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Cationic Scandium Allyl Complexes Bearing Mono(cyclopentadienyl) Ligands: Synthesis, Novel Structural Variety, and Olefin-Polymerization Catalysis

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Dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday

Abstract: The one-pot salt-metathesis reaction of $ScCl_3$, cyclopentadienyl lithium salts, and allylmagnesium chlorides afforded with ease the corresponding base-free half-sandwich scandium di(η^3-allyl) complexes $[(C_5Me_4SiMe_3)Sc(C_3H_5)_2]$ (**1a**), $[(C_5Me_5)Sc(C_3H_5)_2]$ (**1b**), and $[(C_5Me_5)Sc(2\text{-}MeC_3H_4)_2]$ (**1c**) in high yields. Reaction of **1a** with 1 equivalent of $[PhNMe_2H][B(C_6F_5)_4]$ in toluene gave rapidly the *N*,*N*-dimethylaniline-coordinated cationic mono(η^3-allyl) complex $[(C_5Me_4SiMe_3)Sc(\eta^3\text{-}C_3H_5)(\eta^6\text{-}PhNMe_2)][B(C_6F_5)_4]$ (**2**). The similar reaction of **1a** with $[Ph_3C][B(C_6F_5)_4]$ yielded the analogous toluene-separated ion pair $[(C_5Me_4SiMe_3)Sc(\eta^3\text{-}C_3H_5)(\eta^6\text{-}PhMe)][B(C_6F_5)_4]$ (**3**). When $[PhNMe_2H][BPh_4]$ was treated with **1a**, the contact ion pair $[(C_5Me_4SiMe_3)Sc(\eta^3\text{-}C_3H_5)(\mu,\eta^6\text{-}Ph)BPh_3]$ (**4**) was obtained. Recrystallization of **2**, **3**, and **4** in THF yielded the corresponding thf-separated ion pair complexes $[(C_5Me_4SiMe_3)Sc(\eta^3\text{-}C_3H_5)(thf)_2][B(C_6F_5)_4]$ (**5**) and $[(C_5Me_4SiMe_3)Sc(\eta^3\text{-}C_3H_5)(thf)_2][BPh_4]$ (**6**). The *N*,*N*-dimethylaniline-coordinated cationic scandium allyl complex **2** and the toluene-coordinated analogue **3** showed high activity (activity: **3**>**2**) toward the polymerization and copolymerization of isoprene and norbornene to afford random copolymers with a broad range of isoprene content (33–86 mol %). The tight ion pair **4** and the thf-coordinated complexes **5** and **6** showed no activity under the same conditions. These results offer unprecedented insight into the structure–activity relationship of a cationic metal polymerization-catalyst system.

Keywords: allyl ligands · cationic complexes · copolymerization · Lewis bases · metallocenes

Introduction

Cationic rare-earth-metal alkyl complexes have received much current interest as a new family of olefin-polymerization catalysts.[1–3] Among them, the half-sandwich complexes that bear mono(cyclopentadienyl) (Cp) ligands exhibit unique characteristics with regard to reactivity and monomer scope in polymerization catalysis.[1,2] However, structurally well-defined cationic half-sandwich rare-earth alkyl complexes remain scarce,[2c,g,l] in contrast with the large number of Cp-free analogues.[3] A major problem that hampered the isolation and structural characterization of cationic mono(cyclopentadienyl) rare-earth alkyl complexes is facile ligand scrambling in these complexes. From the viewpoint of the balance between stability and reactivity, rare-earth allyl complexes are of much interest because the allyl unit can exhibit both π-η^3 and σ forms, thus offering higher stability as well as appropriate activity. Although a number of rare-earth allyl complexes have been reported,[4,5] cationic rare-earth allyl complexes have received much less attention, and so far only one structurally characterized example, $[Nd(C_3H_5)Cl(thf)_5][B(C_6F_5)_4]$, which is stabilized by five thf ligands and showed no activity toward olefin polymerization, was reported in the literature.[5k]

During our recent studies on cationic rare-earth alkyl and hydride complexes,[2a,b,f–k,3a,e,f,6] we became interested in the analogous allyl complexes. We report herein a novel family of cationic mono(cyclopentadienyl)scandium allyl complexes generated by the reactions of neutral di(allyl) precursors

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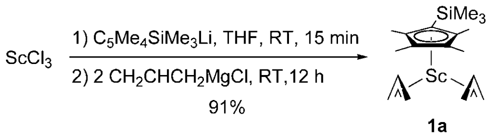
with various activators such as [$PhNMe_2H$][$B(C_6F_5)_4$], [Ph_3C][$B(C_6F_5)_4$], and [$PhNMe_2H$][BPh_4]. Well-defined cationic half-sandwich allyl complexes with various Lewis base ligands such as toluene, *N*,*N*-dimethylaniline, and thf were isolated under appropriate conditions. Novel structure variations with the Cp ligands, the Lewis base ligands, and the counteranions were observed. These cationic complexes were examined as catalysts for the polymerization and copolymerization of isoprene and norbornene, which demonstrated significant influence of the Lewis base ligands and the counteranions on the catalytic activity of the polymerization. Some of these complexes showed unique activity for the copolymerization of isoprene and norbornene to afford random isoprene–norbornene copolymers that were previously unavailable.

Results and Discussion

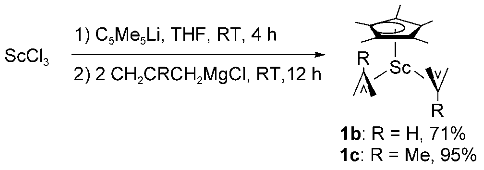
Synthesis and Characterization of Neutral Di(allyl) Complexes

The one-pot reaction of $ScCl_3$ with 1 equivalent of $LiC_5Me_4SiMe_3$ followed by addition of 2 equivalents of allylmagnesium chloride in THF at room temperature afforded the corresponding half-sandwich di(η^3-allyl) complex [$(C_5Me_4SiMe_3)Sc(\eta^3\text{-}C_3H_5)_2$] (**1a**) in 91 % yield (Scheme 1).



Scheme 1. Synthesis of neutral half-sandwich scandium di(η^3-allyl) complex **1a**.

The similar reaction of $ScCl_3$ with LiC_5Me_5 and allylmagnesium chloride or 2-methylallylmagnesium chloride yielded [$(C_5Me_5)Sc(\eta^3\text{-}CH_2CHCH_2)_2$] (**1b**) or [$(C_5Me_5)Sc(\eta^3\text{-}CH_2CMeCH_2)_2$] (**1c**), respectively (Scheme 2). Although complexes **1a–c** were isolated from THF, the incorporation of a thf ligand in these complexes was not observed, which is in contrast with the previously reported η^1-alkyl analogues such as [$(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)_2(thf)$], from which removal of the strongly coordinating thf ligand was difficult.[2b,h,i,k] These results demonstrate that the allyl group is more suitable for the preparation of a thf-free rare-earth complex than a simple alkyl group because of the π-η^3 bonding mode of the former.



Scheme 2. Synthesis of neutral half-sandwich scandium di(η^3-allyl) complexes **1b** and **1c**.

