complex $(C_5Me_4SiMe_3)Sc(C_6H_4OMe\text{-}o)_2$ (**4**) in 93% yield (Scheme 4). Complex **4** was not stable in C_6D_6 at room temperature, and more than half decomposed in 24 h. Nevertheless, recrystallization of **4** in hexane at −30 °C afforded single crystals suitable for X-ray diffraction studies. The ORTEP drawing of **4** is shown in Figure 2. The two anisyl units in **4** are bonded to the Sc atom through both the methoxy oxygen atom and the ortho phenyl carbon atom in a trans orientation. The Sc−C(anisyl) bond lengths in **4** (2.2567(19) and 2.2512(19) Å) are slightly shorter than that in $\{Me_2Si(C_5Me_4)(N\mathit{t}Bu)\}Sc(C_6H_4OMe\text{-}o)(thf)$ (2.271(3) Å).[9a] The Sc−O(anisyl) bond lengths in **4** (2.2371(13) and 2.2442(14) Å) are also shorter than that in $\{Me_2Si(C_5Me_4)(N\mathit{t}Bu)\}Sc(C_6H_4OMe\text{-}o)(thf)$ (2.575(2) Å), suggesting that the bidentate chelation of the anisyl ligands in **4** is stronger. The reaction of **4** with 1 equiv of $[Ph_3C][B(C_6F_5)_4]$ in toluene-d_8 at room temperature took place rapidly but did not give a characterizable product as monitored by ^{1}H NMR.

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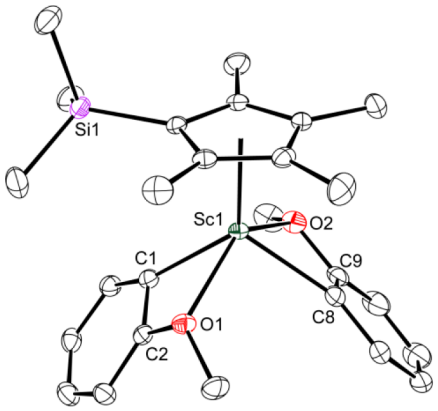


Figure 2. ORTEP drawing of complex **4** with thermal ellipsoids set at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sc−C(1) 2.2567(19), Sc(1)−C(8) 2.2512(19), Sc(1)−O(1) 2.2371(13), Sc(1)−O(2) 2.2442(14), Sc(1)−Cp(av) 2.467(2); Sc(1)−C(1)−C(2) 92.68(12), Sc(1)−C(8)−C(9) 93.27(13), O(1)−Sc(1)−C(1) 62.17(6), O(2)−Sc(1)−C(8) 62.05(7), O(1)−C(2)−C(1) 111.03(16), O(2)−C(9)−C(8) 111.10(17).

When the reaction of **4** with 1 equiv of $[Ph_3C][B(C_6F_5)_4]$ was carried out in THF, the stable product **5** assignable to the ion-pair complex $[(C_5Me_4SiMe_3)Sc(C_6H_4OMe\text{-}o)(thf)_2][B(C_6F_5)_4]$ bearing two THF ligands at the Sc atom was isolated in 85% yield as a white powder (Scheme 4). Addition of 2 equiv of hexamethylphosphoric triamide (HMPA) to a chlorobenzene solution of **5** gave the corresponding HMPA-coordinated cationic scandium anisyl complex $[(C_5Me_4SiMe_3)Sc(C_6H_4OMe\text{-}o)(hmpa)_2][B(C_6F_5)_4]$ (**6**) in 95% yield (Scheme 4).[18] Recrystallization of **6** from a hexane/chlorobenzene/THF mixed solvent at −30 °C afforded single crystals suitable for X-ray diffraction studies. It was revealed that **6** is a HMPA-separated ion-pair complex, in which the Sc atom is bonded to one cyclopentadienyl ligand, one bidentate anisyl ligand, and two HMPA ligands in a four-legged piano-stool configuration (Figure 3). The Sc−C(anisyl) bond distance in **6** (2.231(7) Å) is comparable to those in **4** (2.2567(19) and 2.2512(19) Å), while the Sc−O(anisyl) bond distance in **6** (2.649(8) Å) is significantly longer than those in **4** (2.2390(15) and 2.2440(16) Å), probably due to the strong coordination power of HMAP.[19] Complex **6** represents the first example of a structurally characterized cationic rare-earth metal anisyl complex, as far as we are aware.

