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Mono(boratabenzene) rare-earth metal dialkyl complexes: synthesis, structure and catalytic behaviors for styrene polymerization†

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Four mono(boratabenzene) rare-earth metal dialkyl complexes, [(3,5-Me_2-C_5H_3BR)Ln(CH_2SiMe_3)$_2$(THF)] (**1**: R = NEt_2, Ln = Sc; **2**: R = NEt_2, Ln = Lu; **3**: R = Ph, Ln = Sc; **4**: R = Ph, Ln = Lu), were synthesized efficiently *via* a one-pot strategy with Li[3,5-Me_2-C_5H_3BR] (R = NEt_2, Ph), $LnCl_3(THF)_x$ (Ln = Sc, x = 3; Ln = Lu, x = 0), and $LiCH_2SiMe_3$. The solid-state structures of **1** and **2** were determined by single-crystal X-ray diffraction. Variable-temperature NMR studies indicated that the energy barrier for the rotation of amino-boratabenzene in **1** ($\Delta G^{\ddagger} \approx 71$ kJ mol^{-1}) is higher than that of phenylboratabenzene in **3** ($\Delta G^{\ddagger} \approx 59$ kJ mol^{-1}). These mono(boratabenzene) rare-earth metal dialkyl complexes' catalytic behaviors for styrene polymerization were investigated, and found that mono(boratabenzene) scandium dialkyl complexes show high catalytic activities for syndiotactic polymerization upon activation with cocatalysts.

Introduction

Organometallic complexes of the rare-earth metals are of importance. These complexes not only have rich coordination properties but also promote a variety of useful transformations,[1] and have been widely used in organic[2] and polymer synthesis.[3] The most widely investigated organometallic complexes of rare-earth metals are those bearing Cp-type ligands. To further explore the chemistry of rare-earth metal complexes, ancillary ligands other than Cp and Cp derivatives have been introduced recently.[4]

Boratabenzene is a heterocyclic, 6π-electron aromatic anion that has been introduced into organometallic chemistry as an isoelectronic analogue of the well-known cyclopentadienide anion (Cp).[5] A large number of transition-metal complexes bearing boratabenzenes, in particular the derivatives of Group 4, 6, and 8 metals, have been reported.[6] On the other hand, only a handful examples of boratabenzene derivatives of rare-earth metals have been synthesized before 2007, and most of them are chloride derivatives.[7] Recently, our group carried out a study on the chemistry of boratabenzene rare-earth metal complexes, and were able to synthesize a series of bis(boratabenzene) trivalent rare-earth metal chlorides, amides and alkyl complexes,[8] bis(boratabenzene) divalent rare-earth metal complexes,[9] *ansa*-heteroborabenzene divalent ytterbium,[10] and amidino-boratabenzene trivalent rare-earth metal complexes,[11] some of which show interesting activities.[8c,d,9] Herein we report the synthesis and structural characterization of mono (boratabenzene) rare-earth metal alkyl complexes. The catalytic activity of these complexes for styrene polymerizations is also presented.

Results and discussion

Our choice of the specific boratabenzene ligands to use in our studies was based on stability considerations, which are crucial for isolation of the targeted complexes and catalytic behavior studies. One challenge in the synthesis of mono-Cp rare-earth metal complexes is ligand redistribution, which results in the formation of bis- and/or tris-Cp rare-earth metal complexes, and the sterically demanding Cp ligands are generally required to prevent ligand redistribution. Thus, we selected the multi-substituted boratabenzene ligands [3,5-Me_2-C_5H_3BR]$^-$ (R = NEt_2, Ph). Li[3,5-Me_2-$C_5H_3BNEt_2$] (**LiL1**) and Li[3,5-Me_2-C_5H_3BPh] (**LiL2**) were prepared by a modified procedure (Scheme 1) reported by Herberich and co-workers.[12] A salt elimination reaction between dipotassium salt of 2,4-dimethyl-1,3-pentadiene and diethylaminoboron dichloride or dichlorophenylborane gave 1-(diethylamino)-5-methyl-3-methylene-1,2,3,6-tetrahydro-borinine or 1-phenyl-3,5-dimethyl-1,6-dihydroborinine,

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† Electronic supplementary information (ESI) available: Molecular structure of complex **2**, ^{1}H (^{13}C,^{11}B) NMR spectra of complexes **1–4**. CCDC 1041234 (**1**) and 1041235 (**2**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt04043k