Complexes **1a–c** were structurally characterized by X-ray diffraction. Selected bond lengths and angles are summarized in Table 1. The ORTEP drawing of **1a** is shown in Figure 1, and those of **1b** and **1c** are given in Figure 2. The overall structural features of **1a–c** are similar: the Sc metal center and the centroids of the Cp ring and the two allyl units are coplanar. Complex **1b** contains a mirror plane that bisects the C_5Me_5 and allyl ligands (Figure 2, left). In **1b** and **1c**, one allyl ligand adopts a prone orientation, whereas the other is supine. In contrast, the two allyl ligands in **1a** are all prone, probably due to steric repulsion between the bulky $C_5Me_4SiMe_3$ ligand and the terminal allyl protons. The bond lengths of the terminal Sc–C(allyl) bonds in **1a** (average 2.445(5) Å) are comparable with those of the central Sc–C(allyl) bonds (average

Table 1. Selected bond lengths/distances (Å) and angles (°) for **1a–c**.

	1a	**1b**	**1c**
Sc–C(Cp) (average)	2.477(3)	2.463(3)	2.485(3)
Sc–C_{AT}[a]	2.433(4)	2.424(3)	2.397(2)
	2.460(4)	2.434(3)	2.397(2)
	2.419(4)	2.460(3)	2.435(2)
	2.466(5)	2.440(3)	2.435(2)
Sc–C_{AC}[b]	2.430(5)	2.415(3)	2.494(3)
	2.452(6)	2.439(3)	2.512(3)
C_{AT}–C_{AC}–C_{AT}[a,b]	130.2(6)	125.3(3)	121.7(3)
	131.8(8)	134.8(4)	122.5(3)
Cent1–Sc–Cent2[c]	121.65	120.10	123.14
Cent1–Sc–Cent3[c]	118.70	124.79	124.75
Cent2–Sc–Cent3[c]	119.11	115.09	112.11

[a] C_{AT} = terminal allylic carbon atom. [b] C_{AC} = central allylic carbon atom. [c] Cent1, Cent2, and Cent3 are the centroids of the cyclopentadienyl ring and the two allyl ligands, respectively.

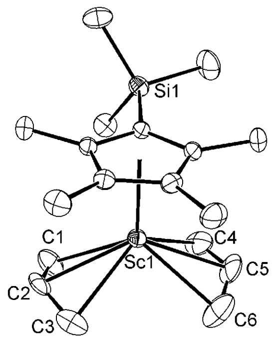


Figure 1. ORTEP drawing of **1a** with thermal ellipsoids at 30 % probability. Hydrogen atoms are omitted for clarity.

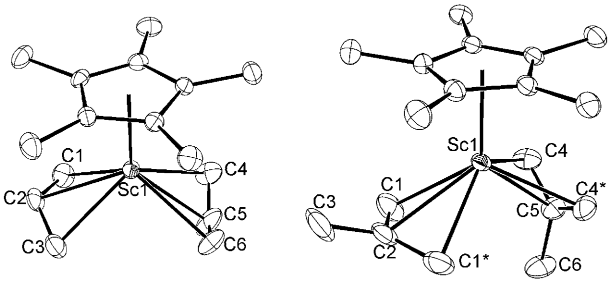


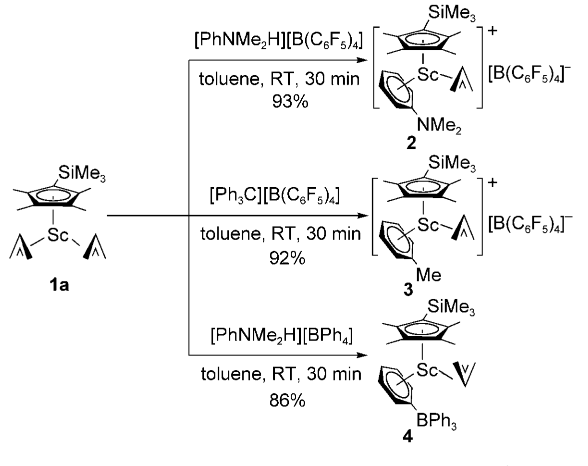
Figure 2. ORTEP drawings of **1b** (left) and **1c** (right) with thermal ellipsoids at 30 % probability. Hydrogen atoms are omitted for clarity.

2.441(6) Å); so are those in **1b** (terminal: 2.440(3) Å; central: 2.427(3) Å). However, the central Sc–C(allyl) bonds (average 2.503(3) Å) in **1c** are significantly longer than those of the terminal Sc–C(allyl) bonds (average 2.416(2) Å), which indicates that the central Sc–C(allyl) bonds in **1c** are weaker than the terminal Sc–C(allyl) bonds, probably due to steric hindrance of the methyl group at the central atom of the allyl unit. The bond lengths of the Sc–C(Cp) bonds of **1a–c** fall in the normal range of cyclopentadienyl–Sc complexes.

The ^{1}H NMR spectra of **1a–c** in [D$_8$]toluene are temperature-dependent, which indicates that these complexes are fluxional in solution. At room temperature, complex **1a** showed two broad signals for the terminal allylic protons (H_{syn} and H_{anti}) and one multiplet for the central allylic protons. At −80 °C, however, the terminal allylic protons showed four doublets, and the central allylic protons gave two multiplets, which suggest that the two allyl units in **1a** are no longer equivalent: one could be in the prone orientation and the other might be supine, an arrangement different from that of its solid structure. At 100 °C, the central allylic protons showed one doublet, which demonstrates a rapid exchange between the two isomers. A similar fluxionality was also observed previously in *ansa*-scandocene allyl complexes.[5m,o]

Synthesis and Characterization of Cationic Allyl Complexes

The reaction of the di(allyl) complex **1a** with 1 equivalent of [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] in toluene or chlorobenzene took place rapidly to give the cationic mono(allyl) complex **2**, which bears an *N*,*N*-dimethylaniline ligand at the metal center (Scheme 3). In contrast, the similar reaction of **1a** with [Ph$_3$C][B(C$_6$F$_5$)$_4$] in toluene yielded the toluene-coordinated analogue **3**. The use of chlorobenzene as a solvent for the reaction of **1a** with [Ph$_3$C][B(C$_6$F$_5$)$_4$] in the absence of toluene gave unidentified oily products. These results suggest that the coordination of a Lewis base (even one as weak as toluene) to the metal center could play an important role in the stabilization of the cationic species. Addition of 1 equivalent of *N*,*N*-dimethylaniline to **3** in [D$_5$]chlorobenzene led to rapid formation of **2** and free toluene as monitored by ^{1}H NMR spectroscopy, which suggests that *N*,*N*-dimethylaniline is a more strongly coordinating ligand than toluene.



Scheme 3. Synthesis of cationic half-sandwich scandium η^3-allyl complexes.