The 1:1 combination of **4** and $[Ph_3C][B(C_6F_5)_4]$ showed high activity for the polymerization of styrene at room temperature in toluene, quantitatively converting 500 equiv of styrene to the *o*-anisyl-end-functionalized sPS (M_n = 139400, M_w/M_n = 2.1) in 1 min. This clearly demonstrates that the cationic half-sandwich scandium anisyl species is highly active for the syndiospecific polymerization of styrene.[20] To gain information about the reversibility of the generation of an anisyl species from **3** or from the reaction of **2** with anisole, the reaction of **4**/$[Ph_3C][B(C_6F_5)_4]$ with 2 equiv of *N*,*N*-dimethyl-*o*-toluidine in toluene was examined, which afforded the cationic anisole-coordinated scandium aminobenzyl complex **3** in 59% yield in 10 min (Scheme 4). This clearly shows that the C(sp^3)−H activation (deprotonation) of the *o*-methyl group in *N*,*N*-dimethyl-*o*-toluidine by an anisyl species (a reverse reaction of the formation of an anisyl species such as **A** from **3**) is highly facile. No reaction was observed between the

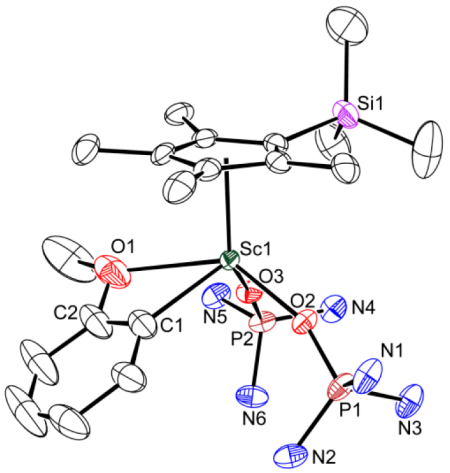
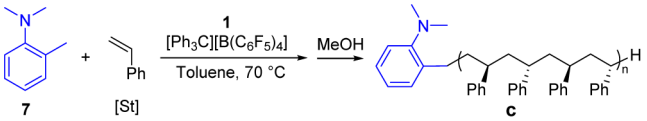


Figure 3. ORTEP drawing of the cationic part of complex **6** with thermal ellipsoids set at the 20% probability level. Hydrogen atoms and the methyl groups of HMPA are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sc(1)−C(1) 2.231(7), Sc(1)−O(1) 2.649(8), Sc(1)−O(2) 2.058(3), Sc(1)−O(3) 2.070(3), P(1)−O(2) 1.503(3), P(2)−O(3) 1.496(3), Sc(1)−Cp(av) 2.492(6); Sc(1)−C(1)−C(2) 104.7(7).

THF- or HMPA-coordinated scandium anisyl complex (**5** or **6**) with *N*,*N*-dimethyl-*o*-toluidine, probably because of the difficulty for *N*,*N*-dimethyl-*o*-toluidine to access the coordination sphere of the Sc atom bearing THF or HMPA ligands.

Using *N*,*N*-Dimethyl-*o*-toluidine as a CTA for Styrene Polymerization. The easy formation of **3** from **4** suggests that *N*,*N*-dimethyl-*o*-toluidine may serve as a CTA for the scandium-catalyzed polymerization of styrene through C(sp^3)−H activation (deprotonation) of the *o*-methyl group. Indeed, the polymerization of styrene by **1**/$[Ph_3C][B(C_6F_5)_4]$ (0.2 mol %) in the presence of 25 equiv of *N*,*N*-dimethyl-*o*-toluidine (relative to the catalyst) at 70 °C afforded the end-aminobenzyl-functionalized sPS with M_n = 3400 (13.7 polymer chains per Sc). This is in sharp contrast with the polymerization of styrene by **1**/$[Ph_3C][B(C_6F_5)_4]$ without extra *N*,*N*-dimethyl-*o*-toluidine,[7,21] which gave a much higher molecular weight (M_n = 228000) (0.2 polymer chain per Sc) (Scheme 5). This represents the first example of using *N*,*N*-dimethyl-*o*-toluidine as a CTA in a polymerization reaction.

