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Alternating and Random Copolymerization of Isoprene and Ethylene Catalyzed by Cationic Half-Sandwich Scandium Alkyls

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Abstract: The acid−base reactions between the scandium trialkyl complex $Sc(CH_2SiMe_3)_3(THF)_2$ and 1 equiv of Cp′−H afforded straightforwardly the corresponding mono(cyclopentadienyl)scandium dialkyl complexes $Cp'Sc(CH_2SiMe_3)_2(THF)$ (Cp′ = C_5H_5 (**1**), C_5MeH_4 (**2**), C_5Me_4H (**3**), C_5Me_5 (**4**), $C_5Me_4SiMe_3$ (**5**)) in 65−80% isolated yields. The analogous half-sandwich complexes having a heteroatom-containing side arm, $(C_5Me_4R)Sc(CH_2SiMe_3)_2$ (R = $CH_2CH_2PPh_2$ (**6**), C_6H_4OMe-*o* (**7**)), were obtained by the one-pot metathetical reactions of $ScCl_3(THF)_3$ with 1 equiv of the potassium salts of the ligands and 2 equiv of $LiCH_2SiMe_3$. The similar reactions of $ScCl_3(THF)_3$ with $KC_5Me_4(C_6H_4NMe_2$-*o*) and $LiCH_2SiMe_3$ gave a methylene-bridged binuclear complex $[\{C_5Me_4(o\text{-}C_6H_4N(Me)CH_2\text{-}\mu\}Sc(CH_2SiMe_3)]_2$ (**8**). Complexes **1**−**8** were fully characterized by ^1H, ^{13}C NMR, X-ray, and microelemental analyses. The reactions of **5** and **7** with 1 equiv of $[PhMe_2NH][B(C_6F_5)_4]$ in THF afforded quantitatively the structurally characterizable cationic monoalkyl complexes $[(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)(THF)_2][B(C_6F_5)_4]$ (**10**) and $[(C_5Me_4C_6H_4OMe\text{-}o)Sc(CH_2SiMe_3)(THF)_2][B(C_6F_5)_4]$ (**11**), respectively. In the presence of an activator such as $[Ph_3C][B(C_6F_5)_4]$, $[PhMe_2NH][B(C_6F_5)_4]$, or $B(C_6F_5)_3$, all of the half-sandwich dialkyl complexes **1**−**7** were active for isoprene polymerization and isoprene−ethylene copolymerization, with the activity and selectivity being significantly dependent on the substituents at the cyclopentadienyl ligands to yield the corresponding homo- and copolymer materials with different microstructures and compositions. In the homopolymerization of isoprene, the less sterically demanding complexes **1** and **2** showed high *cis*-1,4 selectivity (up to 95%), whereas the more sterically demanding complexes **3**−**5** yielded 3,4-polyisoprene (51−65%) as a major product. The ether side arm coordinated complex **7** preferred *trans*-1,4-polyisoprene formation (60−79%), whereas the phosphine analogue **6** showed high *cis*-1,4 selectivity (84−90%) under the same conditions. In the copolymerization of isoprene and ethylene, complexes **1** and **2** afforded the random copolymers with high isoprene contents (85−92 mol %) and predominant *cis*-1,4-microstructures (up to 90%), thus constituting the first example of *cis*-1,4-selective copolymerization of isoprene with ethylene. In contrast, the copolymerization of isoprene and ethylene by **3**, **4**, **6**, and **7** gave, for the first time, almost perfect alternating isoprene−ethylene copolymers. Possible mechanisms of the polymerization and copolymerization processes were proposed on the basis of the DFT calculations.

Introduction

The precise control of the copolymerization of conjugated dienes (butadiene, isoprene) with ethylene is an attractive research subject and has drawn continued attention from both academic and industrial researchers for more than half a century, because of the large availability and low cost of the starting monomers and the high potential of industrial application of the resulting copolymer products.[1−7] The copolymers of conjugated dienes and ethylene are expected to show various novel properties, such as high tensile and tear strength, high impact resistance, low environmental stress cracking, and good rubber compatibility. Further functionalization of the remaining C−C double bonds in the copolymers could also be possible to afford a broad range of new functionalized polymers with improved properties. However, the copolymerization of conjugated dienes

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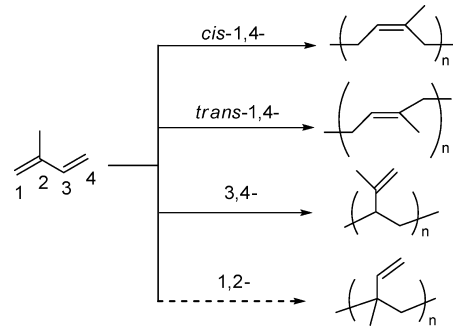
with ethylene is usually rather difficult, because these two classes of monomers show very different reactivity characteristics for a given catalyst and in some cases conjugated dienes could act as poisons for the catalysts designed for ethylene or higher olefin polymerization.[1f,3a,8] So far, many studies have been carried out in this area, but most of them were limited to the copolymerization of butadiene (the smallest, most reactive 1,3-conjugated diene) with ethylene.[1−4] In contrast, the copolymerization of the more sterically demanding isoprene (2-methyl-1,3-butadiene) with ethylene has hardly been investigated.[6,7] In particular, the precise control of the isoprene content and microstructure of the isoprene−ethylene copolymers has remained a challenge to date.

Isoprene is a very attractive and interesting conjugated diene. It is industrially available for a low price, and moreover, the methyl substituent on the conjugated diene could force it to be polymerized in unusual reaction paths, leading to new polymeric structures. Generally, the homopolymerization of isoprene can yield polyisoprenes with various microstructures which show different chemical, physical, and mechanical properties (cf. Scheme 1).[9−12] *cis*-1,4-Polyisoprene is a major component of natural rubber and acts as an excellent elastomer, whereas *trans*-1,4-polyisoprene and *iso*-3,4-polyisoprene are crystalline polymers. 1,2-Polyisoprene is usually not available in coordination polymerization because of the steric reason. In consideration of the limited supply of natural rubber and the increasing demands for various high-performance synthetic rubbers, the development of high-quality elastomers via (co)polymerization of isoprene has grown in importance. So far, a large number of catalysts has been reported for the homopolymerization of isoprene.[9−12] However, catalysts suitable for the copolymerization of isoprene with ethylene remained scarce. Very recently, Carpentier and co-workers described briefly the copolymerization of isoprene with ethylene by an *ansa*-neodymocene allyl catalyst, which yielded an isoprene-rich (76 mol %) isoprene−ethylene copolymer with predominant *trans*-1,4-polyisoprene microstructures.[6] Visseaux and co-workers reported the incorporation of some amount of α-olefins (6−10 mol %) or nonconjugated dienes (4−8 mol %) into *trans*-1,4-polyisoprene by a Sm/Li bimetallic allyl catalyst $(Me_2CC_5H_4)_2Sm(C_3H_5)_2Li(DME)$ (DME = $MeOCH_2CH_2OMe$).[7] The *cis*-1,4- or 3,4-selective copolymerization of isoprene with ethylene has not been reported previously, and neither has the alternating copolymerization of these two monomers, as far as we are aware. The search for

Scheme 1. Polymerization of Isoprene Leading to Polymers with Various Microstructures



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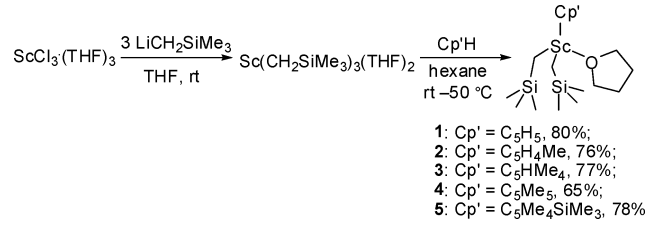
more efficient, selective catalysts for the copolymerization of isoprene with ethylene is therefore of significant importance and interest.

We have recently reported that the cationic scandium alkyl species, generated by the reaction of the half-sandwich dialkyl precursors such as $(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)_2(THF)$ with 1 equiv of a borate compound such as $[Ph_3C][B(C_6F_5)_4]$, can serve as excellent catalysts for the polymerization and copolymerization of a wide range of olefin monomers, such as syndiospecific copolymerization of styrene with isoprene (or ethylene), alternating copolymerization of norbornene (or dicyclopentadiene) with ethylene, and terpolymerization of norbornene (or dicyclopentadiene), ethylene, and styrene.[13,14] During these studies, we found that the scandium catalysts of this type are also active for the copolymerization of isoprene with ethylene to afford the corresponding copolymers unavailable previously.[15] To gain more insight into the structure−activity relation of the catalysts and to develop more efficient, selective catalysts for the copolymerization of isoprene and ethylene, we then synthesized a new series of half-sandwich scandium dialkyl complexes bearing the cyclopentadienyl (Cp) ligands with different substituents. In this article, we report a detailed, systematic study on the copolymerization of isoprene with ethylene catalyzed by the cationic half-sandwich scandium alkyl species generated from these dialkyl precursors. By modifying the Cp ligands, both random and alternating isoprene−ethylene copolymerization have been achieved for the first time to afford a new family of isoprene−ethylene copolymers with a wide range of isoprene contents and controlled microstructures. The isolation and structural characterization of some of the cationic scandium alkyl species and DFT calculations on the coordination and insertion of isoprene at the scandium metal center are also carried out, which shed new light on the mechanistic aspects of the polymerization processes.

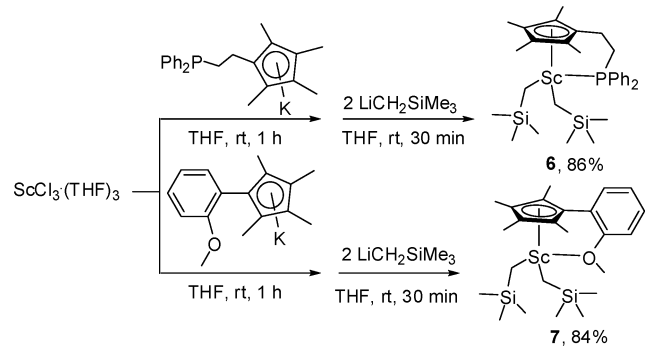
Results and Discussion

Synthesis and Structures of Half-Sandwich Scandium Dialkyl Complexes with Different Cyclopentadienyl Ligands. The acid−base reactions between the scandium trialkyl complex $Sc(CH_2SiMe_3)_3(THF)_2$ and 1 equiv of cyclopentadiene or its methyl- and trimethylsilyl-substituted derivatives gave straightforwardly the corresponding mono(cyclopentadienyl)scandium dialkyl complexes $Cp'Sc(CH_2SiMe_3)_2(THF)$ (**1**: Cp′ = C_5H_5, 80%; **2**: Cp′ = C_5MeH_4, 76%; **3**: Cp′ = C_5Me_4H, 77%; **4**: Cp′ = C_5Me_5, 65%; **5**: Cp′ = $C_5Me_4SiMe_3$, 78%) (Scheme 2).

Scheme 2. Synthesis of Half-Sandwich Scandium Dialkyl Complexes Bearing Mono(cyclopentadienyl) Ligands



Scheme 3. Synthesis of Half-Sandwich Scandium Dialkyl Complexes Bearing Cyclopentadienyl Ligands with a Phosphine or Ether Side Arm



Formation of a bis(cyclopentadienyl) compound of type "Cp′$_2$ScR" was not observed even in the case of the smallest C_5H_5 ligand.[16] In contrast, the analogous reaction of $Sc(CH_2SiMe_3)_3(THF)_2$ with cyclopentadiene derivatives having a heteroatom-containing side arm such as $HC_5Me_4CH_2CH_2PPh_2$ and $HC_5Me_4(C_6H_4OMe\text{-}o)$ was very slow. Alternatively, the one-pot metathetical reactions of $ScCl_3(THF)_3$ with 1 equiv of the potassium salts of the ligands followed by addition of 2 equiv of $LiCH_2SiMe_3$ in THF at 25 °C afforded easily the corresponding half-sandwich scandium dialkyl complexes $(C_5Me_4R)Sc(CH_2SiMe_3)_2$ (**6**: R = $CH_2CH_2PPh_2$, 86%; **7**: R = $C_6H_4OMe\text{-}o$, 84%) (Scheme 3). The similar reactions of $ScCl_3(THF)_3$ with $KC_5Me_4(C_6H_4NMe_2\text{-}o)$ and $LiCH_2SiMe_3$ gave a methylene-bridged binuclear complex $[\{C_5Me_4(o\text{-}C_6H_4N(Me)CH_2\text{-}\mu\}Sc(CH_2SiMe_3)]_2$ (**8**), probably through dehydrogenation of a methyl group of the NMe_2 unit by a $Sc-CH_2SiMe_3$ unit in the initially formed half-sandwich dialkyl species followed by intermolecular interaction between the resulting methylene unit and the Sc atom (Scheme 4). The reactions of $KC_5Me_4(C_6H_4O^iPr\text{-}o)$ with $ScCl_3(THF)_3$ and $LiCH_2SiMe_3$ yielded unidentified insoluble precipitates under the similar conditions probably due to the similar subsequent C−H bond cleavage reactions.