The allyl ligands in both **2** and **3** adopt the prone orientation, as shown by X-ray analysis (Figures 3 and 4). The Sc–C$_{allyl}$ bond lengths in **2** (average 2.561(7) Å) are significantly longer than those in **3** (average 2.459(4) Å) (Table 2), apparently due to the influence of the coordination of *N*,*N*-dimethylaniline to the metal center in **2**, which is stronger than that of toluene in **3** (see below). Notably, the *N*,*N*-dimethylaniline ligand in **2** is bonded to the metal center only through the phenyl ring in a highly tilted η^6 manner, in which the Sc–C(*para*) bond is the shortest (2.495(4) Å) and the Sc–C(*ipso*) bond is the longest (2.881(1) Å), whereas an interaction between the amine group and the metal center was not observed (Sc···N separation: 3.846 Å) (Figure 3). This bonding mode is in sharp contrast with that proposed previously for the interaction between *N*,*N*-dimethylaniline

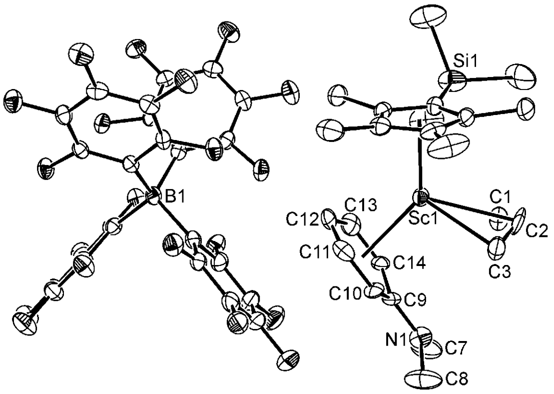


Figure 3. ORTEP drawing of **2** with thermal ellipsoids at 20 % probability. Hydrogen atoms are omitted for clarity.

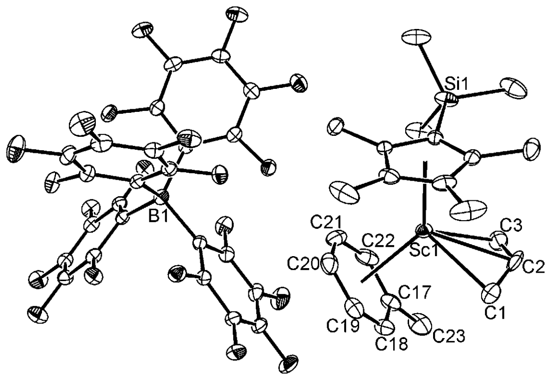


Figure 4. ORTEP drawing of **3** with thermal ellipsoids at 20 % probability. Hydrogen atoms are omitted for clarity.

Table 2. Selected bond lengths/distances (Å) and angles (°) for **2**–**4**.

	2	3	4
Sc1–C(Cp) (average)	2.456(4)	2.464(2)	2.486(2)
Sc1–C1	2.575(6)	2.454(3)	2.409(2)
Sc1–C2	2.584(9)	2.498(5)	2.452(2)
Sc1–C3	2.523(5)	2.417(3)	2.515(2)
Sc1–C(arene)	2.881(7)	2.920(3)	2.816(2)
	2.760(7)	2.888(3)	2.765(2)
	2.539(4)	2.746(3)	2.679(2)
	2.495(4)	2.630(3)	2.629(2)
	2.528(4)	2.621(3)	2.632(2)
	2.701(6)	2.750(3)	2.670(2)
C1–C2–C3	126.3(11)	126.9(6)	125.7(3)
Cent1–Sc1–Cent2[a]	135.67	135.67	133.14
Cent1–Sc1–Cent3[a]	112.06	112.64	117.14
Cent2–Sc1–Cent3[a]	111.87	111.32	109.65

[a] Cent1, Cent2, and Cent3 are the centroids of the Cp ring, the coordinated arene ring, and the allyl ligand, respectively.

and cationic Group 4 metal centers, in which the bonding interaction between the amine group and the metal center was thought to be essential.[7] To the best of our knowledge, complex **2** represents the first example of a crystallographically characterized *N,N*-dimethylaniline-coordinated cationic metal complex.[7,8] The average bond distance of the Sc–C_{arene} bonds in **2** (2.651(5) Å) is around 0.1 Å shorter than that in **3** (2.759(3) Å), in agreement with the fact that *N,N*-dimethylaniline is much more electron-donating than toluene. The π–π stacking interactions between the phenyl plane of the *N,N*-dimethylaniline ligand and one C_6F_5 group of the counteranion $[B(C_6F_5)_4]^-$ in both **2** and **3** were observed. The distances between the phenyl plane of the *N,N*-dimethylaniline ligand and the C_6F_5 plane of the counteranion $[B(C_6F_5)_4]^-$ in **2** and **3** are 3.30(1) and 3.40(1) Å, with dihedral angles of 7.6(3) and 3.8(2)°, respectively (Figures 3 and 4).

To see the influence of the counteranion on the structure of the cationic species, the reaction of $[PhNMe_2H][BPh_4]$ with **1a** in toluene was carried out, which gave the Lewis base free contact-ion-pair complex $[(C_5Me_4SiMe_3)Sc(\eta^3\text{-}C_3H_5)(\mu,\eta^6\text{-}PhBPh_3)]$ (**4**) in 86% yield (Scheme 3). This is in contrast with the formation of the solvent/Lewis base separated ion pairs **2** and **3** in the cases of perfluorophenyl borates $(PhNMe_2H)[B(C_6F_5)_4]$ and $[Ph_3C][B(C_6F_5)_4]$, and is in accordance with the fact that $[BPh_4]^-$ is more strongly coordinating than $[B(C_6F_5)_4]^-$. Interestingly, only one of the four Ph groups in $[BPh_4]^-$ showed bonding interactions with the Sc atom in **4** in an η^6 manner (Figure 5 and Table 2). In most of the previously reported rare-earth tetraphenyl borate complexes, such as $[(Me_3Si)_2NYb(\mu\text{-}\eta^6\text{:}\eta^1\text{-Ph})_2BPh_2(thf)]$,[9a] $[(C_5Me_5)Sm(\mu\text{-}\eta^6\text{:}\eta^1\text{-Ph})_2BPh_2]$,[9b] $[(C_5Me_5)Sm(\mu,\eta^6\text{:}\eta^1\text{-Ph})BPh_3(N_2Ph_2)]$,[9b] and $[(C_5Me_5)_2M(\mu,\eta^2\text{-Ph})_2BPh_2)]$ (M = Y,[5b] Nd,[5p] Sm,[5e] Gd,[5b] Lu[5e]), a chelating interaction between two phenyl groups of the $[BPh_4]^-$ anion and the metal center was observed. The allyl ligand in **4** is oriented in a supine manner, in contrast with the prone configuration in **2** and **3**, apparently due to steric hindrance of the $[B(C_6F_5)_4]^-$ unit in **4**.