Scheme 5. Syndiospecific Chain-Transfer Polymerization of Styrene Using *N*,*N*-Dimethyl-*o*-toluidine as a CTA



7 c

[1] : [7] : [St]	Time (min)	Yield (%)	M_n	M_w/M_n	Chain/Sc	*rrrr*
1 : 0 : 500	1	98	228,000	1.7	0.2	99%
1 : 25 : 500	60	89	3,400	2.6	13.7	99%

Reaction Mechanism of Chain-Transfer Polymerization of Styrene via C−H Activation. On the basis of the experimental results described above, possible scenarios of the chain-transfer polymerization of styrene by **2** or **1**/$[Ph_3C][B(C_6F_5)_4]$ using anisole and *N*,*N*-dimethyl-*o*-toluidine as CTAs are summarized in Scheme 6. Initially, the reaction of **1** with $[Ph_3C][B(C_6F_5)_4]$ would easily generate the cationic scandium

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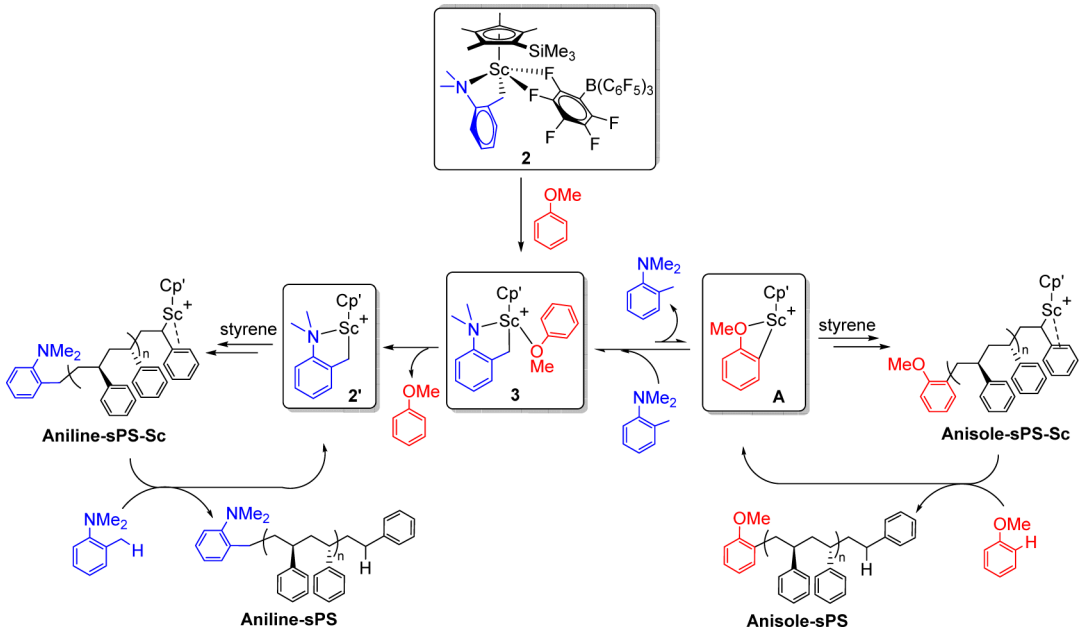
Scheme 6. Possible Scenarios of Sc-Catalyzed Chain Transfer Polymerization of Styrene Using Anisole and *N*,*N*-Dimethyl-*o*-toluidine as CTAs[a]



[a]The $[B(C_6F_5)_4]^-$ counteranion is not shown, except in the structure of **2**.