Complexes **1**−**8** were fully characterized by ^1H and ^{13}C NMR, X-ray, and microelemental analyses. The ORTEP drawings of **1**−**8** are shown in Figure 1. Their selected bond lengths and angles are summarized in Table 1. Despite the large difference in steric hindrance of the Cp′ ligands in these complexes, complexes **1**−**7** adopt a similar overall structure, in which the Sc metal center is boned to one Cp′ unit, two alkyls, and one Lewis base. In **1**−**5**, THF serves as a Lewis base ligand, whereas in **6** and **7** a heteroatom (P or O) in the side arm is coordinated to the metal center instead of THF. Complex **8** adopts a dimeric

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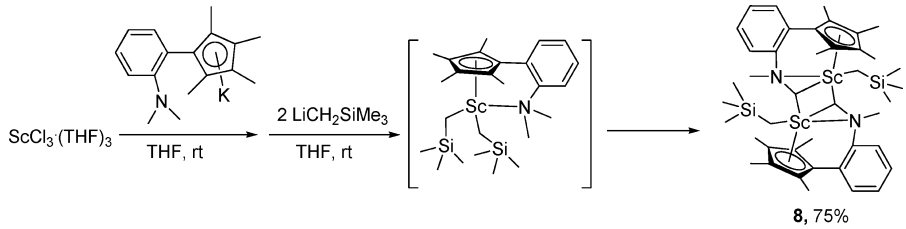
Scheme 4. Synthesis of a Binuclear Scandium Alkyl Complex bearing Mono(cyclopentadienyl) Ligand with an Amine Side Arm



structure, in which the two metal centers are bridged by two aminomethylene units and each metal center is also bonded to one η^5-Cp unit and one η^1-CH_2SiMe_3 ligand. A crystallographic inversion center exists at the center of the whole molecule of **8**.

The bond distances of the Sc−Cp′ bonds as well as the Sc−CH_2SiMe_3 bonds in **1**−**7** are comparable among each other (Table 1). The bond distance of the chelating Sc−O bond in **7** (2.208(1) Å) is longer than those of the Sc−O (THF) bonds found in **1**−**5** (2.139(1)−2.168(1) Å). The Sc−P bond distance in **6** (2.794(1) Å) is much longer than that of the Sc−O bond in **7** (2.208(1) Å), but shorter than that of the Sc−PMe_3 bond found in $[Me_2Si(C_5Me_4)(N^tBu)Sc(\mu\text{-}H)(PMe_3)]_2$ (2.996(1) Å).[17] Among **1**−**5**, differences in the orientation of the THF and CH_2SiMe_3 ligands were observed, possibly as a result of the steric influence of the Cp′ ligands. In **1** and **2**, which bear the relatively small C_5H_5 and C_5MeH_4 ligands, respectively, the THF ring plane is oriented almost vertically toward the Cp′ ring plane, and the two CH_2SiMe_3 groups adopt a supine configuration (Figure 1). When the steric hindrance of the Cp′ ligand becomes bigger in **3** (Cp′ = C_5Me_4H), the orientation of the THF ligand is changed to parallel to the Cp′ ring, and only one CH_2SiMe_3 group is in a supine fashion, whereas the other CH_2SiMe_3 group adopts a prone form. In the case of **4** and **5**, which bear further sterically demanding persubstituted ligands C_5Me_5 and $C_5Me_4SiMe_3$, respectively, both CH_2SiMe_3 groups adopt a prone fashion, together with a parallel THF orientation to the Cp′ ring. In **6** and **7**, the CH_2SiMe_3 groups adopt a prone fashion similar to those in **4** and **5**.

All complexes **1**−**8** are soluble in common organic solvents such as THF, toluene, and hexane and gave well resolved ^1H NMR spectra in C_6D_6, without ligand redistribution being observed. Complexes **1**−**3** each showed one singlet for the methylene protons of the CH_2SiMe_3 groups at −0.22, −0.21, and −0.33 ppm, respectively. In contrast, the methylene protons of the CH_2SiMe_3 groups in **4** and **5** gave two doublets (**4**: −0.40, −0.33 ppm, J_{H-H} = 15.0 Hz; **5:** −0.30, −0.25 ppm, J_{H-H} = 11.5 Hz). The methylene groups of the CH_2SiMe_3 units in **7** appeared as a singlet at −0.18 ppm, while those in **6** showed two doublets at 0.02 and 0.16 ppm with a germinal H−H

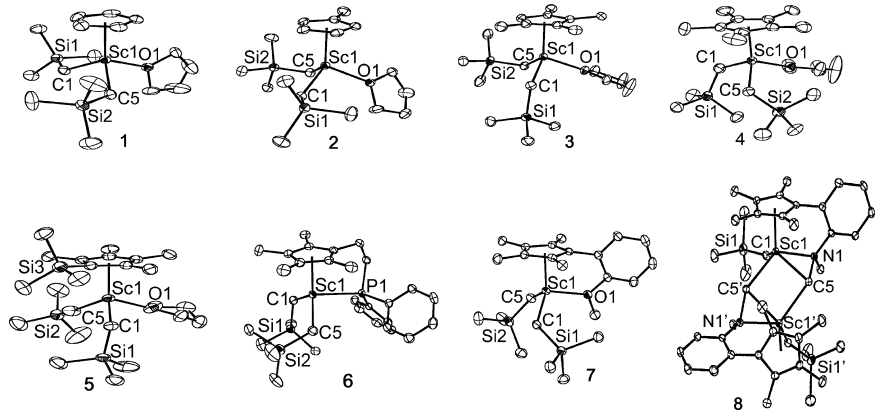
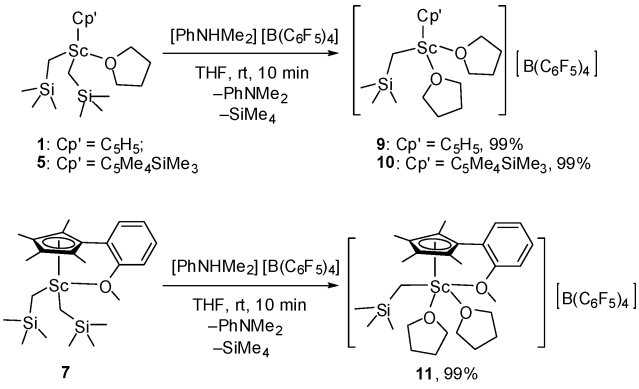


Figure 1. ORTEP drawings of **1**−**8** with thermal ellipsoids at 30% probability. Hydrogen atoms have been omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) of Complexes **1**−**8**

	1	2	3	4	5	6	7	8
Sc−$Cp_{av.}$	2.486(2)	2.486(2)	2.487(3)	2.493(3)	2.498(2)	2.491(4)	2.470(2)	2.496(2)
Sc−C1	2.220(2)	2.204(2)	2.242(3)	2.239(3)	2.240(2)	2.222(4)	2.221(2)	2.228(2)
Sc−C5	2.211(2)	2.215(2)	2.221(3)	2.221(3)	2.206(2)	2.217(4)	2.243(2)	2.400(2)
Sc−C5′								2.432(2)
Sc−O/P/N	2.145(1)	2.139(1)	2.168(2)	2.166(2)	2.158(1)	2.794(1)	2.208(1)	2.246(2)
O/P/N−Sc−C1	97.02(6)	100.09(6)	96.29(9)	95.26(9)	95.88(6)	96.91(11)	104.73(6)	96.57(8)
O/P/N−Sc−C5	100.48(7)	93.64(6)	96.40(9)	105.64(8)	106.36(10)	103.05(12)	98.51(7)	37.93(7)
C5−Sc−C1	102.50(7)	103.95(7)	107.90(12)	105.19(10)	101.78(8)	113.88(15)	111.69(8)	116.21(9)
C5′−Sc−C1								95.49(9)
Si1−C1−Sc	127.69(10)	131.05(9)	124.61(15)	125.08(14)	124.09(10)	126.6(2)	128.27(10)	141.73(13)
Si2−C5−Sc	128.46(11)	127.48(10)	126.91(15)	133.10(13)	147.3(2)	149.2(3)	125.07(11)	−
Sc−$Cp_{Cent(1)}$	2.186	2.182	2.177	2.188	2.189	2.180	2.155	2.186
$Cp_{Cent(1)}$−Sc−O/P/N	113.6	114.7	112.8	115.5	112.2	98.2	100.4	101.5
$Cp_{Cent(1)}$−Sc−C1	118.8	120.1	117.7	115.3	118.8	118.7	118.3	119.7
$Cp_{Cent(1)}$−Sc−C5/C5′	120.5	119.5	120.8	117.2	119.0	119.5	118.8	112.8/113.9

Scheme 5. Synthesis of the Cationic Half-Sandwich Scandium Alkyl Complexes **9**−**11**



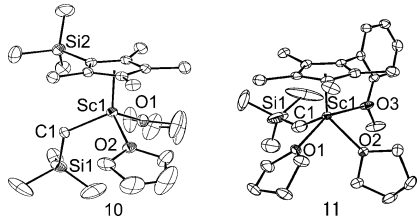


Figure 2. ORTEP drawings of the cation part of **10** (left) and **11** (right) with thermal ellipsoids at 30% probability. Hydrogen atoms have been omitted for clarity.

coupling constant of 11.1 Hz. These results may suggest that free rotation of the CH_2SiMe_3 groups in **1**−**3** and **7** could be possible, whereas the CH_2SiMe_3 groups in **4**−**6** are fixed to some extent at the NMR time scale. The ^{1}H NMR spectrum of the binuclear complex **8** showed two doublets at −1.29 and −0.51 ppm with a germinal H−H coupling constant of 10.6 Hz for the methylene protons of the CH_2SiMe_3 groups, indicative of a rather rigid structure.

Isolation and Structural Characterization of the Cationic Half-Sandwich Scandium Alkyl Complexes. ^{1}H NMR monitoring of the reactions of **1**−**7** with 1 equiv of $[PhMe_2NH][B(C_6F_5)_4]$ in C_6D_5Cl at 25 °C suggested instant formation of $PhNMe_2$ and $SiMe_4$, but an unambiguous identification of the resulting cationic scandium species was difficult because of rapid decomposition. However, when the reactions were carried out in THF, much better resolved ^{1}H NMR spectra of the cationic scandium species were observed. Complexes **1**, **5**, and **7** were then chosen for further detailed investigations, as representative examples with different steric hindrances in this series of half-sandwich complexes. Thus, the reactions of **1**, **5**, and **7** with 1 equiv of $[PhMe_2NH][B(C_6F_5)_4]$ in THF afforded quantitatively the corresponding bis(THF)-coordinated, cationic half-sandwich scandium monoalkyl complexes **9**−**11**, respectively (Scheme 5). Single crystals of **9**−**11** were obtained from a THF/hexane solution. The crystal structures of **10** and **11** were unambiguously determined by X-ray diffraction studies. In the case of **9**, the overall structure was identified to be similar to those of **10** and **11**, but a well-refined structure was not obtained because of the disorder problems.