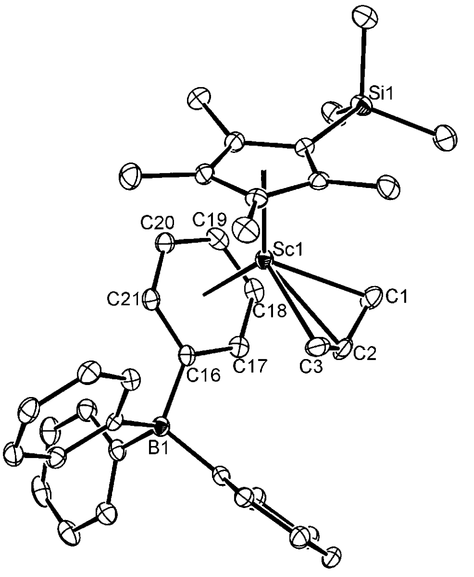
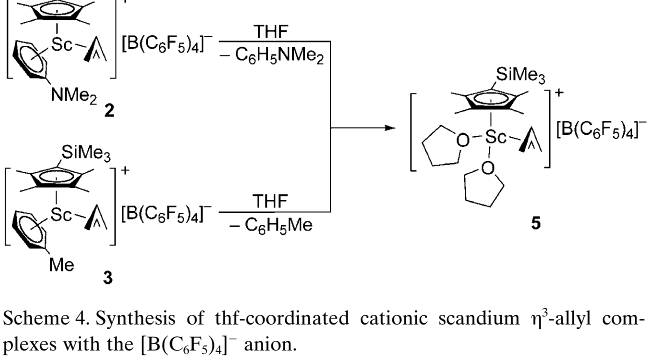


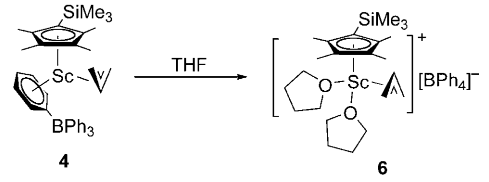
Figure 5. ORTEP drawing of **4** with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity.

The cationic allyl complexes **2**–**4** are fluxional in solution, as shown by the ^{1}H NMR spectra in [D$_5$]chlorobenzene. However, interaction between the *N,N*-dimethylaniline ligand and the metal ion in **2** is evident, as indicated by the downfield shift of its ^{1}H NMR peaks relative to those of free *N,N*-dimethylaniline.[7,10] The methyl group of the toluene ligand in **3** showed a sharp singlet at 2.18 ppm, which was shifted slightly downfield to that of free toluene (2.14 ppm).

The *N,N*-dimethylaniline ligand in **2** and the toluene ligand in **3** could be easily replaced by thf. Recrystallization of **2** and **3** in THF gave quantitatively the thf adduct $[(C_5Me_4SiMe_3)Sc(\eta^3\text{-}C_3H_5)(thf)_2][B(C_6F_5)_4]$ (**5**; Scheme 4). Similarly, recrystallization of the contact ion pair **4** in THF yielded the thf-separated ion pair $[(C_5Me_4SiMe_3)Sc(\eta^3\text{-}C_3H_5)(thf)_2][BPh_4]$ (**6**; Scheme 5). The allyl ligand in **6** adopts a prone configuration (Figure 6), in contrast with the supine orientation in the precursor **4**, apparently due to the re-



Scheme 4. Synthesis of thf-coordinated cationic scandium η^3-allyl complexes with the $[B(C_6F_5)_4]^-$ anion.



Scheme 5. Synthesis of a thf-coordinated cationic scandium η^3-allyl complex with the $[BPh_4]^-$ anion.

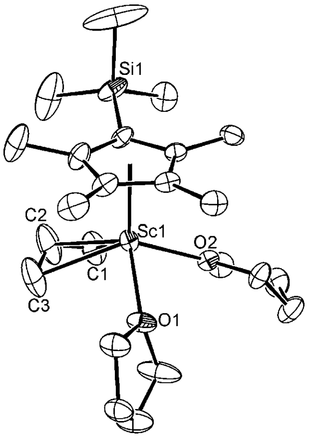


Figure 6. ORTEP drawing of the cationic part of **6** with thermal ellipsoids at 30% probability. Hydrogen atoms and the solvent THF molecule in the lattice are omitted for clarity. Selected bond lengths/distances [Å] and angles [°]: Sc1-C(Cp) (average) 2.484(4), Sc1-C1 2.370(5), Sc1-C2 2.431(5), Sc1-C3 2.485(5), Sc1-O1 2.174(3), Sc1-O2 2.185(3); C1-C2-C3 127.0(7), O1-Sc1-O2 82.45(10).

placement of the sterically demanding BPh_4 ligand by thf at the metal center.

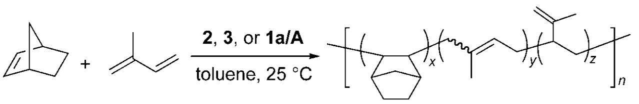
Polymerization and Copolymerization of Isoprene and Norbornene

The *N*,*N*-dimethylaniline-coordinated complex **2** and the toluene-coordinated analogue **3** showed high activity toward the polymerization of isoprene at room temperature in toluene to afford polyisoprene with mixed 1,4- and 3,4-microstructures and a narrow molecular-weight distribution (Table 3, entries 1 and 2), similar to the analogous cationic alkyl catalyst system $[(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)_2(thf)]/[Ph_3C][B(C_6F_5)_4]$.[2b] In this polymerization, the toluene-coordinated complex **3** exhibited higher activity than the *N*,*N*-dimethylaniline adduct **2**, in agreement with the above observation that the coordination of toluene to the metal center is weaker than that of *N*,*N*-dimethylaniline. Complexes **5** and **6**, which bear more strongly coordinating thf ligands, showed no activity under the same conditions. These results clearly indicate that replacement of a Lewis base or solvent ligand with an olefin monomer at the metal center is essential for initiating the polymerization reaction. The neutral complex **1a** and the cationic complex **4**, which bears $[BPh_4]^-$ as a counteranion, were inactive under the same conditions, in contrast with the highly active perfluorophenyl borate complexes **2** and **3**, thus demonstrating that the formation of a cationic species with a weakly coordinating counteranion is critically important for generating an active polymerization catalyst. Although significant influences of solvent and activator on the catalytic activity of various cationic metal polymerization-catalyst systems have been observed previously, as far as we are aware this is the first example to clarify these effects on the basis of a family of well-defined cationic metal complexes. More remarkably, complexes **2** and **3** were also active toward the polymerization of norbornene and led to the selective copolymerization of isoprene and norbornene in the presence of the two monomers (Table 3, entries 3–6). The use of the isolated cationic allyl complexes was not necessarily required for these polymerization reactions. The combination of the neutral complex **1a** with $[PhNMe_2H][B(C_6F_5)_4]$ was also effective (Table 3, entries 7–10). Isoprene incorporation in the present copolymerization reactions was easily controlled simply by changing the isoprene/norbornene feed ratio to give the corresponding random copolymers with a wide range of isoprene content (33–86 mol%; Table 3, entries 5–10). It is usually difficult to incorporate isoprene into a cyclic olefin copolymer by other catalysts.[11] The only previously reported isoprene–norbornene copolymerization was catalyzed by a nickel-based catalyst, but with much lower isoprene incorporation.[12] The present allyl catalyst systems are also highly active toward the copolymerization of ethylene with norbornene and the copolymerization of ethylene with styrene, as reported previously for analogous alkyl catalysts.[1b,2a,g–k]