aminobenzyl species **2**, which upon reaction with anisole yields the anisole-coordinated ion-pair complex **3**. The *o*-C−H activation (deprotonation) of the anisole ligand by the aminobenzyl unit in **3** could generate the anisyl species **A** with release of *N*,*N*-dimethyl-*o*-toluidine. This process is reversible, and the aminobenzyl complex **3** is thermodynamically more favored. In the presence of excess styrene, the continuous insertion of styrene into the Sc−anisyl bond in **A** would yield the end-anisyl-functionalized polymer (**Anisole-sPS-Sc**). Similarly, the insertion of styrene into the Sc−aminobenzyl bond in **3** or its anisole-free analogue **2′** should yield the end-aminobenzyl-functionalized polymer (**Aniline-sPS-Sc**). DFT studies have shown that the energy barrier for styrene insertion into a scandium−anisyl bond (8 kcal/mol) is much lower than that for a scandium−aminobenzyl bond (22 kcal/mol).[22] Therefore, the insertion of styrene into the Sc−anisyl bond in **A** and the subsequent styrene insertion into the resulting Sc−styrenyl bond would be kinetically much easier and faster than that into the Sc−aminobenzyl bond in **3** or its anisole-free analogue **2′**. This could account for the formation of the anisyl-end-functionalized sPS (**a**) (rather than the dimethylaminobenzyl-end-capped sPS (**b**)) as a major product in the polymerization of styrene by **3** (see Scheme 3). When anisole exists (as a CTA), the *o*-hydrogen abstraction of anisole by the Sc−benzyl bond in **Anisole-sPS-Sc** would finally give the anisyl-end-functionalized sPS (**Anisole-sPS**) and regenerate the anisyl active species **A**. Similarly, the reaction of **Aniline-sPS-Sc** with *N*,*N*-dimethyl-*o*-toluidine (CTA) via activation of the *o*-methyl C−H bond would yield the dimethylaminobenzyl-end-functionalized sPS (**Aniline-sPS**) with regeneration of the active catalyst species **2′**.

CONCLUSION

We have examined the formation and reactivity of the cationic scandium anisyl species in the scandium-catalyzed chain-transfer polymerization of styrene using anisole as a CTA as well as in related reactions. The structurally well-defined, anisole-coordinated scandium aminobenzyl complex **3** was obtained from the reaction of the base-free aminobenzyl complex **2**. Although the formation of a anisyl species from **3** was not observed by ^{1}H NMR, the polymerization of styrene by **3** yielded the anisyl-functionalized sPS **a** as a major product in addition to the aminobenzyl-functionalized sPS **b**, suggesting that the cationic scandium aminobenzyl complex **3** should exist in an equilibrium with an anisyl species such as **A**. The latter is kinetically more active for styrene polymerization, although it is thermodynamically less favored than **3**. The reaction of *N*,*N*-dimethyl-*o*-toluidine with the half-sandwich bis(anisyl) complex **4** and $[Ph_3C][B(C_6F_5)_4]$ in toluene yielded the anisole-coordinated scandium aminobenzyl complex **3** through C−H activation (deprotonation) of the *o*-methyl group by the Sc−anisyl bond, which confirmed the reversibility of the transformation of **3** to a cationic scandium anisyl species. The reaction of **4** with $[Ph_3C][B(C_6F_5)_4]$ in THF afforded the isolable THF-coordinated cationic scandium anisyl complex **5**, which upon reaction with HMPA gave the structurally characterizable HMPA-coordinated analogue **6**. This constitutes the first example of a structurally characterized cationic rare-earth anisyl complex. The selective formation of the anisyl-functionalized sPS in the polymerization of styrene by **4**/$[Ph_3C][B(C_6F_5)_4]$ demonstrates well that a cationic half-sandwich scandium anisyl species such as **A** is highly efficient for the syndiospecific polymerization of styrene. Consistent with the facile formation of **3** from *N*,*N*-dimethyl-*o*-toluidine and **4**/$[Ph_3C][B(C_6F_5)_4]$, *N*,*N*-dimethyl-*o*-toluidine has also been found to act as an efficient CTA for the syndiospecific chain-transfer polymerization of styrene by **1**/$[Ph_3C][B(C_6F_5)_4]$ through C−H activation of the *o*-methyl group, thus constituting the first example of using *N*,*N*-dimethyl-*o*-toluidine as a CTA in a polymerization reaction.