The ORTEP drawings of **10** and **11** are shown in Figure 2. Their selected bond lengths and angles are summarized in Table 2. These complexes are solvent-separated ion pairs, in which the $[B(C_6F_5)_4]^-$ anion has no bonding interaction with the scandium center. In each complex, the Sc metal center is bonded to two THF, one Cp′, and one alkyl ligands. In **11**, an additional coordination of the oxygen atom of the side arm in the Cp′ ligand is also present, and therefore **11** has a higher coordination number than that of **10** and that of its neutral precursor **7** as well. Because of the higher electron deficiency of the cationic metal center in **10**, the bond distances of the Sc−Cp′ bonds (av. 2.454(3) Å) are significantly shorter than those found in its neutral precursor **5** (av. 2.498(2) Å), and so are the Sc−CH_2SiMe_3 (**10**: 2.193(3) Å, **5**: 2.240(2) Å) and Sc−O (**10**: 2.136(2) Å, **5**: 2.158(1) Å) bond distances. The average bond length of the Sc−CH_2SiMe_3 bond in **11** (2.115(9) Å) is also shorter than that of its neutral precursor **7** (2.221(2) Å). However, the bond distances of the Sc−Cp′ bonds (av. 2.485(7) Å) and Sc−O bonds (av. 2.255(4) Å) in **11** are longer than those found in the neutral precursor **7** (av. 2.470(2) Å, 2.208(1) Å, respectively), probably because of the higher coordination number in **11**.[18] Complexes **10** and **11** represent rare examples of structurally characterized cationic half-sandwich rare earth metal complexes with an η^1-alkyl ligand.[19]

Table 2. Selected Bond Distances (Å) and Angles (deg) of Complexes **5**, **7**, **10** and **11**

	5	10	7	11
Sc−C(Cp)(av.)	2.498(2)	2.454(3)	2.470(2)	2.486(7)
Sc−C1(av.)	2.240(2)	2.193(3)	2.221(2)	2.115(9)
Sc−O (av.)	2.158(1)	2.136(2)	2.208(1)	2.255(5)
O1−Sc−C1	95.88(6)	106.22(11)	104.73(6)	87.7(3)
O2−Sc−C1		95.96(12)		110.9(3)
O1−Sc−O2		99.15(10)		77.66(16)
O3−Sc−C1		−		86.6(3)
O1−Sc−O3		−		151.25(17)
O2−Sc−O3		−		78.13(16)
Si1−C1−Sc	124.09(10)	127.12(17)	128.27(10)	154.2(5)
Sc−$Cp_{Cent(1)}$	2.189	2.136	2.155	2.174
$Cp_{Cent(1)}$−Sc−O	112.2	116.3, 114.6	100.4	97.2, 109.4, 125.4
$Cp_{Cent(1)}$−Sc−C1	118.8	120.7	118.3	123.1

All complexes **9**−**11** showed well-resolved ^{1}H NMR spectra in C_6D_5Cl or THF-d_8, which are in agreement with their solid structure. No ligand redistribution was observed even in the case of the C_5H_5-ligated complex **9**.

Homopolymerization of Isoprene (IP). To gain fundamental information on the ligand influences on the catalyst activity and selectivity, the homopolymerization of isoprene was first examined by use of complexes **1**−**8**. $[Ph_3C][B(C_6F_5)_4]$ (**A**), $[PhMe_2NH][B(C_6F_5)_4]$ (**B**), and $B(C_6F_5)_3$ (**C**) were used as activators to generate the corresponding cationic scandium alkyl active species. Representative results are summarized in Table 3.

Generally, the trityl and anilinium borate activators **A** and **B** showed similar influences on the polymerization activity and

(17) Shapiro, P. J.; Bunel, E. E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867.

(18) A higher coordination usually results in longer bond distances around the metal center. See: Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

(19) The isolation of a cationic half-sandwich rare earth metal complex with an η^1-alkyl ligand is usually difficult because of facile ligand scrambling. Only two examples were reported previously: (a) Robert, D.; Spaniol, T. P.; Okuda, J. *Eur. J. Inorg. Chem.* **2008**, 2801. (b) Henderson, L. D.; Maclnnis, G. D.; Piers, W. E.; Parvez, M. *Can. J. Chem.* **2004**, *82*, 162. For η^2-aminobenzyl and η^3-allyl cationic half-sandwich Sc complexes, see (c) Li, X.; Nishiura, M.; Mori, K.; Mashiko, T.; Hou, Z. *Chem. Commun.* **2007**, 4137. (d) Yu, N.; Nishiura, M.; Li, X.; Xi, Z.; Hou, Z. *Chem. Asian. J.* **2008**, *3*, 1406. Cationic rare earth alkyls with multidentate non-Cp ligands are relatively easier to isolate.[14]

Table 3. Isoprene Polymerization by Using the Complexes **1**−**8**/Activator Systems[a]

entry	comp.	act.[b]	*t* (min)	yield (%)	microstructure (%)[c] *cis*-1,4-	*trans*-1,4-	3,4-	M_n[d] (× 10^3)	M_w/M_n[d]	T_g[e] (°C)	Eff.[f] (%)
1	**1**	**A**	5	100	95	0	5	120	2.39	−57	0.3
2	**1**	**B**	5	100	92	3	5	85	1.64	−60	0.5
3	**1**	**C**	240	68	82	13	5	25	2.20	−64	1.1
4	**2**	**A**	5	100	91	0	9	122	2.26	−60	0.3
5	**2**	**B**	5	100	87	4	9	105	1.63	−62	0.4
6	**2**	**C**	240	50	69	22	9	30	1.65	−62	0.7
7	**3**	**A**	60	100	41	8	51	67	1.10	−32	0.6
8	**3**	**B**	60	100	39	10	51	70	1.08	−33	0.6
9	**3**	**C**	60	100	30	29	41	72	1.09	−44	0.6
10	**4**	**A**	180	100	25	20	55	75	1.07	−32	0.5
11	**4**	**B**	180	100	23	22	55	66	1.07	−27	0.6
12	**4**	**C**	180	95	7	61	32	57	1.11	−50	0.7
13	**5**	**A**	180	100	20	15	65	77	1.07	−18	0.5
14	**5**	**B**	180	100	17	18	65	69	1.07	−21	0.6
15	**5**	**C**	180	91	3	57	40	59	1.08	−43	0.6
16	**6**	**A**	120	100	90	0	10	73	1.12	−59	0.6
17	**6**	**B**	120	100	90	0	10	77	1.07	−60	0.5
18	**6**	**C**	120	100	84	0	16	107	1.14	−58	0.4
19	**7**	**A**	120	100	29	60	11	77	1.05	−61	0.5
20	**7**	**B**	120	100	28	61	11	69	1.08	−63	0.6
21	**7**	**C**	120	100	10	79	11	114	1.11	−65	0.4
22	**8**	**A**	120	8	77	0	23	7	1.37	−44	0.5

[a] Conditions: 25 μmol of Sc, 25 μmol of activator, 15 mmol of isoprene, 10 mL of C_6H_5Cl, 25 °C. [b] Activator: **A** = $[Ph_3C][B(C_6F_5)_4]$, **B** = $[PhMe_2NH][B(C_6F_5)_4]$, **C** = $B(C_6F_5)_3$. [c] Determined by ^1H and ^{13}C NMR. [d] Determined by GPC in THF at 45 °C. [e] Measured by DSC. [f] Catalyst efficiency = M_n(Calculated)/M_n(Measured).

selectivity, while the neutral borane compound **C** showed lower activity and gave polyisoprene with higher *trans*-1,4-configuration (cf. Table 3, entries 1−3, 4−6, 10−12, and 13−15). Significant influences of the Cp′ ligands on the polymerization activity and selectivity were observed. Among these complexes, **1** and **2**, which bear the smallest Cp′ ligands (C_5H_5 and C_5MeH_4, respectively), showed the highest activity, converting quantitatively 600 equiv of isoprene into polyisoprene within 5 min in the presence of 1 equiv of **A** or **B** at room temperature (Table 3, entries 1−2 and 4−5). High *cis*-1,4 selectivity (up to 95%) was observed. As the steric hindrance of the Cp′ ligands increased in **3** (C_5Me_4H), **4** (C_5Me_5) and **5** ($C_5Me_4SiMe_3$), the polymerization became slower and much longer reaction time was required for completion. The formation of 3,4-polyisoprene (51−65%) was preferred in the case of **3**−**5** under the same conditions (Table 3, entries 7−8, 10−11, and 13−14). The phosphine side arm coordinated complex **6** showed the similar activity as that of the ether analogue **7**. However, a distinct difference in selectivity was observed between these two complexes. Complex **6** showed high *cis*-1,4 selectivity (84−90%), whereas **7** preferred *trans*-1,4-polyisoprene formation (60−79%) (Table 3, entries 16−18 and 19−21). The binuclear complex **8** showed much lower activity than those of the mononuclear complexes **1**−**7** under the same conditions (Table 3, entry 22). The neutral complexes **1**−**8** alone were inactive under the same conditions, suggesting that the generation of a cationic metal alkyl species is essential for the present polymerization. The isolated, THF-solvated cationic complexes **9**−**11** were inactive under the same conditions, obviously due to the strongly coordinating THF ligands.

Copolymerization of Isoprene (IP) with Ethylene (E). The copolymerization reactions were carried out by feeding varying amounts of isoprene under an atmosphere of ethylene (1 atm) in C_6H_5Cl at 25 °C, in the presence of a scandium complex and an activator. Representative results are shown in Table 4.

In consistence with the selectivity observed in the homopolymerization of isoprene, the copolymerization of isoprene with ethylene by **1**/**A** or **2**/**A** afforded the corresponding copolymers with high isoprene contents and predominant *cis*-1,4-microstructures (up to 90%) (Table 4 entries 1−8). As the isoprene feed was raised gradually from 30 to 60 mmol under 1 atm of ethylene, the copolymerization activity (or the copolymer yield) increased significantly (from 456 to 1598 kg/mol-Sc·h for **1** and 744 to 1234 kg/mol-Sc·h for **2**) and the isoprene content in the resulting random copolymers also increased gradually in the range of 80−90 mol %. These results suggest that an increase of isoprene feed under 1 atm of ethylene could accelerate the copolymerization of these two monomers. When the more sterically demanding complexes **3**−**5**/**A** were used as catalysts, the copolymerization activity generally increased at first and then decreased after reaching a peak value, as the isoprene feed was raised in the range of 30−60 mmol under 1 atm of ethylene (Table 4, entries 9−20). The copolymers produced by **3,4/A** possessed almost perfect alternating isoprene−ethylene sequences with 3,4-rich polyisoprene microstructures (isoprene content: 47−51 mol % for **3** and 38−50 mol % for **4**; 3,4-selectivity: 58−68%) (Table 4, entries 9−20), whereas the copolymers produced by **5**/**A** adopted a random microstructure with lower isoprene incorporation (isoprene content: 29−40 mol %; 3,4-selectivity: 55%). In all the cases, the copolymerization activity was much higher than that of the homopolymerization of isoprene. Such "co-monomer effect" was observed previously in the alternating copolymerization of cycloolefins (norbornene, dicyclopentadiene) with ethylene catalyzed by **5**/**A**.[13b,c]

Similarly, the side arm-coordinated complexes **6** and **7** also exhibited high activity for the copolymerization of isoprene with ethylene (Table 4, entries 21−34), although their activity for the homopolymerization of isoprene was rather low under the similar conditions. Predominant alternating isoprene−ethylene copolymers with high molecular weights and narrow molecular weight distributions were obtained (isoprene content around 50 mol %, M_n up to 4.6×10^5, M_w/M_n = 1.12−1.87) (Table 4, entries 21−34). It is also noteworthy that the isoprene units in all the copolymers produced by **6** and **7** adopted predominantly the 3,4-configuration (68−82%). This is distinctly different from