Conclusions

We have demonstrated that base-free half-sandwich scandium di(η^3-allyl) complexes such as **1a**–**c** can be easily prepared by one-pot salt-metathesis reactions of $ScCl_3$, cyclopentadienyl lithium salts, and allylmagnesium chloride. By treatment of the diallyl complex **1a** with 1 equivalent of $[PhNMe_2H][B(C_6F_5)_4]$ in toluene, the structurally characterizable *N*,*N*-dimethylaniline-coordinated cationic allyl complex **2** was isolated. In contrast, the similar reaction of **1a** with $[Ph_3C][B(C_6F_5)_4]$ afforded the toluene-coordinated analogue **3**, whereas the reaction of **1a** with $[PhNMe_2H][BPh_4]$ yielded the solvent/Lewis base free contact-ion-pair complex **4**. These results demonstrate well that *N*,*N*-dimethylaniline is more strongly coordinating than toluene, and that $[B(C_6F_5)_4]^-$ is a more weakly coordinating anion than $[BPh_4]^-$. When **2**–**4** were dissolved in more strongly coordinating THF, the corresponding thf-coordinated cationic complexes **5** and **6** were obtained. Complexes **2**–**6** constitute a novel family of structurally well-defined cationic allyl complexes with different Lewis base/solvent ligands and different counteranions, thus offering an unprecedented structural basis for the understanding of the effects of activator and solvent on the activity of cationic rare-earth and related polymeri-

Table 3. Polymerization and copolymerization of isoprene (IP) and norbornene (NB) by cationic η^3-allyl scandium complexes.[a]



Entry	Cat.	NB [mmol]	IP [mmol]	Yield [%]	Activity [kg-(polymer) mol(Sc)$^{-1}$ h^{-1}]	M_n[c] (10^4)	M_w/M_n[c]	IP content[d] [mol %]	T_g[e] [°C]
1	**2**	0	5	85	46.4	3.3	1.12	100	−1.9
2	**3**	0	5	91	49.6	2.2	1.12	100	−6.9
3[b]	**2**	5	0	59	0.93	0.5	1.70	–	380.0
4[b]	**3**	5	0	66	1.03	0.4	1.81	–	384.7
5	**2**	5	5	35	44.8	2.5	1.33	81	13.4
6	**3**	5	5	44	57.6	2.3	1.13	69	20.2
7	**1a/A**	5	5	37	48.0	1.5	1.29	86	9.4
8	**1a/A**	25	5	7	30.4	1.3	1.45	56	45.6
9	**1a/A**	35	5	3	18.4	1.4	1.43	43	53.4
10	**1a/A**	50	5	1	5.6	0.9	1.59	33	66.1

[a] Conditions: [Sc] (25 μmol), **A** = [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] (25 μmol), toluene (25 mL), 25 °C, 15 min, unless otherwise noted. [b] Polymerization time = 12 h. [c] Determined by GPC against polystyrene standard. [d] Determined by ^{1}H NMR spectroscopy; 1,4-/3,4-IP ≈ 30:70. [e] Measured by DSC.

zation-catalyst systems. The high incorporation of isoprene in the copolymerization of isoprene and norbornene catalyzed by **2**, **3**, and **1a**/[PhNMe$_2$H][B(C$_6$F$_5$)$_4$] demonstrates that cationic half-sandwich rare-earth metal allyl complexes can serve as a new family of polymerization catalysts.

Experimental Section

General Procedure and Materials

All manipulations were performed under pure argon with rigorous exclusion of air and moisture by using standard Schlenk techniques or in a nitrogen-filled Mbraun glovebox. Argon (>99.9 %, research grade, Takachiho Chemical Industrial Co., Ltd.) was purified by passing it 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. Samples for NMR spectroscopic measurements were prepared in the glovebox with J. Young valve NMR tubes. NMR (^{1}H, ^{13}C, ^{11}B, ^{19}F) spectra were recorded on JNM-AL 300, JNM-AL 400, and JEOL ECA-600 spectrometers. ^{19}F and ^{11}B NMR spectra were referenced to external CFCl$_3$ and BF$_3$·Et$_2$O, respectively. Elemental analysis was performed on a MICRO CORDER JM10 instrument (J-SCIENCE LAB Co.). Molecular weights and molecular-weight distributions of polymer samples were determined by gel permeation chromatography on a TOSOH HLC-8220 GPC chromatograph (column: Super HZM-H × 3) at 40 °C with THF as an eluent at a flow rate of 0.35 mL min^{-1} against polystyrene standards. DSC measurements were performed on an SII DSC6220 instrument at a heating rate of 20 °C min^{-1} under nitrogen atmosphere. ScCl$_3$ was purchased from Strem. [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] and [Ph$_3$C][B(C$_6$F$_5$)$_4$] were obtained from Tosoh Finechem Corporation and used without purification. [PhNMe$_2$H][BPh$_4$][13] was prepared according to literature procedures. Allylmagnesium chloride (2.0 M in THF) and 2-Me-allylmagnesium chloride (2.0 M in THF) were purchased from Aldrich. Isoprene was purchased from Junsei Chemical Co., Ltd., dried over CaH$_2$, vacuum transferred, and degassed by two freeze–pump–thaw cycles. Norbornene was purchased from Aldrich, dried over sodium, vacuum transferred, and degassed by two freeze–pump–thaw cycles. Deuterated solvents [D$_5$]chlorobenzene (99 atom % D), [D$_6$]benzene (99.6 atom % D), and 1,1,2,2,-[D$_2$]tetrachloroethane (99.6 atom % D) were purchased from Cambridge Isotope.

Syntheses

1a: *n*BuLi (0.38 mL, 1 mmol, 2.63 M in hexane) was added dropwise to a solution of C$_5$Me$_4$H(SiMe$_3$) (195 mg, 1 mmol) in THF (10 mL). After 15 min, the reaction mixture (containing LiC$_5$Me$_4$SiMe$_3$ prepared in situ) was added to a suspension of ScCl$_3$ (151 mg, 1 mmol) in THF (20 mL). The mixture was stirred for 30 min to afford a clear solution, to which C$_3$H$_5$MgCl (1 mL, 2 mmol, 2.0 M in THF) was added. The resulting light-yellow solution was left overnight. Removal of volatiles yielded a yellow residue, which was extracted with hexane. Evaporation of the solvent gave **1a** as a red crystalline solid (291 mg, 91 %). Recrystallization from hexane gave single crystals suitable for X-ray analysis. ^{1}H NMR (C$_6$D$_6$, 25 °C): δ = 7.03–7.19 (m, 2H, CH$_2$C*H*CH$_2$), 3.76 (br s, 4H, C*H$_2$*CHC*H$_2$*), 2.92 (br s, 4H, C*H$_2$*CHC*H$_2$*), 2.22 (s, 6H, C$_5$Me$_4$), 1.73 (s, 6H, C$_5$Me$_4$), 0.17 ppm (s, 9H, C$_5$Me$_4$Si*Me$_3$*); ^{13}C NMR (C$_6$D$_6$, 25 °C): δ = 157.9 (CH$_2$*C*HCH$_2$), 130.7 (*C$_5$*Me$_4$SiMe$_3$), 125.8 (*C$_5$*Me$_4$SiMe$_3$), 119.1 (C$_{ipso}$ of *C$_5$*Me$_4$SiMe$_3$), 79.3 (*C*H$_2$CH*C*H$_2$), 16.0 (C$_5$*Me$_4$*SiMe$_3$), 12.2 (C$_5$*Me$_4$*SiMe$_3$), 2.2 ppm (C$_5$Me$_4$Si*Me$_3$*); elemental analysis: calcd for C$_{18}$H$_{31}$ScSi: C 67.46, H 9.75; found: C 67.40, H 9.22.