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EXPERIMENTAL SECTION

General Procedures and Materials. All manipulations of air- and moisture-sensitive compounds were performed under a dry nitrogen atmosphere by use of standard Schlenk techniques or an mBRAUN Labmaster glovebox. Nitrogen was purified by passing it through a DC-A4 drying column (4 A molecular sieves, Nikka Seiko Co.) and a Gasclean GC-RX column (Nikka Seiko Co.). The nitrogen in the glovebox was constantly circulated through a copper/molecular sieves catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O_2/H_2O Combi-Analyzer (Mbraun) to ensure that both were always below 0.1 ppm. Hexane, THF and toluene (dehydrated, stabilizer-free) were obtained from Kanto Kagaku Co., purified by an mBRAUN SPS-800 solvent purification system, and dried over fresh Na chips in a glovebox. Styrene (Junsei Chemical Co., Ltd.) was dried by stirring with CaH_2 overnight (>12 h) and distilled under reduced pressure prior to polymerization experiments. Anisole was obtained commercially and distilled from an appropriate drying agent such as sodium/benzophenone before use. $[Ph_3C][B(C_6F_5)_4]$ was purchased from Strem Chemicals and used without purification. $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**1**)[13] was synthesized according to the literature. 1,1,2,2-Tetrachloroethane-d_2 and chlorobenzene-d_5 were dried over molecular sieves. Benzene-d_6 was dried over Na chips. The ^1H NMR and ^{13}C NMR data of polymers and complexes were obtained on a Bruker AVANCE III HD 500 NMR spectrometer. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, m = multiplet, br = broad signal), integration, and coupling constant (Hz). The DSC measurements were performed on a DSC6220 instrument (SII Co.) at a rate of 20 °C/min. Any thermal history difference in the polymers was eliminated by first heating the specimen to 300 °C, cooling at 20 °C/min to −25 °C, and then recording the second DSC scan. The molecular weights and molecular weight distributions (M_w/M_n) of the polymers were determined by gel permeation chromatography (GPC) with a refractive index (RI) detector against polystyrene standards on a TOSOH HLC-8121 GPC instrument (3 columns of TSK gel GMHHR-H(20) HT 7.8 mm i.d.× 30 cm were calibrated against 10 standard polystyrene samples (M_n = 3150000−1010, M_w/M_n < 1.16)) at 145 °C using 1,2,4-trichlorobenzene as a solvent at a flow rate of 1.0 mL/min or on a TOSOH HLC-8321 GPC instrument (2 columns of TSK gel GMHHR-H(S) HT 7.8 mm I.D.× 30 cm were calibrated against 10 standard polystyrene samples (M_n = 3150000−1010, M_w/M_n < 1.16)) at 145 °C using *o*-dichlorobenzene as a solvent at a flow rate of 1.0 mL/min.

X-ray Crystallographic Studies. Suitable single crystals for X-ray crystallographic studies were obtained as described below. These were manipulated under a microscope in a glovebox filled with dinitrogen. X-ray diffraction data collections were performed on a Bruker D8 QUEST diffractometer equipped with a CMOS area detector, using a IμS (Incoatec Microfocus Source) microfocus sealed tube with Mo Kα radiation (λ = 0.71073 Å) at 173 K. The Bravais lattice and the unit cell parameters were determined by the Bruker APEX2 software package.[23] The raw frame data were processed, and absorption corrections were done using SAINT and SADABS embedded in Bruker APEX2 to yield the reflection data (*hkl*) file.[23] All of the structures were solved using SHELXS-2013.[24] Structural refinement was performed using the WINGX-Version 2014.1 system[25] on F^2 anisotropically for all of the non-hydrogen atoms by the full-matrix least-squares method. Analytical scattering factors for neutral atoms were used throughout the analysis. The hydrogen atoms were placed at calculated positions, which were then refined using a riding model. The residual electron densities in all of the structures were of no chemical significance. The disordered hexane and THF molecules in **6** were refined with isotropic thermal parameters. The crystallographic figures were drawn by using ORTEP-III software.[26] CCDC numbers 1556771 (for **3**), 1556772 (for **4**), and 1556773 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of $[(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)][B(C_6F_5)_4]$ (2). In a glovebox, a toluene solution (30 mL) of $[Ph_3C][B(C_6F_5)_4]$ (1.84 g, 2 mmol) was added dropwise to a well-stirred toluene solution (20 mL) of $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (1.01 g, 2 mmol) at room temperature in a 200 mL flask. After 10 min, the volatiles were removed under reduced pressure. The residue was washed with hexane (20 mL × 4 times) mL and dried under vacuum to give a brown powder (1.9 g, 90%).