Table 4. Copolymerization of Isoprene with Ethylene by Using the Complexes **1**−**7**/Activator Systems[a]

entry	comp.	A[b]	IP (mmol)	yield (g)	act.[c]	IP cont.[d](mol %)	3,4-IP[d](%)	1,4-IP[d](%)(*C*/*T*)[e]	M_n[f] (10^3)	M_w/M_n[f]	T_g[g] (°C)
1	**1**	**A**	30	0.95	456	82	11	89 (85/4)	86	1.40	−61
2	**1**	**A**	40	1.83	878	83	10	90 (86/4)	150	1.42	−62
3	**1**	**A**	50	2.73	1310	87	8	92 (90/2)	249	1.33	−62
4	**1**	**A**	60	3.33	1598	90	8	92 (90/2)	261	1.56	−62
5	**2**	**A**	30	1.55	744	80	17	83 (78/5)	110	1.48	−61
6	**2**	**A**	40	1.78	854	86	15	85 (n.d.)[h]	181	1.31	−59
7	**2**	**A**	50	2.00	960	88	15	85 (80/5)	227	1.48	−60
8	**2**	**A**	60	2.57	1234	89	15	85 (n.d.)	281	1.56	−60
9	**3**	**A**	30	1.18	566	47	68	32 (n.d.)	440	1.13	−37
10	**3**	**A**	40	1.66	797	49	68	32 (15/17)	256	1.25	−38
11	**3**	**A**	50	2.01	965	50	68	32 (14/18)	429	1.11	−38
12	**3**	**A**	60	1.58	758	51	68	32 (11/21)	352	1.30	−38
13	**4**	**A**	30	1.24	595	38	57	43 (n.d.)	294	1.55	−51
14	**4**	**A**	40	2.42	1162	44	58	42 (7/35)	595	1.38	−52
15	**4**	**A**	50	2.15	1032	48	58	42 (n.d.)	423	1.40	−52
16	**4**	**A**	60	1.99	955	50	57	43 (4/39)	310	1.31	−50
17	**5**	**A**	30	1.26	605	29	55	45 (n.d.)	303	1.29	−53
18	**5**	**A**	40	1.39	667	32	55	45 (6/39)	327	1.22	−51
19	**5**	**A**	50	1.52	730	36	55	45 (5/40)	256	1.25	−50
20	**5**	**A**	60	1.42	682	40	55	45 (n.d.)	238	1.26	−48
21	**6**	**A**	30	1.35	648	43	68	32 (5/27)	296	1.14	−52
22	**6**	**A**	40	1.69	811	46	71	29 (2/27)	407	1.19	−31
23	**6**	**A**	50	2.13	1022	52	81	19 (2/17)	487	1.12	−20
24	**6**	**A**	60	2.09	1003	55	81	19 (2/17)	483	1.12	−22
25	**6**	**B**	40	1.90	912	52	75	25 (1/24)	413	1.12	−24
26	**6**	**C**	40	2.03	974	49	81	19 (1/18)	309	1.22	−24
27	**6**	**C**	50	1.56	749	50	80	20 (1/19)	283	1.37	−24
28	**7**	**A**	40	1.95	936	50	75	25 (n.d.)	356	1.87	−30
29	**7**	**B**	20	1.59	763	46	81	19 (n.d.)	346	1.24	−35
30	**7**	**B**	30	2.17	1042	48	81	19 (n.d.)	417	1.34	−31
31	**7**	**B**	40	2.66	1277	49	81	19 (12/7)	363	1.40	−31
32	**7**	**B**	50	2.71	1301	49	81	19 (12/7)	393	1.25	−31
33	**7**	**B**	60	2.15	1032	50	81	19 (12/7)	462	1.45	−30
34	**7**	**C**	40	2.22	1066	47	82	18 (11/7)	267	1.48	−30

[a] Conditions: 25 μmol of Sc, 25 μmol of activator, 1 atm of ethylene, 40 mL of C_6H_5Cl, 25 °C, 5 min. [b] Activator: **A** = $[Ph_3C][B(C_6F_5)_4]$, **B** = $[PhMe_2NH][B(C_6F_5)_4]$, **C** = $B(C_6F_5)_3$. [c] Kilograms of copolymer/mol-Sc·h·atm. [d] Determined by ^{1}H NMR. [e] Determined by ^{13}C NMR, *C* = *cis*, *T* = *trans*. [f] Determined by GPC in *o*-dichlorobenzene at 145 °C. [g] Measured by DSC. [h] n.d. = not detected.

what was observed in the homopolymerization of isoprene, where either *cis*-1,4- (**6**: 84−90%) or *trans*-1,4-configuration (**7**: 60−79%) was predominant (see Table 3).

The reactivity ratios ($r_E = k_{EE}/k_{EIP}$ and $r_{IP} = k_{IPIP}/k_{IPE}$) for the **3/A** system ($r_E = 0.4$ and $r_{IP} = 0.003$) and the **7/B** system ($r_E = 0.7$ and $r_{IP} = 0.007$) were obtained from the Fineman−Ross plots at very low monomer conversion (<5%).[20] These results suggest that the ethylene-isoprene alternating insertion should be much faster than successive insertion of either monomer in the present catalytic systems. The reactivity ratios for **5/A** were found to be $r_E = 6.7$ and $r_{IP} = 0.020$, indicating a preference for the coordination/insertion of ethylene over those of isoprene in this catalyst system. The product of the reactivity ratios ($r_E r_{IP} = 0.134$) demonstrates a tendency to form random copolymers, in agreement with the microstructures of the resulting copolymers determined by ^{13}C NMR analysis. Attempts to obtain the reactivity ratios for **1** or **2** from the Fineman−Ross plot were not successful because the copolymerization reaction in these cases was too fast.

As far as we are aware, the catalyst system based on **1** or **2** represents the first example of a catalyst for the *cis*-1,4-selective copolymerization of isoprene with ethylene, and those based on **3**, **4**, **6**, and **7** are the first examples for the alternating copolymerization of isoprene with ethylene. It should also be noted that the use of the analogous nonmetallocene Sc or Y complexes bearing an ancillary (phosphinophenyl) amido (PNP) or amidinate ligand, which had shown excellent regio- and stereoselectivity for the homopolymerization of isoprene,[10k,l] yielded only a mixture of the homopolymers under the same conditions, while an isoprene−ethylene copolymer product was not observed. These results may demonstrate that the half-sandwich scandium systems are unique for the copolymerization of isoprene and ethylene.

Characterization of Isoprene-Ethylene Copolymers. The copolymers obtained above are white elastomers (no gel formation) and have good solubility in $C_2H_2Cl_4$ and $C_6H_4Cl_2$. GPC curves revealed that these copolymers possess high molecular weights (M_n = 86,000−595,000 g/mol) and unimodal molecular weight distributions (1.11−1.87), indicative of the predominance of a homogeneous single-site catalyst species. Differential scanning calorimetry (DSC) demonstrated that the T_g values of these polymers vary in the range of −64 to −22 °C depending on the relative amount of the 3,4-isoprene units in the copolymers. An endothermic peak corresponding to the melting point of polyethylene expected in the temperature range of 100−130 °C was not observed even in the samples with high ethylene contents.

Because very little NMR information on the isoprene−ethylene copolymers could be found in the literature,[6] we then carried out the full characterization of our copolymers by the ^{1}H, ^{13}C, DEPT-^{13}C, ^{1}H−^{1}H, and ^{1}H−^{13}C NMR analyses (see Supporting Information) to establish the comonomer incorporation and distribution in the copolymer chains. The aliphatic parts of the ^{13}C NMR spectra of some representative copolymers are shown

(20) Fineman, M.; Ross, S. D. *J. Polym. Sci.* **1949**, *2*, 259.

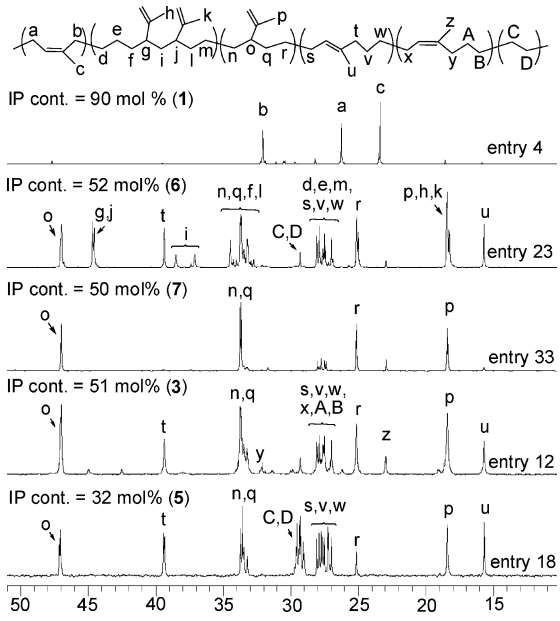


Figure 3. Aliphatic parts of the ^{13}C NMR spectra of some representative copolymers obtained in Table 4.

in Figure 3. The ^{13}C NMR spectra of the random copolymers (IP content = 82−90 mol %) prepared by **1**,**2**/**A** are very simple, consisting mainly of *cis*-1,4-PIP sequences and small amounts of *cis*-1,4-IP-*alt*-E, isolated 3,4-IP and isolated *trans*-1,4-IP units. In contrast, the copolymers prepared by **3** (e.g., Table 4, entry 12, IP content = 51 mol %) and **7** (e.g., Table 4, entry 33, IP content = 50 mol %) showed almost perfect alternating microstructures, in which the 3,4-IP-*alt*-PE sequence is dominant, with small amounts of *cis*-1,4-IP-*alt*-E and *trans*-1,4-IP-*alt*-E sequences (Figure 3). The PE units (at 29.4 ppm) are negligible in these copolymers. In the alternating copolymers produced by **6**, a significant amount of (3,4-IP)(3,4-IP)EE sequences was observed in addition to 3,4-IP-*alt*-E and *trans*-1,4-IP-*alt*-E sequences. In the ethylene-rich copolymers prepared by **5** (Table 4, entry 18, IP content = 32 mol %), the signals of the 3,4-IP-*alt*-PE units decreased, while those of PE and *trans*-1,4-IP-*alt*-E increased compared with those found in the polymers prepared by **3** (Figure 3).

Polymerization Mechanism. To gain more insight into the influence of the steric hindrance around the scandium center on the polymerization processes, the DFT calculations on four cationic species $[Cp'Sc(CH_2SiMe_3)(THF)_n][B(C_6F_5)_4]$ (**1a**: Cp′ = C_5H_5, n = 1; **4a**: Cp′ = C_5Me_5, n = 1; **6a**: Cp′ = $C_5Me_4CH_2CH_2PPh_2$, n = 0; **7a**: Cp′ = $C_5Me_4C_6H_4OMe$, n = 0) were carried out. In all the cases, it was revealed that the coordination of isoprene to the metal center in an η^2-*trans*-3,4 fashion is the most favored among four possible isoprene coordination modes (η^4-*cis*-1,4, η^4-*trans*-1,4, η^2-*cis*-3,4, η^2-*trans*-3,4) (See Supporting Information). Therefore, the η^2-*trans*-3,4-coordination (e.g., **b** in Scheme 6) might be prevailing in the chain initiation process of the present catalyst systems. The subsequent 3,4-isoprene insertion into the Sc−alkyl bond could lead to the formation of an η^3-σ-allyl intermediate (**c**) as a secondary growing chain. There could be three competitive pathways to carry through the chain propagation process from **c** (Scheme 6). One is the coordination (in a *trans*-3,4-mode) of another molecule of isoprene at the metal center of **c** to give **h**, others are the isomerization of **c** to give the *syn*-η^3-π-allylic intermediate (**d**) or that to the *anti*-η^3-π-allylic intermediate (**l**) via rotation of the C3−C2 single bond of the η^1-σ-allyl intermediate (**k**). These competitive pathways would result in different microstructures (3,4-, *trans*-1,4- and *cis*-1,4-) in the polymer chains. The DFT calculations showed that the π−η^3-allylic intermediates (**d** and **l**) have lower energies than that of the σ-allyl intermediate (**c**), and the *anti*-η^3-allylic intermediate (**l**) is further more stable (ca. 1.5−2.0 kcal/mol) than the *syn*-η^3-allylic intermediate (**d**). These energy differences could provide a driving force for the σ−π and *syn*-*anti* isomerizations among these allyl intermediates, especially when the complexes have small steric hindrance around the metal center. Therefore, for the less steric catalysts **1** and **2**, all these processes should be faster and the equilibrium would shift to the thermodynamically more stable *anti* π−η^3-allylic intermediate (**l**), and thus afford the *cis*-1,4-polyisoprene sequences as a major component (cf. **m**−**p**, Scheme 6). This scenario is in agreement with the experimental results (see Table 3). As to a possible chain termination reaction, the growing-polymer-chain-containing species (similar to **o**) could have enough space for β-hydrogen elimination. The resulting olefin/hydride species would be susceptible to ligand exchange with an incoming isoprene monomer, thus leading to chain termination/transfer.