1b: *n*BuLi (0.38 mL, 1 mmol, 2.63 M in hexane) was added dropwise to a solution of C$_5$Me$_5$H (136 mg, 1 mmol) in THF (10 mL). After 15 min, the reaction mixture (containing LiC$_5$Me$_5$ prepared in situ) was added to a suspension of ScCl$_3$ (151 mg, 1 mmol) in THF (20 mL). The mixture was stirred for 4 h to afford a clear solution, to which C$_3$H$_5$MgCl (1 mL, 2 mmol, 2.0 M in THF) was added. The resulting light-yellow solution was left overnight. Removal of volatiles yielded a yellow residue, which was extracted with hexane. Evaporation of the solvent gave **1b** as a red crystalline solid (187 mg, 71 %). Recrystallization from hexane gave single crystals suitable for X-ray analysis. ^{1}H NMR (C$_6$D$_6$, 25 °C): δ = 6.72–6.91 (m, 2H, CH$_2$C*H*CH$_2$), 3.03 (br s, 8H, C*H$_2$*CHC*H$_2$*), 1.61 ppm (s, 15H, C$_5$Me$_5$); ^{13}C NMR (C$_6$D$_6$, 25 °C): δ = 158.1 (CH$_2$CHCH$_2$), 120.7 (*C$_5$*Me$_5$), 78.4 (*C*H$_2$CH*C*H$_2$), 11.8 ppm (C$_5$*Me$_5$*); elemental analysis: calcd for C$_{16}$H$_{25}$Sc: C 73.26, H 9.61; found: C 72.79, H 9.76.

1c: *n*BuLi (0.38 mL, 1 mmol, 2.63 M in hexane) was added dropwise to a solution of C$_5$Me$_5$H (136 mg, 1 mmol) in THF (10 mL). After 15 min, the reaction mixture (containing LiC$_5$Me$_5$ prepared in situ) was added to a suspension of ScCl$_3$ (151 mg, 1 mmol) in THF (20 mL). The mixture was stirred for 4 h to afford a clear solution, to which 2-Me-C$_3$H$_4$MgCl (1 mL, 2 mmol, 2.0 M in THF) was added. The resulting light-yellow solution was left overnight. Removal of volatiles yielded a yellow residue, which was extracted with hexane. Evaporation of the solvent left **1c** as a red crystalline solid (275 mg, 95 %). Recrystallization from hexane gave single crystals suitable for X-ray analysis. ^{1}H NMR (C$_6$D$_6$, 25 °C): δ = 2.87 (br s, 8H, C*H$_2$*CMeC*H$_2$*), 1.81 (s, 6H, CH$_2$C*Me*CH$_2$), 1.71 ppm (s, 15H, C$_5$Me$_5$); ^{13}C NMR (C$_6$D$_6$, 25 °C): δ = 167.6 (CH$_2$CMeCH$_2$), 120.6 (*C$_5$*Me$_5$), 74.9 (*C*H$_2$CMe*C*H$_2$), 27.9 (CH$_2$C*Me*CH$_2$), 12.0 ppm (C$_5$*Me$_5$*); elemental analysis: calcd for C$_{18}$H$_{29}$Sc: C 74.45, H 10.07; found: C 73.72, H 9.85.

2: A 30-mL flask was charged with [(C$_5$Me$_4$SiMe$_3$)Sc(η^3-C$_3$H$_5$)$_2$] (64 mg, 0.20 mmol) and (PhNMe$_2$H)[B(C$_6$F$_5$)$_4$] (162 mg, 0.20 mmol), and toluene (10 mL) was added to the mixture. The resulting red suspension was stirred for 30 min at 25 °C, and the solvent was then removed under vacuum. The dark-red residue was washed with hexane (3 × 5 mL) to give **2** (200 mg, 93 %) as a fine brick-red powder. Layering of hexane on the reaction mixture of [(C$_5$Me$_4$SiMe$_3$)Sc(η^3-C$_3$H$_5$)$_2$] and [PhNMe$_2$H][B-

(C$_6$F$_5$)$_4$] in chlorobenzene yielded dark-red crystals suitable for X-ray diffraction. ^{1}H NMR (C$_6$D$_5$Cl, 25 °C): δ = 7.17–7.21 (m, 2 H, *m*-Ph), 6.95–7.03 (m, 1 H, *p*-Ph), 6.65–6.81 (m, 1 H, CH$_2$C*H*CH$_2$), 6.63–6.66 (m, 2 H, *o*-Ph), 2.35–2.60 (m, 4 H, C*H*$_2$CHC*H*$_2$), 2.61 (s, 6 H, NMe$_2$), 2.05 (s, 6 H, C$_5$Me$_4$), 1.61 (s, 6 H, C$_5$Me$_4$), 0.09 ppm (s, 9 H, C$_5$Me$_4$Si*Me*$_3$); the ^{13}C NMR spectrum of **2** was not informative due to decomposition of **2** during the recording time; ^{19}F NMR (C$_6$D$_5$Cl, 25 °C): δ = −132.3, −162.6, −166.6 ppm; ^{11}B NMR (C$_6$D$_5$Cl, 25 °C): δ = −16.6 ppm; elemental analysis: calcd for $C_{47}H_{38}BF_{20}NScSi$: C 52.29, H 3.45, N 1.30; found: C 52.15, H 3.62, N 1.49.