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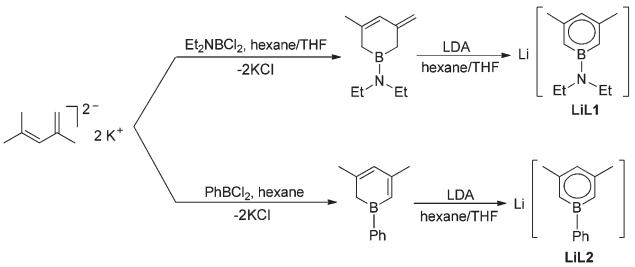
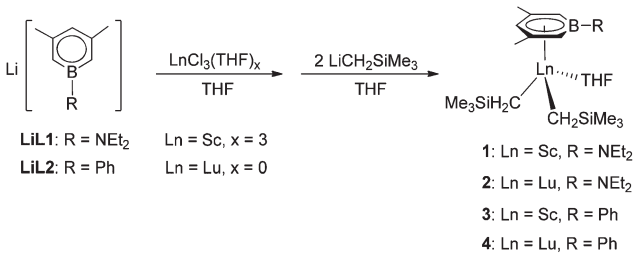


Scheme 1 Synthesis of **LiL1** and **LiL2**.

which was subsequently deprotonated by LDA to produce **LiL1** or **LiL2**.

The ^{1}H NMR spectral monitoring of the reaction of one equivalent of **LiL1** with $ScCl_3(THF)_3$ in THF-d_8 at ambient temperature showed that the corresponding mono(boratabenzene) scandium dichloride was produced in nearly quantitative yield after 15 min. Followed by the salt elimination reaction with two equivalents of $LiCH_2SiMe_3$, the desired mono(boratabenzene) scandium dialkyl complex $[(3,5\text{-}Me_2\text{-}C_5H_3BNEt_2)Sc(CH_2SiMe_3)_2(THF)]$ (**1**) was formed in 10 min with high yield. The reaction was subsequently scaled up in THF, and complex **1** was obtained in 99% yield (Scheme 2). Accordingly, $[(3,5\text{-}Me_2\text{-}C_5H_3BR)Ln(CH_2SiMe_3)_2(THF)]$ (**2**: R = NEt_2, Ln = Lu; **3**: R = Ph, Ln = Sc; **4**: R = Ph, Ln = Lu) was synthesized by reactions between **LiL1** (or **LiL2**), $LnCl_3(THF)_x$ (Ln = Sc, x = 3; Ln = Lu, x = 0) and $LiCH_2SiMe_3$ in THF at ambient temperature in 86–94% yields (Scheme 2). Attempts to prepare the yttrium analogues by reactions of $LiCH_2SiMe_3$ with *in situ* generated mono(boratabenzene) yttrium dichlorides failed as the formed mono(boratabenzene) yttrium dialkyls readily decomposed at room temperature.

Single crystals of **1** and **2** were obtained from hexane solutions at −30 °C and characterized by X-ray diffraction. An ORTEP diagram of **1** is shown in Fig. 1, while that of **2** is presented in the ESI.† The structural features of **1** and **2** are very similar and **1** was taken as an example to analyse the structural features. A scandium ion is four-coordinated by an anionic boratabenzene, two $-CH_2SiMe_3$ groups and one THF molecule. The geometry at the metal center can be described as a pseudo-tetrahedral with the boratabenzene taking an apical position. Inspection of the Sc–C(boratabenzene) bond lengths in **1**



Scheme 2 Synthesis of mono(boratabenzene) rare-earth metal dialkyl complexes **1–4**.

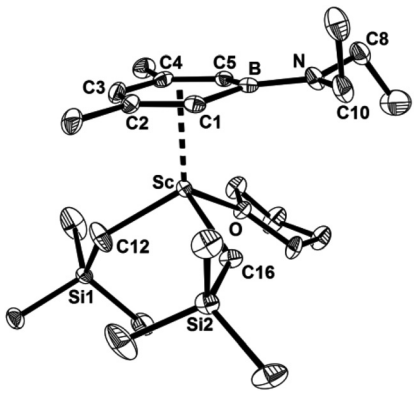


Fig. 1 Molecular structure of **1** with thermal ellipsoids set at 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Sc–B 2.741(3), Sc–C1 2.569(3), Sc–C2 2.547(3), Sc–C3 2.539(3), Sc–C4 2.615(3), Sc–C5 2.626(3), Sc–C12 2.202(3), Sc–C16 2.221(3), Sc–O 2.157(2), B–N 1.428(4), B–N–C8 122.8(2), B–N–C10 122.1(2), C8–N–C10 114.6(2).