Synthesis of $[(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)(C_6H_5OMe\text{-}o)][B(C_6F_5)_4]$ (3). In a glovebox, a toluene solution (2 mL) of anisole (0.50 g, 2.5 mmol) was added dropwise to a well-stirred toluene solution (3 mL) of **2** (0.50 g, 0.5 mmol) in a 30 mL flask. After 5 min, the volatiles were removed under reduced pressure. The residue was washed with hexane (3 mL × 3 times) and dried under vacuum to give a yellow powder (0.57 g, 98%). Recrystallization from a hexane/chlorobenzene solution at −30 °C gave single crystals suitable for X-ray analysis. ^1H NMR (C_6D_5Cl, 500 MHz, 26.8 °C): δ 0.24 (s, 9H, $SiMe_3$), 1.40 (d, 1H, $J_{H,H}$ = 12.4 Hz, CH_2), 1.76 (d, 1H, $J_{H,H}$ = 12.4 Hz, CH_2), 1.83 (s, 6H, NMe_2), 1.96 (s, 3H, C_5Me_4), 2.00 (s, 3H, C_5Me_4), 2.08 (s, 3H, C_5Me_4), 2.26 (s, 3H, C_5Me_4), 3.44 (s, 3H, OMe), 6.13 (br, 2H, aryl[anisole]), 6.44 (d, 1H, $J_{H,H}$ = 8.1 Hz aryl[aminobenzyl]), 6.70 (d, 1H, $J_{H,H}$ = 7.3 Hz, aryl[aminobenzyl]), 6.81 (dd, 1H, $J_{H,H}$ = 7.6 Hz, aryl[aminobenzyl]), 6.93−7.00 (m, 1H, aryl[aminobenzyl]), 7.02−7.08 (m, 3H, *m*- and *p*-aryl[anisole]). $^{13}C\{^1H\}$ NMR (C_6D_5Cl, 125 MHz, 26.8 °C): δ 1.8 ($SiMe_3$) 11.6 (NMe_2), 14.3, 14.6, 40.4, 47.3 (C_5Me_4), 58.7 (CH_2), 62.9 (OMe), 124.4, 130.0, 131.0, 133.5, 135.5, (Cp ring carbons), 120.2, 126.3, 130.4, 132.6, 136.4, 138.2, (aminobenzyl aromatic carbons), 115.2, 128.9, 131.7, 151.9, (anisole aromatic carbons), 124.8 (m, C_6F_5-1), 136.8 (dt, $^1J_{C,F}$ = 247.5 Hz, $^2J_{C,F}$ = 13.5 Hz, C_6F_5-3), 138.7 (dt, $^1J_{C,F}$ = 245.2 Hz, $^2J_{C,F}$ = 13.3 Hz, C_6F_5-4). Anal. Calcd for $C_{52}H_{41}BF_{20}NOScSi$: C, 53.85; H, 3.56; N, 1.21. Found: C, 54.19; H, 3.64; N, 1.42.