3: A 30-mL flask was charged with [(C$_5$Me$_4$SiMe$_3$)Sc(η^3-C$_3$H$_5$)$_2$] (64 mg, 0.20 mmol) and (Ph$_3$C)[B(C$_6$F$_5$)$_4$] (184 mg, 0.20 mmol), and toluene (10 mL) was added to the mixture. The resulting red suspension was stirred for 30 min at 25 °C, and the solvent was then removed under vacuum. The dark-red residue was washed with hexane (3 × 5 mL) to give **3** (193 mg, 92 %) as a fine brick-red powder. Layering of toluene on the reaction mixture of [(C$_5$Me$_4$SiMe$_3$)Sc(η^3-C$_3$H$_5$)$_2$] and [Ph$_3$C][B(C$_6$F$_5$)$_4$] in chlorobenzene yielded dark-red crystals suitable for X-ray diffraction. ^{1}H NMR (C$_6$D$_5$Cl, 25 °C): δ = 6.95–7.20 (m, 5 H, *Ph*Me), 6.65–6.81 (m, 1 H, CH$_2$C*H*CH$_2$), 3.08 (d, *J* = 8.7 Hz, 2 H, *syn*-C*H*$_2$CHC*H*$_2$), 2.74 (d, *J* = 15.2 Hz, 2 H, *anti*-C*H*$_2$CHC*H*$_2$), 2.15 (s, 3 H, Ph*Me*), 2.06 (s, 6 H, C$_5$Me$_4$), 1.69 (s, 6 H, C$_5$Me$_4$), 0.14 ppm (s, 9 H, C$_5$Me$_4$Si*Me*$_3$); ^{13}C NMR (C$_6$D$_5$Cl, 25 °C): δ = 160.3 (CH$_2$CHCH$_2$), 149.0 (d, $J_{C,F}$ = 239.6 Hz, 2-C$_6$F$_5$), 139.3 (d, $J_{C,F}$ = 246.1 Hz, 4-C$_6$F$_5$), 138.4 (C$_{ipso}$ of *Ph*Me), 137.1 (d, $J_{C,F}$ = 243.7 Hz, 3-C$_6$F$_5$), 132.8, 130.5 (C$_{arom}$ and Cp), 124.5 (br m, 1-C$_6$F$_5$), 87.4 (*C*H$_2$CH*C*H$_2$), 21.7 (Ph*Me*), 15.5 (C$_5$*Me*$_4$SiMe$_3$), 11.8 (C$_5$*Me*$_4$SiMe$_3$), 1.3 ppm (C$_5$Me$_4$Si*Me*$_3$); some peaks for the aromatic and Cp ring carbon atoms could not be assigned due to overlap with the solvent peaks; ^{19}F NMR (C$_6$D$_5$Cl, 25 °C): δ = −132.1, −161.8, −166.1 ppm; ^{11}B NMR (C$_6$D$_5$Cl, 25 °C): δ = −16.6 ppm; elemental analysis: calcd for $C_{46}H_{34}BF_{20}ScSi$: C 52.59, H 3.26; found: C 53.14, H 3.33.

4: A 30-mL flask was charged with [(C$_5$Me$_4$SiMe$_3$)Sc(η^3-C$_3$H$_5$)$_2$] (64 mg, 0.20 mmol) and [PhNMe$_2$H][BPh$_4$] (88 mg, 0.20 mmol), and toluene (10 mL) was added to the mixture. The resulting red suspension was stirred for 30 min at 25 °C, and the solvent was then removed under vacuum. The dark-red residue was washed with hexane (3 × 5 mL) to give **4** (103 mg, 86 %) as a fine brick-red powder. Layering of hexane on the reaction mixture of [(C$_5$Me$_4$SiMe$_3$)Sc(η^3-C$_3$H$_5$)$_2$] and [PhNMe$_2$H][BPh$_4$] in chlorobenzene yielded dark-red crystals suitable for X-ray diffraction. ^{1}H NMR (C$_6$D$_5$Cl, 25 °C): δ = 7.61 (d, *J* = 7.5 Hz, 8 H, *o*-Ph), 7.43 (t, *J* = 7.5 Hz, 8 H, *m*-Ph), 7.12 (t, *J* = 6.9 Hz, 4 H, *p*-Ph), 6.43–6.70 (m, 1 H, CH$_2$C*H*CH$_2$), 3.12 (br s, 4 H, C*H*$_2$CHC*H*$_2$), 2.34 (s, 6 H, C$_5$*Me*$_4$), 1.86 (s, 6 H, C$_5$*Me*$_4$), 0.15 ppm (s, 9 H, C$_5$Me$_4$Si*Me*$_3$); the ^{13}C NMR spectrum of **4** in C$_6$D$_5$Cl was not informative due to decomposition during the recording time; ^{11}B NMR (C$_6$D$_5$Cl, 25 °C): δ = −6.3 ppm; elemental analysis: calcd for $C_{39}H_{46}BScSi$: C 78.25, H 7.75; found: C 78.36, H 7.69.

5: A 30-mL flask was charged with [(C$_5$Me$_4$SiMe$_3$)Sc(η^3-C$_3$H$_5$)$_2$] (64 mg, 0.20 mmol) and (PhNMe$_2$H)[B(C$_6$F$_5$)$_4$] (162 mg, 0.20 mmol), and THF (5 mL) was added to the mixture. The resulting yellow solution was stirred for 30 min at 25 °C, and the solvent was then removed under vacuum. The residue was washed with hexane (3 × 5 mL) to give **5** quantitatively (220 mg) as a fine light-yellow powder. ^{1}H NMR (C$_6$D$_5$Cl, 25 °C): δ = 6.60–6.76 (m, 1 H, CH$_2$C*H*CH$_2$), 3.69 (br s, 8 H, THF), 2.95 (d, *J* = 12.0 Hz, 4 H, C*H*$_2$CHC*H*$_2$), 2.10 (s, 6 H, C$_5$Me$_4$), 1.78 (br s, 8 H, THF), 1.76 (s, 6 H, C$_5$Me$_4$), 0.28 ppm (s, 9 H, C$_5$Me$_4$Si*Me*$_3$); ^{13}C NMR (C$_6$D$_5$Cl, 25 °C): δ = 155.5 (CH$_2$CHCH$_2$), 148.9 (d, $J_{C,F}$ = 240.6 Hz, 2-C$_6$F$_5$), 138.7 (d, $J_{C,F}$ = 244.3 Hz, 4-C$_6$F$_5$), 136.9 (d, $J_{C,F}$ = 246.9 Hz, 3-C$_6$F$_5$), 134.4 (*C*$_5$Me$_4$SiMe$_3$), 127.8 (*C*$_5$Me$_4$SiMe$_3$), 123.2 (C$_{ipso}$ of *C*$_5$Me$_4$SiMe$_3$), 81.9 (*C*H$_2$CH*C*H$_2$), 73.3 (THF), 25.2 (THF), 15.1 (C$_5$*Me*$_4$SiMe$_3$), 11.6 (C$_5$*Me*$_4$SiMe$_3$), 1.6 ppm (C$_5$Me$_4$Si*Me*$_3$); the peak of 1-C$_6$F$_5$ was not observed due to overlap with solvent peaks; elemental analysis: calcd for $C_{47}H_{42}BF_{20}O_2ScSi$: C 51.19, H 3.84; found: C 51.35, H 4.10.