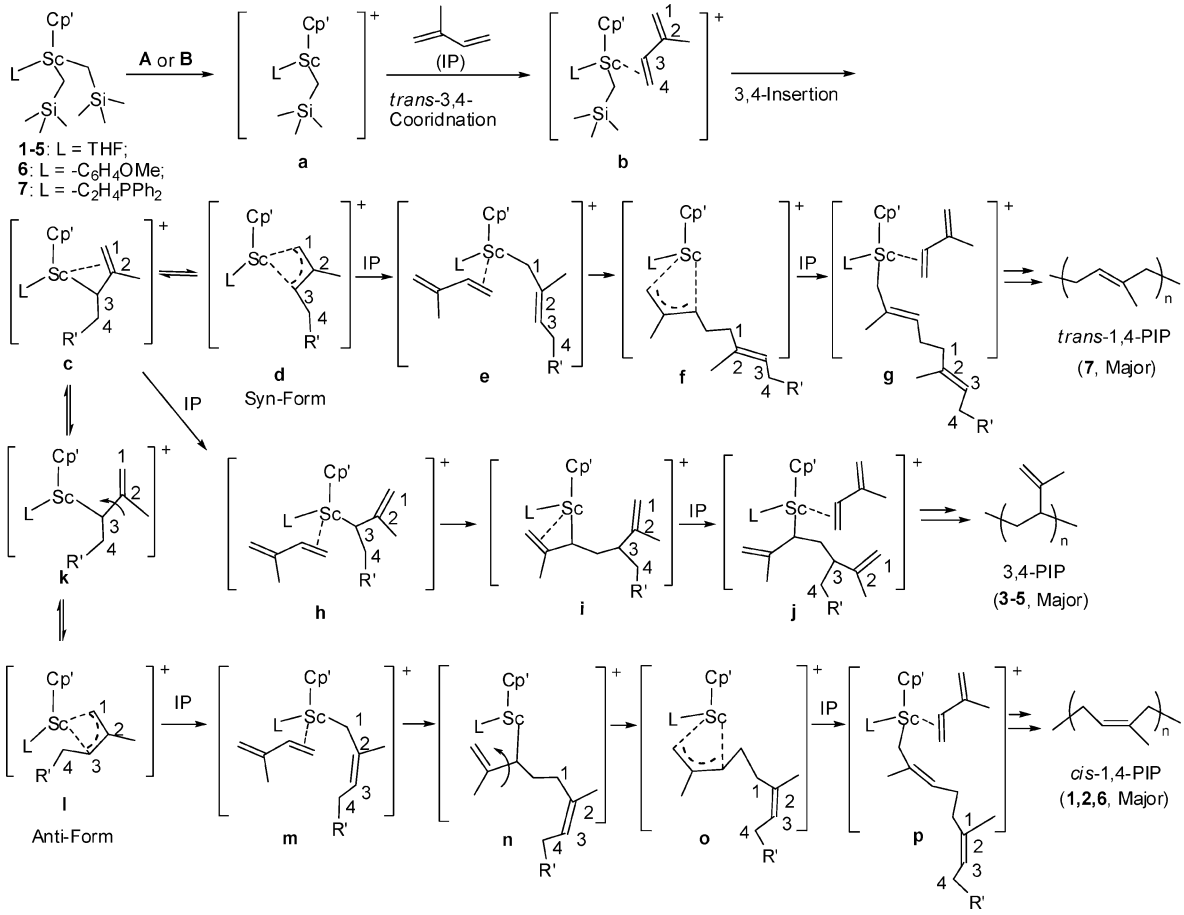
In the case of the THF-free, phosphine side arm coordinated complex **6**, the chain propagation process could follow those in the case of **1** and **2** to give *cis*-1,4-predominant polyisoprene sequences (**c**, **k**, **l**−**p**, Scheme 6) (see also Table 3).[21] However, the larger steric hindrance of the Cp′ ligand in **6** could make its polymerization speed slower than those of **1** and **2**. For the analogous THF-free complex **7**, which bears a more strongly coordinating ether side arm on the Cp ring, the isomerization of the σ-allyl intermediate **c** to the *anti*-η^3-π-allyl species **l** via the η^1-σ-alkyl intermediate **k**, would be kinetically less favored compared with that to the *syn*-η^3-π-allyl species **d** because of the steric hindrance around metal center. Therefore, the coordination of an incoming isoprene monomer to the metal center of **d** would give a primary σ-allyl species such as **e**, which after isoprene insertion should afford **f**, and finally lead to formation of *trans*-1,4-polyisoprene sequences as a major component in the resulting polymers. Regarding a possible chain termination reaction, the steric hindrance of the bulky Cp′ ligands in these catalysts would prevent β-hydrogen elimination from a species like **f** or **o**. Therefore, a chain transfer reaction would be difficult, thus accounting for the living feature of these catalysts (**6** and **7**) for the polymerization of isoprene.

In the case of the further sterically demanding catalysts such as **3**−**5**, which contain both a bulky multisubstituted cyclopentadienyl ligand and a five-membered ring THF ligand, all the reaction processes would be retarded because of steric hindrance. In particular, the isomerization reactions of the σ-allyl intermediate **c** to the π−η^3-allylic intermediates **d** and **l** could be hampered to such an extent that the coordination of an incoming isoprene monomer to the σ-allyl intermediate **c** to give **h** would become relatively favored, thus leading to formation of the 3,4-polyisoprene sequences as a major part in the resulting polymers (cf. **h**−**j**, Scheme 6) (see also Table 3). The steric hindrance of both the Cp′ and the THF ligands could account for the livingness observed in isoprene polymerization, as described above in the case of **6** and **7**.

When the neutral borane compound $B(C_6F_5)_3$ (**C**) was used as an activator, a contact ion pair such as Cp′Sc-

(21) The loosely coordinated phosphine side arm could probably be dissociated from the metal center upon coordination or insertion of isoprene, thus making the isomerization of **c** to **l** possible.

Scheme 6. Possible Scenarios of Isoprene Polymerization Catalyzed by Cationic Half-Sandwich Scandium Species



$(CH_2SiMe_3)(THF)_n(CH_2SiMe_3)B(C_6F_5)_3$ ($n = 0$, 1) would be formed, in which a relatively strong bonding interaction between the metal center and the resulting anionic borate unit $[B(CH_2SiMe_3)(C_6F_5)_3]$ could exist.[19b] Therefore, the cationic metal center would be more crowded and less electropositive compared to those generated by use of $[Ph_3C][B(C_6F_5)_4]$ (**A**) or $[PhMe_2NH][B(C_6F_5)_4]$ (**B**) as an activator. As in the case of **7**, the larger steric hindrance around metal center could account for the higher content of the *trans*-1,4-polyisoprene unit in the polymers obtained when $B(C_6F_5)_3$ (**C**) was used as an activator (cf. Table 3).

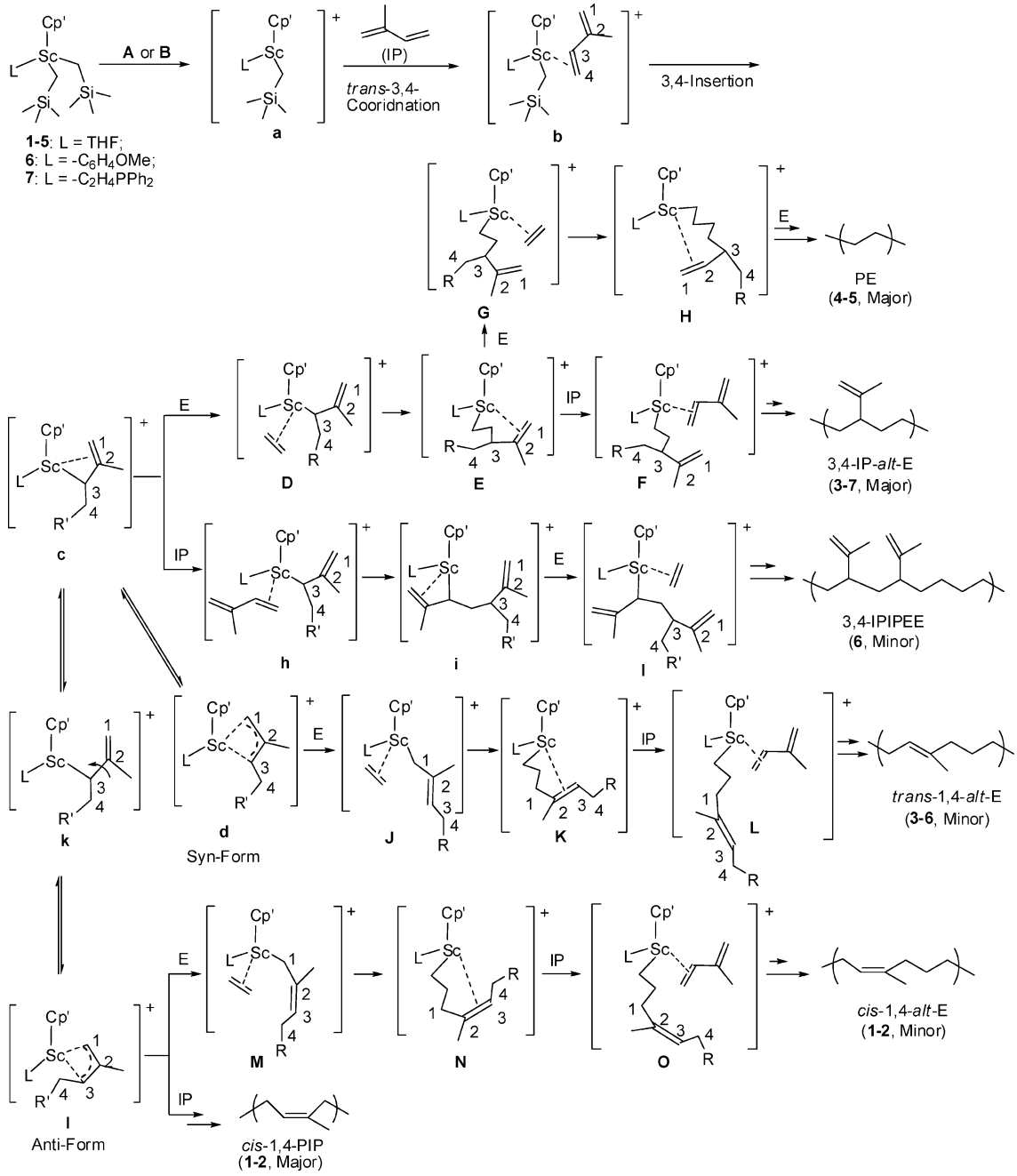
For the copolymerization of isoprene with ethylene, whether the initiation step is the insertion of isoprene or ethylene, the copolymerization reaction should proceed through the allyl intermediates similar to those formed in the homopolymerization of isoprene, such as **c**, **l**, and **d** (Schemes 6 and 7). In the case of the less sterically demanding catalysts **1** and **2**, the copolymerization could take place through the thermodynamically more stable *anti*-η^3-π-allyl intermediate **l** as in the case of isoprene homopolymerization, to afford the copolymers with high *cis*-1,4-polyisoprene sequences (Scheme 7). In the case of the more sterically demanding catalysts **3**−**7**, the coordination of the smaller ethylene molecule to the metal center of **c** could be possible before the isomerization of **c** to **d** or **l**, thus leading to formation of the copolymers with alternating 3,4-isoprene−ethylene units as main sequences via the intermediates **D**−**F**.[22] Among these catalysts, the most bulky complexes **4** and **5**, which bear both a persubstituted cyclopentadienyl ligand and a five-membered ring THF ligand at the metal center, would favor the insertion of the smaller ethylene monomer, to give more ethylene-ethylene sequences in the resulting copolymers (cf. **G** and **H**, Scheme 7). The coordination and insertion of an isoprene monomer at **c** followed by successive insertion of ethylene could explain the formation of some amount of IPIPEE sequences observed in the case of **6** (cf. **h**, **i**, and **I**, Scheme 7). The coordination and insertion of ethylene at the metal center of the *syn*-η^3-π-allyl intermediate **d** followed by those of isoprene would lead to formation of the alternating *trans*-1,4-isoprene−ethylene units, as observed in the case of **3**−**6** (cf. **d**, **J**, **K**, and **L**, Scheme 7).

Concluding Remarks

A series of structurally well-defined half-sandwich scandium dialkyl complexes such as **1**−**7**, which bear mono(cyclopentadienyl) ligands with various substituents including those having a heteroatom side arm, have been synthesized either by the alkane elimination reactions between the trialkyl complex $Sc(CH_2SiMe_3)_3(THF)_2$ and the neutral cyclopentadiene ligands or by the one-pot metathetical reactions of $ScCl_3(THF)_3$ with the potassium salts of the ligands and $LiCH_2SiMe_3$. The reactions of the dialkyl complexes with one equiv of a borate

(22) For similar alternating copolymerization of ethylene with sterically demanding cyclic olefins, see: (a) Li, X.; Baldamus, J.; Hou, Z. *Angew. Chem., Int. Ed.* **2005**, *44*, 962. (b) Li, X.; Hou, Z. *Macromolecules* **2005**, *38*, 6767.