Synthesis of $(C_5Me_4SiMe_3)Sc(C_6H_4OMe\text{-}o)_2$ (4). In a glovebox, THF (20 mL) was added to $ScCl_3$ (0.30 g, 2 mmol) in a 50 mL J. Young Schlenk tube. The closed Schlenk tube was taken out of the glovebox and heated at 120 °C for 1 h. In a glovebox, a THF solution (5 mL) of $Li(C_5Me_4SiMe_3)$ (0.40 g, 2 mmol), prepared by the reaction of $C_5Me_4HSiMe_3$ with *n*-butyllithium in THF, was added dropwise to a well-stirred THF solution (20 mL) of $ScCl_3$ (0.30 g, 2 mmol) in a 50 mL J. Young Schlenk tube at room temperature. After 1 h, a THF solution (5 mL) of 2-lithioanisole (0.46 g, 4 mmol), prepared by the reaction of anisole with *n*- butyllithium in THF at 0 °C, was added dropwise to the reaction mixture. After 1 h, the solvent was removed under reduced pressure. The residue was dissolved with toluene (10 mL) and filtered to remove the lithium salt. The solvent was removed under reduced pressure to give a white powder (0.84 g, 93%). Recrystallization from a hexane solution at −30 °C gave single crystals suitable for X-ray analysis. ^1H NMR (C_6D_6, 400 MHz): δ 0.37 (s, 9H, $SiMe_3$), 1.97 (s, 6H, C_5Me_4), 2.20 (s, 6H, C_5Me_4), 3.44 (s, 6H, OMe), 6.40−6.44 (m, 2H, aryl), 7.02−7.11 (m, 4H, aryl), 7.54−7.60 (m, 2H, aryl). ^1H NMR (C_6D_5Cl, 400 MHz): δ 0.28 (s, 9H, $SiMe_3$), 1.90 (s, 6H, C_5Me_4), 2.16 (s, 6H, C_5Me_4), 3.68 (s, 6H, OMe), 6.50 (dd, 2H, $J_{H,H}$ = 7.3, 1.4 Hz, aryl), 6.93−7.04 (m, 4H, aryl), 7.48 (dd, 2H, $J_{H,H}$ = 1.8, 6.4 Hz, aryl). $^{13}C\{^1H\}$ NMR (C_6D_5Cl, 100 MHz): δ 2.1 ($SiMe_3$), 11.6 (C_5Me_4), 14.2 (C_5Me_4), 57.2 (OMe), 118.0, 126.4, 129.3 (Cp ring carbons), 107.4, 123.2, 127.5, 136.2, 165.8, 166.6, (aromatic carbons). Anal. Calcd for $C_{26}H_{35}O_2ScSi$: C, 69.00; H, 7.79. Found: C, 68.88; H, 7.77.

Synthesis of $[(C_5Me_4SiMe_3)Sc(C_6H_4OMe\text{-}o)(thf)_2][B(C_6F_5)_4]$ (5). In a glovebox, a suspended THF solution (5 mL) of $[Ph_3C][B(C_6F_5)_4]$ (92.2 mg, 0.1 mmol) was added dropwise to a well-stirred THF solution (5 mL) of **4** (45.5 mg, 0.1 mmol) in a 30 mL flask. After the mixture was stirred for 5 min, the solvent was removed under reduced pressure. The residue was washed with hexane and dried under vacuum to give a white powder (99 mg, 85%). ^1H NMR (C_6D_5Cl, 500 MHz, 26.8 °C): δ 0.06 (s, 9H, $SiMe_3$), 1.59−1.68 (m, 8H, THF), 1.71 (s, 6H, C_5Me_4), 1.91 (s, 6H, C_5Me_4), 3.56 (s, 3H, OMe), 3.51−3.65 (m, 8H, THF), 6.51 (d, 1H, $J_{H,H}$ = 8.2 Hz, aryl),

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6.93 (t, 1H, $J_{H,H}$ = 7.1 Hz, aryl), 7.08 (ddd, 1H, $J_{H,H}$ = 8.0, 7.4, 1.5, Hz, aryl), 7.18 (dd, 1H, $J_{H,H}$ = 6.8, 1.4 Hz, aryl). $^{13}C\{^1H\}$ NMR (C_6D_5Cl, 125 MHz, 26.8 °C): δ 1.5 ($SiMe_3$), 11.3 (C_5Me_4), 14.3 (C_5Me_4), 25.2 (THF), 55.1 (OMe), 72.4 (THF), 124.4, 128.0, 133.9 (Cp ring carbons), 105.6, 123.7, 129.4, 137.0, 163.5, 163.9 (aromatic carbons), 124.7 (m, C_6F_5-1), 136.8 (dt, $^1J_{C,F}$ = 247.7 Hz, $^2J_{C,F}$ = 13.8 Hz, C_6F_5-3), 138.7 (dt, $^1J_{C,F}$ = 245.0 Hz, $^2J_{C,F}$ = 13.6 Hz, C_6F_5-4), 148.9 (d, $^1J_{C,F}$ = 240.8 Hz, C_6F_5-2). Anal. Calcd for $C_{51}H_{44}BF_{20}O_3ScSi$: C, 52.41; H, 3.79. Found: C, 52.37; H, 4.02.