6: Complex **6** was prepared quantitatively by a procedure analogous to that for **5**. Recrystallization from THF gave single crystals suitable for X-ray diffraction. ^{1}H NMR (C$_6$D$_5$Cl, 25 °C): δ = 7.83 (br s, 8 H, *o*-Ph), 7.18 (t, *J* = 7.5 Hz, 8 H, *m*-Ph), 7.02 (t, *J* = 6.9 Hz, 4 H, *p*-Ph), 6.54–6.71 (m, 1 H, CH$_2$C*H*CH$_2$), 3.38 (br s, 12 H, THF), 2.75 (d, *J* = 12.0 Hz, 4 H, C*H*$_2$CHC*H*$_2$), 1.92 (s, 6 H, C$_5$Me$_4$), 1.57 (s, 6 H, C$_5$Me$_4$), 1.42 (br s, 12 H, THF), 0.14 ppm (s, 9 H, C$_5$Me$_4$Si*Me*$_3$); ^{13}C NMR (C$_6$D$_5$Cl, 25 °C): δ = 164.8 (q, $J_{B,C}$ = 49.1 Hz, *Ph*BPh$_3$), 154.3 (CH$_2$CHCH$_2$), 136.8, 134.2, 133.8, 127.5, 126.1, 122.2 (C$_{arom}$ and Cp), 81.8 (*C*H$_2$CH*C*H$_2$), 73.0 (THF), 25.4 (THF), 15.3 (C$_5$*Me*$_4$SiMe$_3$), 11.9 (C$_5$*Me*$_4$SiMe$_3$), 1.9 ppm (C$_5$Me$_4$Si*Me*$_3$); elemental analysis: calcd for $C_{51}H_{70}BO_3ScSi$ (**6**·THF): C 75.16, H 8.66; found: C 75.26, H 8.64.

Typical procedure for the random copolymerization of isoprene with norbornene by **2** (Table 1, entry 5): In a glovebox, a solution of **2** (27.0 mg, 25 μmol) in toluene (2 mL) was added to a well-stirred solution of norbornene (0.47 g, 5 mmol) and isoprene (0.34 g, 5 mmol) in toluene (3 mL) in a 20-mL flask at 25 °C. After 15 min, the flask was taken out of the glovebox, and methanol was added to terminate the polymerization. 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 (0.28 g, 35 %). The copolymer is soluble in THF and chloroform at room temperature.

Isoprene (IP) and norbornene (NB) content in copolymer: The norbornene and 1,4-polyisoprene content of the copolymer was calculated according to the following formulae:

$$\mathrm{NB\ (mol\,\%)} = (I_{tot} - 7\,I_{IP\text{-}1,4} - 3\,I_{IP\text{-}3,4})/(I_{tot} + 3\,I_{IP\text{-}1,4} + 2\,I_{IP\text{-}3,4}) \times 100\%$$

$$\mathrm{IP\text{-}1,4\,\%} = 10\,I_{IP\text{-}1,4}/(I_{tot} + 3\,I_{IP\text{-}1,4} + 2\,I_{IP\text{-}3,4}) \times 100\,\%$$

$$\mathrm{IP\text{-}3,4\,\%} = 5\,I_{IP\text{-}3,4}/(I_{tot} + 3\,I_{IP\text{-}1,4} + 2\,I_{IP\text{-}3,4}) \times 100\,\%$$

in which $I_{IP\text{-}1,4}$ is the area of the resonance at 5.0 ppm (one vinyl proton), $I_{IP\text{-}3,4}$ is the area of the resonance at 4.7 ppm (two vinyl protons), and I_{tot} is the total area of the resonances at 2.6–0.7 ppm (all aliphatic protons) in the ^{1}H NMR spectrum.

X-ray Crystallographic Analysis

Crystals for X-ray analysis were sealed in a thin-walled glass capillary under a microscope in a glovebox. Data collection was performed at −100 °C on a Bruker SMART APEX diffractometer with a CCD area detector by using graphite-monochromated Mo$_{K\alpha}$ radiation (λ = 0.71069 Å). Determination of crystal class and unit-cell parameters was carried out by the SMART program package.[14] Raw frame data were processed with SAINT[15] and SADABS[16] to yield the reflection data file. Structures were solved by using the SHELXTL program.[17] Refinements were performed on F^2 anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. Analytical scattering factors for neutral atoms were used throughout the analysis. Hydrogen atoms were placed at 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 central carbon atoms of the allyl groups (C2/C19, C5/C20) in **1a** were disordered (70:30 occupancy). The central carbon atoms in the allyl group and the carbon atoms of the phenyl group of *N*,*N*-dimetylaniline (C2/C51, C10/C4, C9/C5, C14/C6) in **2** were disordered (60:40 occupancy). The central carbon atom of the allyl group (C2/C4) in **3** was disordered (55:45 occupancy). Crystal data, data collection, and processing parameters for compounds **1a**–**c**, **2**–**4**, and **6** are summarized in Table 4. CCDC-648920 (**1a**), 666957 (**1b**), 666958 (**1c**), 648921 (**2**), 648922 (**3**), 648923 (**4**), and 648924 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

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Table 4. Crystallographic data and structure-refinement details for **1a–c**, **2–4**, and **6**.

	1a	**1b**	**1c**	**2**	**3**	**4**	**6**·THF
Formula	$C_{18}H_{31}ScSi$	$C_{16}H_{25}Sc$	$C_{18}H_{29}Sc$	$C_{47}H_{36}BF_{20}NSiSc$	$C_{46}H_{34}BF_{20}SiSc$	$C_{39}H_{46}BSiSc$	$C_{51}H_{70}BO_3SiSc$
M_r	320.48	262.32	290.37	1078.63	1050.59	598.62	814.93
Crystal system	triclinic	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$Pnma$	$P2_1/c$	$C2/c$	$P2_1/c$	$P2_1/c$
a [Å]	7.2641(15)	8.2334(16)	10.620(1)	13.9685(18)	31.845(2)	9.0991(7)	19.865(2)
b [Å]	9.934(2)	14.542(3)	11.8991(12)	14.9902(19)	15.029(1)	18.7657(15)	9.8603(10)
c [Å]	14.340(3)	12.580(3)	13.5515(13)	22.697(3)	21.2478(15)	20.1759(16)	23.929(3)
a [°]	82.359(3)	90	90	90	90	90	90
β [°]	77.838(4)	95.323(4)	90	102.369(2)	119.292(1)	102.297(2)	94.187(2)
γ [°]	69.221(3)	90	90	90	90	90	90
V [Å^3]	943.8(3)	1499.7(5)	1712.5(3)	3164.7(12)	8868.6(11)	3366.0(5)	4674.7(8)
Z	2	4	4	4	8	4	4
ρ_{calcd} [g cm^{-3}]	1.128	1.162	1.126	1.543	1.574	1.181	1.158
μ [mm^{-1}]	0.444	0.469	0.417	0.301	0.312	0.280	0.223
F(000)	348	568	632	2180	4240	1280	1760
θ range [°]	1.46–25.03	2.15–25.01	2.28–25.52	1.49–25.10	1.67–25.03	1.50–25.05	1.71–25.06
No. of reflns. collected	4843	7677	8817	23752	22588	17352	23596
No. of indep. reflns.	3244	2634	1679	8198	7802	5936	8236
No. of variables	198	159	106	685	644	386	489
GOF	1.072	1.005	1.084	1.002	1.000	1.007	1.030
R ($I>2\sigma(I)$)	0.0521	0.0512	0.0372	0.0495	0.0393	0.0406	0.0826
Rw	0.1415	0.1375	0.0965	0.0814	0.0813	0.0725	0.2303

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