Scheme 7. Possible Scenarios of Isoprene−Ethylene Copolymerization Catalyzed by Cationic Half-Sandwich Scandium Species[a]



[a] Structures shown represent the micro-structural units in the copolymer products (e.g., PE represents polyethylene units/blocks in the copolymers, rather than ethylene homopolymer).

compound such as $[Ph_3C][B(C_6F_5)_4]$ or $[PhMe_2NH][B(C_6F_5)_4]$ have afforded easily the corresponding cationic monoalkyl species, some of which (e.g., **10** and **11**) have been structurally characterized by X-ray diffraction studies. In the presence of an activator such as $[Ph_3C][B(C_6F_5)_4]$, $[PhMe_2NH][B(C_6F_5)_4]$ or $B(C_6F_5)_3$, all the dialkyl complexes **1**−**7** are active for the polymerization of isoprene and the copolymerization of isoprene with ethylene, with the activity and selectivity being significantly dependent on the ancillary ligands, to yield a new family of polymer materials with different microstructures and compositions. In the homopolymerization of isoprene, the less sterically demanding complexes **1** and **2** showed high *cis*-1,4 selectivity (up to 95%), while the ether side arm containing complex **7** yielded *trans*-1,4-polyisoprene (60−79%) as a major product. In the case of the more sterically demanding complexes **3**−**5**, the formation of 3,4-polyisoprene (51−65%) was preferred. In the copolymerization of isoprene and ethylene, complexes **1** and **2** afforded the random copolymers with high isoprene contents (85−92 mol %) and predominant *cis*-1,4-microstructures (up to 90%), thus constituting the first example of *cis*-1,4-selective copolymerization of isoprene with ethylene. In contrast, the copolymerization of isoprene and ethylene by **3**, **4**, **6**, and **7** gave, for the first time, almost perfect alternating isoprene−ethylene copolymers. The DFT calculations have offered unprecedented insight into the mechanistic aspects of the polymerization processes. This work has demonstrated that the activity and selectivity of the cationic half-sandwich rare earth alkyl catalysts can be fine-tuned by modifying the substituents on the cyclo-

pentadienyl ligands. Further studies on the polymerization and copolymerization of other monomers by the cationic half-sandwich and related rare earth catalysts are in progress.

Experimental Section

Materials. All manipulations of air and moisture-sensitive compounds were performed under a dry argon atmosphere by use of standard Schlenk techniques or a nitrogen-filled Mbraun glovebox. Argon, nitrogen, and ethylene (Takachiho Chemical Industrial Co., Ltd.) were purified by being passed through a Dryclean column (4 Å molecular sieves, Nikka Seiko Co.) and a Gasclean GC-XR column (Nikka Seiko Co.). Solvents were purified by an Mbraun SPS-800 Solvent Purification System and dried over fresh Na chips in the glovebox. Isoprene was purchased from TCI, dried over CaH_2, vacuum-transferred, and degassed by two freeze−pump−thaw cycles prior to polymerization experiments. $[Ph_3C][B(C_6F_5)_4]$, $[PhMe_2NH][B(C_6F_5)_4]$, and $B(C_6F_5)_3$ were purchased from Tosoh Finechem Corporation and used without purification. $ScCl_3$ was purchased from Strem. $LiCH_2SiMe_3$ (1.0 M solution in pentane), $C_5Me_4H_2$, C_5Me_5H, and $C_5Me_4H(SiMe_3)$ were purchased from Aldrich, and used as received. C_5H_6 and C_5MeH_5 were obtained by cracking of dicyclopentadiene and methylcyclopentadiene dimer at 180 °C, respectively. $Sc(CH_2SiMe_3)_3(THF)_2$,[23] $C_5Me_4(CH_2CH_2PPh_2)Li$,[24] $C_5Me_4H(C_6H_4OMe\text{-}o)$,[25] and $C_5Me_4H(C_6H_4NMe_2\text{-}o)$[26] were synthesized according to literature. The deuterated solvents benzene-d_6 (99.6 atom % D), THF-d_8 (99.6 atom % D), $CDCl_3$ (99.8 atom % D), and 1,1,2,2-tetrachloroethane-d_2 (99.6 atom % D) were obtained from Cambridge Isotope.

General Methods. Samples of rare earth metal complexes for NMR spectroscopic measurements were prepared in the glovebox using J. Young valve NMR tubes. The NMR (^1H, ^{13}C, ^{31}P, ^{11}B, ^{19}F) spectra were recorded on a JEOL JNM-EX 300, JNM-EX 400 or an ECA-600 spectrometer. The ^{31}P, ^{19}F and ^{11}B NMR spectra were referenced to external 85% H_3PO4, $CFCl_3$ and $BF_3\cdot Et_2O$, respectively. Elemental analyses were performed on MICRO CORDER JM10(J-SCIENCE LAB Co.). The NMR data of the polymers and copolymers were obtained on a JNM-EX 300 (FT, 300 MHz for ^1H; 75 MHz for ^{13}C) spectrometer at 45 or 120 °C with $CDCl_3$ or 1,1,2,2-$C_2D_2Cl_4$ as a solvent, respectively. The molecular weights and molecular weight distributions of polyisoprenes were determined by gel permeation chromatography on TOSOH HLC-8220 GPC (Column: Super HZM-H × 3) at 40 °C using THF as an eluent at a flow rate of 0.35 mL/min against polystyrene standards. The molecular weights and molecular weight distributions of the copolymer samples were determined at 145 °C by high temperature gel permeation chromatography (HT-GPC) on a HLC-8121GPC/HT apparatus (Tosoh Co.). 1,2-Dichlorobenzene (DCB) was employed as an eluent at a flow rate of 1.0 mL/min. The calibration was made by polystyrene standard. The DSC measurements were performed on a DSC6220 (SII Co.) at a rate of 20 °C/min. Any thermal history difference in the polymers was eliminated by first heating the specimen to 200 °C, cooling at 10 °C/min to −120 °C, and then recording the second DSC scan.

Synthesis of $(C_5H_5)Sc(CH_2SiMe_3)_2(THF)$ (1). To a colorless hexane solution (5 mL) of $Sc(CH_2SiMe_3)_3(THF)_2$ (0.225 g, 0.50 mmol) was added a solution of cyclopentadiene (0.033 g, 0.50 mmol) in hexane (1.0 mL) at room temperature. The mixture was stirred at room temperature for 3 h. After removal of all volatiles in vacuo, the residue was recrystallized from hexane at −30 °C to give **1** as light yellow crystals (0.143 g, 0.40 mmol, 80% yield). ^1H NMR (C_6D_6, 22 °C, δ/ppm): −0.22 (s, 4H, CH_2SiMe$_3$), 0.30 (s, 18H, $CH_2Si(CH_3)_3$), 1.07 (m, 4H, THF-β-CH_2), 3.40 (m, 4H, THF-α-CH_2), 6.34 (s, 5H, C_5H_5). ^{13}C NMR (C_6D_6, δ/ppm): 4.2 (s, $CH_2Si(CH_3)_3$), 25.2 (s, THF), 40.1 (br, CH_2SiMe_3), 72.2 (s, THF), 112.5 (s, C_5H_5). Anal. calcd for $C_{17}H_{35}OScSi_2$: C, 57.26; H, 9.89. Found: C, 57.20; H, 9.71.

Synthesis of $(C_5MeH_4)Sc(CH_2SiMe_3)_2(THF)$ (2). To a colorless hexane solution (5 mL) of $Sc(CH_2SiMe_3)_3(THF)_2$ (3.268 g, 7.25 mmol), was added C_5H_5Me (0.581 g, 7.25 mmol) at room temperature. The pale-yellow mixture was stirred for 3 h. After reduction of the solution volume (1 mL) under reduced pressure, the oily residue was cooled at −30 °C overnight to give **2** as colorless crystals (2.038 g, 5.50 mmol, 76% yield). ^1H NMR (300 MHz, C_6D_6, 22 °C, δ/ppm): −0.21 (s, 4H, CH_2Si(CH$_3$)$_3$), 0.32 (s, 18H, $CH_2Si(CH_3)_3$), 1.06 (m, 4H, THF-β-CH_2), 2.21 (s, 3H, $C_5H_4CH_3$), 3.41 (m, 4H, THF-α-CH_2), 6.19 (s, 4H, C_5MeH_4). ^{13}C NMR (75 MHz, C_6D_6, 22 °C, δ/ppm): 4.0 (s, $CH_2Si(CH_3)_3$), 15.3 (s, $C_5H_4CH_3$), 24.9 (s, THF), 40.0 (br, $CH_2Si(CH_3)_3$), 71.7 (s, THF), 111.8 (s, $C_5H_4CH_3$), 113.0 (s, C_5MeH_4), 124.8 (s, C_5MeH_4). Anal. calcd for $C_{18}H_{37}OScSi_2$: C, 58.33; H, 10.06. Found: C, 58.61; H, 10.27.

Synthesis of $(C_5Me_4H)Sc(CH_2SiMe_3)_2(THF)$ (3). To a colorless hexane solution (5 mL) of $Sc(CH_2SiMe_3)_3(THF)_2$ (3.268 g, 7.25 mmol) was added $C_5H_2Me_4$ (0.886 g, 7.25 mmol) at room temperature. The pale-yellow mixture was stirred for 3 h. After reduction of the solution volume (1 mL) under reduced pressure, the oily residue was cooled at −30 °C overnight to give **3** as colorless crystals (2.299 g, 5.57 mmol, 77% yield). ^1H NMR (300 MHz, C_6D_6, 22 °C, δ/ppm): −0.33 (s, 4H, CH_2SiMe$_3$), 0.33 (s, 18H, $CH_2Si(CH_3)_3$), 1.15 (br, 4H, THF-β-CH_2), 1.95 (s, 6H, $C_5H(CH_3)_4$), 2.10 (s, 6H, $C_5H(CH_3)_4$), 3.52 (m, 4H, THF-α-CH_2), 5.96 (s, 1H, $C_5H(CH_3)_4$). ^{13}C NMR (75 MHz, C_6D_6, 22 °C, δ/ppm): 4.3 (s, $CH_2Si(CH_3)_3$), 11.6 (s, $C_5H(CH_3)_4$), 13.7 (s, $C_5H(CH_3)_4$), 24.9 (s, THF), 38.9 (s, CH_2SiMe_3), 71.1 (s, THF), 111.3 (s, C_5Me_4H), 120.1 (s, C_5Me_4H), 120.5 (s, C_5Me_4H). Anal. calcd for $C_{21}H_{43}OScSi_2$: C, 61.12; H, 10.50. Found: C, 60.56; H, 10.34.

Synthesis of $(C_5Me_5)Sc(CH_2SiMe_3)_2(THF)$ (4). To a colorless hexane solution (5 mL) of $Sc(CH_2SiMe_3)_3(THF)_2$ (1.470 g, 3.26 mmol) was added C_5Me_5H (0.444 g, 3.26 mmol) at room temperature. The pale yellow mixture was stirred at 50 °C for 48 h. After reduction of the solution volume (1 mL) under reduced pressure, the dark brown oily residue was cooled at −30 °C overnight to give **4** as colorless plate-like crystals (0.900 g, 2.11 mmol, 65% yield). ^1H NMR (C_6D_6, 22 °C, δ/ppm): −0.40 (d, 2H, CH_2Si(CH$_3$)$_3$, $^2J_{H-H}$ = 15 Hz), −0.33 (d, 2H, CH_2Si(CH$_3$)$_3$, $^2J_{H-H}$ = 15 Hz), 0.32 (s, 18H, $CH_2Si(CH_3)_3$), 1.13 (m, 4H, THF-β-CH_2), 2.01 (s, 15H, $C_5(CH_3)_5$), 3.53 (m, 4H, THF- α-CH_2). ^{13}C NMR (C_6D_6, 22 °C, δ/ppm): 4.4 (s, $CH_2Si(CH_3)_3$), 11.9 (s, $C_5(CH_3)_5$), 24.8 (s, THF), 38.8 (s, CH_2SiMe_3), 71.2 (s, THF), 119.0 (s, $C_5(CH_3)_5$). Anal. calcd for $C_{22}H_{45}OScSi_2$: C, 61.92; H, 10.63. Found: C, 61.71; H, 9.92.