Synthesis of [($C_5Me_4SiMe_3$)Sc(C_6H_4OMe-*o*)(hmpa)$_2$][B(C_6F_5)$_4$] (6). In a glovebox, a chlorobenzene solution (1 mL) of hexamethylphosphoric triamide (71.7 mg, 0.4 mmol) was added dropwise to a well-stirred chlorobenzene solution (1 mL) of **5** (234 mg, 0.2 mmol) in a 20 mL flask. After 5 min, the solvent was removed under reduced pressure. The residue was washed with hexane (1 mL × 3 times), and evaporation of the solvent gave the product as a powder. The filtrate was dried under vacuum to give a white powder (264 mg, 95%). Recrystallization from a hexane/chlorobenzene solution with a small amount of THF at −30 °C gave single crystals suitable for X-ray analysis. ^1H NMR (C_6D_5Cl, 500 MHz, 26.8 °C): δ 0.19 (s, 9H, $SiMe_3$), 1.71 (s, 6H, C_5Me_4), 2.10 (s, 6H, C_5Me_4), 2.26 (36 H, $^3J_{H,P}$ = 9.7 Hz, NMe_2), 3.52 (s, 3H, OMe), 6.47 (d, 1H, $J_{H,H}$ = 8.1 Hz, aryl), 6.81 (t, 1H, $J_{H,H}$ = 6.9 Hz, aryl), 7.04−7.12 (m, 2H, aryl). $^{13}C\{^1H\}$ NMR (C_6D_5Cl, 125 MHz, 26.8 °C): δ 2.2 ($SiMe_3$), 11.9, 14.7 (C_5Me_4), 36.4 (d, $^2J_{C,P}$ = 5.4 Hz, NMe_2), 53.6 (OMe), 117.5, 127.3, 128.9 (Cp ring carbons), 106.5, 120.4, 128.1, 136.7, 165.6, 168.0 (aromatic carbons), 124.9 (m, C_6F_5-1), 136.8 (dt, $^1J_{C,F}$ = 249.0 Hz, $^2J_{C,F}$ = 13.6 Hz, C_6F_5-3), 138.7 (dt, $^1J_{C,F}$ = 244.7 Hz $^2J_{C,F}$ = 13.6 Hz, Hz, C_6F_5-4), 148.9 (dm, $^1J_{C,F}$ = 242.1 Hz, C_6F_5-2). Anal. Calcd for $C_{55}H_{64}BF_{20}N_6O_3P_2ScSi$: C, 47.77; H, 4.66; N, 6.08. Found: C, 48.24; H, 4.70; N, 6.30.

Typical Procedure for the Polymerization of Styrene. (Scheme 3). In a glovebox, a toluene solution (1.0 mL) of **3** (23.2 mg, 20 μmol) was placed in a 30 mL flask. A dropping funnel was charged with a toluene solution (2 mL) of styrene (210 mg, 2 mmol) and connected to the flask. The apparatus was moved outside of the glovebox and set in an oil bath for 5 min at 70 °C. The styrene solution was added to the vigorously stirred mixture at 70 °C. After 30 min, polymerization was quenched by addition of methanol. The polymer product was collected by filtration, washed with methanol, and dried under vacuum at 60 °C to a constant weight (210 mg).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00526.

NMR spectra, GPC curves, and DSC charts of representative polymer products, bond lengths and angles, structural refinement details, and ORTEP drawings of **3**, **4**, and **6** with full numbering schemes (PDF)

Accession Codes

CCDC 1556771−1556773 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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(17) The anisyl scandium species may be generated both by the hydrogen abstraction of the coordinated anisole ligand with the benzyl

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