Synthesis of $(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)_2(THF)$ (5). To a colorless hexane solution (10 mL) of $Sc(CH_2SiMe_3)_3(THF)_2$ (1.366 g, 3.03 mmol) was added $C_5Me_4H(SiMe_3)$ (0.589 g, 3.03 mmol) at room temperature. The pale-yellow mixture was stirred at room temperature for 2 h. After reduction of the solution volume under reduced pressure, the oily residue was cooled at −30 °C overnight to give **5** as colorless cubic crystals (1.145 g, 2.36 mmol, 78% yield). ^1H NMR (C_6D_6, 22 °C, δ/ppm): −0.30 (d, 2H, CH_2Si(CH$_3$)$_3$, J_{H-H} = 11.5 Hz), −0.25 (d, 2H, CH_2Si(CH$_3$)$_3$, J_{H-H} = 11.5 Hz), 0.29 (s, 18H, $CH_2Si(CH_3)_3$), 0.43 (s, 9H, $C_5(CH_3)_4Si(CH_3)_3$), 1.19 (m, 4H, THF-β-CH_2), 1.91 (s, 6H, $C_5(CH_3)_4$), 2.22 (s, 6H, $C_5(CH_3)_4$), 3.63 (m, 4H, THF-α-CH_2). ^{13}C NMR (C_6D_6, 22 °C, δ/ppm): 2.8 (s, $C_5Me_4Si(CH_3)_3$), 4.6 (s, $CH_2Si(CH_3)_3$), 12.1 (s, $C_5(CH_3)_4(SiMe_3)$), 15.4 (s, $C_5(CH_3)_4$), 24.9 (s, THF), 40.4 (s, CH_2SiMe_3), 71.5 (s, THF), 116.6 (s, ipso-$C_5Me_4(SiMe_3)$, 124.2 (s, $C_5Me_4(SiMe_3)$), 128.0 (s, $C_5Me_4(SiMe_3)$). Anal. calcd for $C_{24}H_{51}OScSi_3$: C, 59.45; H, 10.60. Found: C, 59.20; H, 10.19.

Synthesis of $(C_5Me_4(C_2H_4PPh_2))Sc(CH_2SiMe_3)_2$ (6). $ScCl_3$ (0.378 g, 2.50 mmol) was refluxed in 10 mL of THF at 80 °C for 12 h, the solution was cooled down with stirring to room temperature to give a white suspension of $ScCl_3(THF)_3$.

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$[C_5Me_4(CH_2CH_2PPh_2)]Li$ (0.851 g, 2.50 mmol) in THF (5 mL) was added slowly and stirred at room temperature for 1 h. A THF solution (3 mL) of Me_3SiCH_2Li (0.471 g, 5.00 mmol) was then added slowly. After the mixture was stirred at room temperature for 30 min, the solvent was removed in vacuum, and the residue was extracted with toluene. The toluene extract was dried in vacuum and washed with cold hexane to give **6** (1.189 g, 2.15 mmol, 86% yield) as white micro crystals. Single crystals suitable for X-ray analysis were grown from a hexane solution at −30 °C. ^{1}H NMR (300 MHz, C_6D_6, r.t., δ/ppm): 0.02 (d, 2H, J = 11.1 Hz, CH_2SiMe$_3$), 0.16 (d, 2H, J = 11.1 Hz, CH_2SiMe$_3$), 0.34 (s, 18H, CH$_2$Si(CH_3)$_3$), 1.87 (s, 6H, C$_5$(CH_3)$_4$), 2.19 (s, 6H, C$_5$(CH_3)$_4$), 2.45 (br, 4H, C$_2H_4$PPh$_2$), 7.00 (m, 6H, C$_2$H$_4$P(C$_6H_5$)$_2$), 7.39 (m, 4H, C$_2$H$_4$P(C$_6H_5$)$_2$). ^{13}C NMR (75 MHz, C_6D_6, r.t., δ/ppm): 4.5 (s, CH$_2$Si(CH_3)$_3$), 12.1 (s, C$_5$(CH_3)$_4$), 12.2 (s, C$_5$(CH_3)$_4$), 21.9 (s, CH_2CH$_2$PPh$_2$), 31.8 (br, CH_2SiMe$_3$), 47.3 (s, CH$_2$CH_2PPh$_2$), 120.5, 121.4, 124.6, 129.2, 130.7, 133.1 (aromatics and Cp ring carbons). ^{31}P NMR (75 MHz, C_6D_6, r.t., δ/ppm): −7.2. Anal. calcd for $C_{31}H_{48}PScSi_2$: C, 67.35; H, 8.75. Found: C 67.48; H 8.88.

Synthesis of (C$_5$Me$_4$(C$_6$H$_4$OMe-o))Sc(CH$_2$SiMe$_3$)$_2$ (7). $ScCl_3$ (0.076 g, 0.50 mmol) was refluxed in 10 mL of THF at 80 °C for 12 h, the solution was cooled down with stirring to room temperature to give a white suspension of $ScCl_3(THF)_3$. A THF solution (5 mL) of [C$_5$Me$_4$(C$_6$H$_4$OMe-*o*)]K (0.133 g, 0.50 mmol), which was prepared by the reaction of C$_5$Me$_4$H(C$_6$H$_4$OMe-*o*) with KH, was added slowly and stirred at room temperature for 1 h. A THF solution (3 mL) of Me_3SiCH_2Li (0.094 g, 1.00 mmol) was then added slowly. After the mixture was stirred at room temperature for 30 min, the solvent was removed in vacuum, and the residue was extracted with toluene. The toluene extract was dried in vacuum and washed with cold hexane to give **7** (0.188 g, 0.42 mmol, 84% yield) as white micro crystals. Single crystals suitable for X-ray analysis were grown from a hexane solution at −30 °C. ^{1}H NMR (300 MHz, C_6D_6, r.t., δ/ppm): −0.16 (s, 4H, CH_2SiMe$_3$), 0.28 (s, 18H, CH$_2$Si(CH_3)$_3$), 1.88 (s, 6H, C$_5$(CH_3)$_4$), 2.19 (s, 6H, C$_5$(CH_3)$_4$), 3.60 (s, 3H, OCH_3), 6.26 (dd, J = 8.4, 1.1 Hz, 1H, -C$_6H_4$OMe), 6.83 (dt, J = 7.3, 1.1 Hz, 1H, -C$_6H_4$OMe), 6.91 (dt, J = 7.9, 1.8 Hz, 1H, -C$_6H_4$OMe), 7.04 (dd, J = 7.3, 2.0 Hz, 1H, -C$_6H_4$OMe). ^{13}C NMR (75 MHz, C_6D_6, r.t., δ/ppm): 4.1 (s, CH$_2$Si(CH_3)$_3$), 11.8 (s, C$_5$(CH_3)$_4$), 11.9 (s, C$_5$(CH_3)$_4$), 38.6 (br, CH_2SiMe$_3$), 58.9 (s, OCH_3), 110.5, 120.5, 120.7, 122.0, 124.4, 126.9, 128.5, 132.5, 160.0 (aromatics and Cp ring carbons). Anal. calcd for $C_{24}H_{41}OScSi_2$: C, 64.53; H, 9.25. Found: C 64.57; H 9.17.

Synthesis of [C$_5$Me$_4${o-C$_6$H$_4$N(Me)CH$_2$-μ}Sc(CH$_2$SiMe$_3$)]$_2$ (8). $ScCl_3$ (0.454 g, 3.00 mmol) was refluxed in 20 mL of THF at 80 °C for 12 h, the solution was cooled down with stirring to room temperature to give a white suspension of $ScCl_3(THF)_3$. A THF solution (15 mL) of [C$_5$Me$_4$(C$_6$H$_4$NMe$_2$-*o*)]K·0.5Et$_2$O (0.950 g, 3.00 mmol), which was prepared by the reaction of C$_5$Me$_4$H(C$_6$H$_4$NMe$_2$-*o*) with KH, was added slowly and stirred at room temperature for 1 h. A THF solution (5 mL) of Me_3SiCH_2Li (0.565 g, 6.00 mmol) was then added slowly. After the mixture was stirred at room temperature for 30 min, the solvent was removed in vacuum, and the residue was extracted with toluene. The solution was kept at −30 °C for 12 h, and was decanted. The solvent was removed in vacuum. The residue was washed with hexane and diethyl ether to give **8** (0.839 g, 1.13 mmol, 75% yield) as white powder. Single crystals (with one molecule of hexane as a lattice solvent) suitable for X-ray analysis were grown from a hexane solution at −30 °C. ^{1}H NMR of *anti*-complex (400 MHz, C_6D_6, r.t., δ/ppm): −1.29 (d, J = 10.6 Hz, 2H, CH_2SiMe$_3$), −0.51 (d, J = 10.6 Hz, 2H, CH_2SiMe$_3$), 0.07 (s, 18H, CH$_2$Si(CH_3)$_3$), 1.44 (d, J = 13.3 Hz, 2H, NCH_2), 1.54 (d, J = 13.1 Hz, 2H, NCH_2), 1.89 (s, 6H, C$_5$(CH_3)$_4$), 2.00 (s, 6H, C$_5$(CH_3)$_4$), 2.15 (s, 6H, C$_5$(CH_3)$_4$), 2.36 (s, 6H, C$_5$(CH_3)$_4$), 2.68 (s, 6H, NCH_3), 6.95−7.15 (m, 8H, C$_6H_4$). ^{13}C NMR (75 MHz, C_6D_6, 50 °C, δ/ppm): 4.4 (s, CH$_2$Si(CH_3)$_3$), 12.2 (s, C$_5$(CH_3)$_4$), 13.0 (s, C$_5$(CH_3)$_4$), 13.1 (s, C$_5$(CH_3)$_4$), 13.4 (s, C$_5$(CH_3)$_4$), 39.0 (br, CH_2SiMe$_3$), 48.5 (NCH_3), 72.8 (NCH_2), 117.0, 119.3, 120.0, 120.5, 122.3, 123.5, 126.6, 128.7, 131.6, 133.9, 159.3 (aromatics and Cp ring carbons). Anal. calcd for $C_{48}H_{78}N_2Sc_2Si_2$ (**8**·C$_6$H$_{14}$): C, 69.52; H, 9.48; N, 3.38. Found: C, 69.52; H, 9.48; N, 3.59.

Synthesis of [(C$_5$H$_5$)Sc(CH$_2$SiMe$_3$)(THF)$_2$][B(C$_6$F$_5$)$_4$] (9). To a THF solution (5 mL) of (C$_5$H$_5$)Sc(CH$_2$SiMe$_3$)$_2$(THF) (**1**) (0.007 g, 21 μmol) was added 1 equiv of [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] (0.017 g, 21 μmol) in THF (5 mL) at room temperature. The pale-yellow mixture was stirred for 10 min. The solvent was removed in vacuum. The residue was washed with hexane several times and dried in vacuum to give **9** (0.021 g, 20.8 μmol, 99% yield) as white micro crystals. Single crystals for X-ray analysis were grown from a mixed solvent of THF/hexane (5/20 mL/mL) at −30 °C. Unfortunately, the X-ray structure of **9** could not be unambiguously determined completely because of the disorder of the cyclopentadienyl ligand. ^{1}H NMR (C$_4$D$_8$O, 22 °C, δ/ppm): −0.45 (s, 2H, CH_2SiMe$_3$), 0.01 (s, 9H, CH$_2$Si(CH_3)$_3$), 1.69−1.73 (br, 4H, THF-α-CH_2), 3.55−3.58 (br, 4 H, THF-β-CH_2), 6.47 (s, C$_5H_5$). ^{13}C NMR (C$_4$D$_8$O, 22 °C, δ/ppm): 4.2 (s, CH$_2$Si(CH_3)$_3$), 25.2 (s, THF), 40.1 (br, CH_2SiMe$_3$), 72.2 (s, thf), 112.5 (s, C$_5$H$_5$), 125.4 (m, C$_6$F$_5$-1), 137.2 (d, $^1J_{CF}$ = 245.7 Hz, C$_6$F$_5$-3), 139.1 (d, $^1J_{CF}$ = 242.0 Hz, C$_6$F$_5$-4), 149.3 (d, $^1J_{CF}$ = 241.5 Hz, C$_6$F$_5$-2). Anal. calcd for $C_{41}H_{32}BF_{20}O_2ScSi$: C, 48.25; H, 3.16. Found: C, 49.53; H, 3.66.

Synthesis of [(C$_5$Me$_4$SiMe$_3$)Sc(CH$_2$SiMe$_3$)(THF)$_2$][B(C$_6$F$_5$)$_4$] (10). To a 5 mL of THF solution of complex **5** (C$_5$Me$_4$SiMe$_3$)-Sc(CH$_2$SiMe$_3$)$_2$(THF) (0.012 g, 25 μmol) was added 1 equiv of [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] (0.020 g, 25 μmol) in THF (5 mL) at room temperature. The pale yellow mixture was stirred for 10 min. The solvent was removed in vacuum. The residue was washed with hexane several times and dried in vacuum to give **10** (0.028 g, 24.7 μmol, 99% yield) as white micro crystals. Single crystals suitable for X-ray analysis were grown from a mixed solvent of THF/hexane (5/20 mL/mL) at −30 °C. ^{1}H NMR (400 MHz, *o*-C$_6$D$_4$Cl$_2$, 23 °C, δ/ppm): −0.09 (s, 9H, CH$_2$Si(CH_3)$_3$), −0.02 (s, 2H, CH_2SiMe$_3$), 0.24 (s, 9H, C$_5$Me$_4$Si(CH_3)$_3$), 1.82 (s, 6H, C$_5$(CH_3)$_4$), 1.92 (br s, 8H, THF), 2.09 (s, 6H, C$_5$(CH_3)$_4$), 3.95 (m, 8 H, THF). ^{13}C NMR (99 MHz, *o*-C$_6$D$_4$Cl$_2$, 23 °C, δ/ppm): δ 1.9 (s, C$_5$Me$_4$Si(CH_3)$_3$), 3.4 (s, CH$_2$Si(CH$_3$)$_3$), 11.6 (s, C$_5$(CH_3)$_4$), 15.0 (s, C$_5$(CH_3)$_4$), 25.5 (s, THF), 50.9 (b, CH_2SiMe$_3$), 73.8 (s, THF), 124.4 (m, C$_6$F$_5$-1), 125.5 (s, *ipso*-C$_5$Me$_4$(SiMe$_3$)), 129.6 (s, C$_5$Me$_4$(SiMe$_3$)), 134.1 (s, C$_5$Me$_4$(SiMe$_3$)), 137.0 (d, $^1J_{CF}$ = 240.7 Hz, C$_6$F$_5$-3), 138.8 (d, $^1J_{CF}$ = 244.0 Hz, C$_6$F$_5$-4), 149.0 (d, $^1J_{CF}$ = 240.5 Hz, C$_6$F$_5$-2). ^{19}F NMR (*o*-C$_6$D$_4$Cl$_2$, 564 MHz, 25 °C, CFCl$_3$): −132.4 (s, *o*-C$_6$F$_5$), −162.8 (t, *p*-C$_6$F$_5$) −166.8 (s, *m*-C$_6$F$_5$). ^{11}B NMR (*o*-C$_6$D$_4$Cl$_2$, 192 MHz, 25 °C, BF$_3$·Et$_2$O): −16.8. Anal. calcd for $C_{48}H_{48}BF_{20}O_2ScSi_2$: C, 50.18; H, 4.21. Found: C, 50.50; H, 4.61.

Synthesis of [{C$_5$Me$_4$(C$_6$H$_4$OMe)}Sc(CH$_2$SiMe$_3$)(THF)$_2$]-[B(C$_6$F$_5$)$_4$] (11). To a THF solution (5 mL) of {C$_5$Me$_4$(C$_6$H$_4$OMe)}-Sc(CH$_2$SiMe$_3$)$_2$ (**7**) (0.011 g, 25 μmol) was added 1 equiv of [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] (0.020 g, 25 μmol) in THF (5 mL) at room temperature. The pale-yellow mixture was stirred for 10 min. The solvent was removed in vacuum. The residue was washed with hexane several times and dried in vacuum to give **11** (0.029 g, 24.7 μmol, 99% yield) as white micro crystals. Single crystals suitable for X-ray analysis were grown from a mixed solvent of THF/hexane (5/20 mL/mL) at −30 °C. ^{1}H NMR (C$_4$D$_8$O, 396 MHz, 23 °C, δ/ppm): −0.17 (s, 2H, CH_2SiMe$_3$), −0.06 (s, 9H, C$_5$Me$_4$Si(CH_3)$_3$), 1.78 (br s, 8H, THF), 2.01 (s, 6H, C$_5$(CH_3)$_4$), 2.31 (s, 6H, C$_5$(CH_3)$_4$), 3.62 (m, 8H, THF), 4.20 (s, 3H, OCH_3), 7.24 (d, 2H, -C$_6H_4$OMe), 7.34 (d, 1H, -C$_6H_4$OMe), 7.47 (m, 1H, -C$_6H_4$OMe). ^{13}C NMR (C$_4$D$_8$O, 99 MHz, 23 °C): δ 4.0 (s, C$_5$Me$_4$Si*Me*$_3$), 12.0 (s, C$_5$*Me*$_4$), 14.5 (s, C$_5$*Me*$_4$), 26.4 (s, THF), 32.6 (s, CH_2SiMe$_3$), 60.2 (s, OMe), 68.3 (s, THF), 112.2, 113.6, 117.7, 123.5, 124.9, 129.7, 130.3, 132.3, 159.0 (aromatics and Cp ring carbons), 125.7 (m, C$_6$F$_5$-1), 137.2 (d, $^1J_{CF}$ = 251.0 Hz, C$_6$F$_5$-3), 139.3 (d, $^1J_{CF}$ = 241.1 Hz, C$_6$F$_5$-4), 149.3 (d, $^1J_{CF}$ = 238.7 Hz, C$_6$F$_5$-2). ^{19}F NMR (C$_4$D$_8$O, 564 MHz, 25 °C, CFCl$_3$): −132.7 (s, *o*-C$_6$F$_5$), −165.0 (t, *p*-C$_6$F$_5$) −168.5 (s, *m*-C$_6$F$_5$). ^{11}B NMR (C$_4$D$_8$O, 192 MHz, 25 °C, BF$_3$·Et$_2$O): −16.6. Anal. calcd for $C_{52}H_{46}BF_{20}O_3ScSi$: C, 52.81; H, 3.92. Found: C, 53.42; H, 4.25.

A Typical Procedure for Isoprene (IP) Polymerization (Table 3, entry 1). In a glovebox, a chlorobenzene solution (5 mL) of $[Ph_3C][B(C_6F_5)_4]$ (0.023 g, 25 μmol) was added to a well-stirred chlorobenzene solution (5 mL) of complex **1** (0.009 g, 25 μmol) and isoprene (1.022 g, 15 mmol) at 25 °C in a 30-mL flask. The reaction mixture became viscous rapidly. After 5 min, the flask was taken outside and the polymerization was quenched by addition of methanol (50 mL, containing 5% butylhydroxytoluene (BHT) as a stabilizing agent). Then the mixture was poured into methanol (200 mL) to precipitate the polymer product. The precipitated polymer was dried under vacuum at 60 °C to a constant weight (1.020 g, 100% yield). The resulting polymer is soluble in THF and chloroform at room temperature.

The isomer contents of the polyisoprene products were calculated from the ^{1}H and ^{13}C NMR spectra according to the following formula (eqs 1−5):

$$\text{Mol 1,4-IP\%} = \{I_{H1}/(I_{H1} + 0.5I_{H2})\} \times 100 \quad (1)$$

$$\text{Mol 3,4-IP\%} = \{0.5I_{H2}/(I_{H1} + 0.5I_{H2})\} \times 100 \quad (2)$$

in which I_{H1} is the integration of the resonance at 5.13 ppm (one vinyl proton of the 1,4-isoprene unit), and I_{H2} is the integration of the resonance at 4.72 ppm (two vinyl protons of the 3,4-isoprene unit) in the ^{1}H NMR spectrum.

$$\text{Mol } \textit{cis}\text{-1,4-IP\%} = \{I_{C1}/(I_{C1}+I_{C2}+I_{C3})\} \times 100 \quad (3)$$

$$\text{Mol } \textit{trans}\text{-1,4-IP\%} = \{I_{C3}/(I_{C1}+I_{C2}+I_{C3})\} \times 100 \quad (4)$$

$$\text{Mol 3,4-IP\%} = \{I_{C2}/(I_{C1}+I_{C2}+I_{C3})\} \times 100 \quad (5)$$

in which I_{C1} is the integration of the signals at 23.2 ppm assigned as the methyl carbon of the *cis*-1,4-isoprene unit, and I_{C2} is the integration of the signals at 18.5 ppm assigned as the methyl carbon of the 3,4-isoprene unit, while I_{C3} is the integration of the signals at 15.9 ppm assigned as the methyl carbon of the *trans*-1,4-isoprene unit in the ^{13}C NMR spectrum.

A Typical Procedure for the Copolymerization of Isoprene (IP) with Ethylene (E) (Table 4, entry 32). In a glovebox, a chlorobenzene solution (30 mL) of isoprene (3.406 g, 50 mmol) was charged into a two-necked flask with a magnetic stir bar. The flask was taken outside, set in a water bath (25 °C), and connected to a well-purged Schlenk ethylene line and a mercury-sealed stopper by use of a three-way cock. Ethylene (1 atm) was introduced into the system and was saturated in the solution by stirring for 2 min. A chlorobenzene solution (10 mL) of $(C_5Me_4(C_6H_4OMe\text{-}o))Sc(CH_2SiMe_3)_2$ (**7**) (0.011 g, 25 μmol) and $[PhNMe_2H][B(C_6F_5)_4]$ (0.020 g, 25 μmol) was then added through a syringe under vigorous stirring. The reaction mixture became viscous rapidly. The polymerization was quenched after 5 min by addition of methanol (300 mL, containing 5% butylhydroxytoluene (BHT) as a stabilizing agent). The polymer product was collected by filtration, washed with methanol, and then dried *in vacuum* at room temperature to a constant weight (2.71 g, 1.3×10^3 kg of copolymer/mol-Sc·h·atm). The resulting polymer is soluble in dichlorobenzene and 1,1,2,2-tetrachloroethane.

The IP contents in the copolymers were calculated from the ^{1}H and ^{13}C NMR spectra according to eq 6, whereas the isoprene isomer units in the copolymer chains were calculated according to eqs 1−5 as described above.

$$\text{Mol IP\%} = \{(I_{H1} + 0.5I_{H2})/(I_{H1} + 0.5I_{H2} + 0.25(I_{H5} - I_{H2}))\} \times 100 \quad (6)$$

in which I_{H5} is the integration of the broad signals at 1.3 ppm as the total methylene protons in both 3,4-isoprene units and ethylene units in the ^{1}H NMR spectrum.

X-Ray Crystallographic Analysis. A crystal was selected and sealed in a thin-walled glass capillary under a microscope in a glovebox. Data collections were performed at −100 °C on a Bruker SMART APEX diffractometer with a CCD area detector using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). The determination of crystal class and unit cell was carried out by SMART program package.[27] The raw frame data were processed using SAINT[28] and SADABS[29] to yield the reflection data file. The structures were solved by using SHELXTL program.[30] Refinements were performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The analytical scattering factors for neutral atoms were used throughout the analysis. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. The residual electron densities were of no chemical significance. The methyl carbon and silicon atoms of CH_2SiMe_3 (Si2/Si3, C7/C9) in **6** were disordered (50:50 occupancy). Crystal data, data collection and processing parameters for compounds **1**−**8**, **10**, and **11** are summarized in Supporting Information. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-738570 (**1**), −738573 (**2**), −738574 (**3**), −738575 (**4**), −256379 (**5**), −738576 (**6**), −738577 (**7**), −738578 (**8**), −738571 (**10**), and −738572 (**11**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Details. The geometry optimizations and energy estimations were carried out with B3LYP density functional method,[31] which is adopted in Gaussian 03 program.[32] The 6-31G(D) basis set was considered for the entire coordinate complexes. The initial structures of active species were from their crystal structures. Since there is no symmetry in these complexes, A C1 symmetry point group was used throughout all calculations, and no higher molecular symmetry restriction was imposed. All calculations were performed utilizing the Gaussian 03 program.

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Supporting Information Available: Detailed experimental procedures and spectra of representative polymer products. Complete ref 32. This material is available free of charge via the Internet at http://pubs.acs.org.

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