shows that the Sc–C(boratabenzene) distances are significantly longer for C5 (2.626(3) Å) and C4 (2.615(3) Å) *vs.* C1 (2.569(3) Å), C2 (2.547(3) Å), and C3 (2.539(3) Å), which minimizes steric interactions between the boratabenzene ring and the $-CH_2SiMe_3$ groups. The average Sc–C (boratabenzene) bond length in **1** is 2.579(3) Å, which is significantly longer than that in its Cp analogue $[C_5Me_5Sc(CH_2SiMe_3)_2(THF)]$ (2.493(3) Å).[13] It is also noteworthy that the bonding situation in **1** is rather different from that in the amidino-boratabenzene scandium dialkyl complex $[\{C_5H_5BN(^iPr)C(H)N(^iPr)\}Sc(CH_2SiMe_3)_2(THF)]$,[11] where the scandium ion is far from the *para* and *meta* carbon atoms (2.679(2), 2.674(2) and 2.676(2) Å) and closer to the *ortho* carbon atoms (2.606(2) and 2.604(2) Å) and the boron atom (2.573(2) Å). The B–N bond length (1.428(4) Å) in **1** is much shorter than that in $[\{C_5H_5BN(^iPr)C(H)N(^iPr)\}Sc(CH_2SiMe_3)_2(THF)]$ (1.512(3) Å). The trigonal-planar geometry around the nitrogen atom ($\sum$N = 395.5°) and the rather shorter B–N bond length in **1** indicate a fairly strong π-interaction between boron and nitrogen.

The rotation barriers of boratabenzene in the mono(boratabenzene) rare-earth metal dialkyls are influenced by the substituents on the boron atom. For example, the ^{1}H NMR spectra of the scandium complexes **1** and **3** in toluene-d_8 at 25 °C showed an AB system (−0.02 and −0.15 ppm) and a singlet (−0.10 ppm) for the methylene protons in Sc-CH_2SiMe$_3$, respectively. Increasing the temperature of a solution of **1** from 25 to 85 °C results in broadening and coalescence of the Sc-CH_2SiMe$_3$ resonances followed by sharpening of the resulting coalesced peak (Fig. 2). The coalescence temperature (*ca.* 348 K) and the $\Delta\delta$ for the individual ^{1}H NMR resonances due to Sc-CH_2SiMe$_3$ groups (*ca.* 69 Hz) have been used to estimate a $\Delta G^{\ddagger}$ value of *ca.* 71 kJ mol^{-1} for the rotation of the diethylamino-substituted boratabenzene.[14] For **3**, the Sc-CH_2SiMe$_3$ resonance splits into an AB system upon lowering the temperature from 25 to −50 °C (Fig. 3). The coalescence temperature (*ca.* 288 K) and the $\Delta\delta$ (*ca.* 42 Hz) gives a $\Delta G^{\ddagger}$ value of

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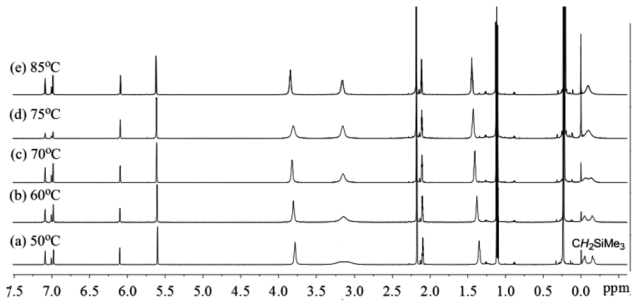

Fig. 2 Variable-temperature ^{1}H NMR spectra of **1** (toluene-d_8, 600 MHz). The complex slowly decomposes at elevated temperature.

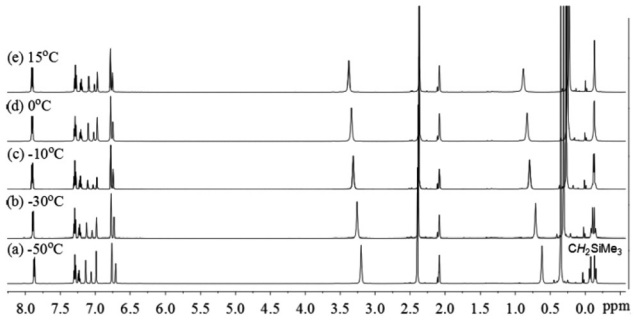

Fig. 3 Variable-temperature ^{1}H NMR spectra of **3** (toluene-d_8, 600 MHz).

ca. 59 kJ mol^{-1} for the rotation of the phenyl-substituted boratabenzene. The observed rotation barrier difference is consistent with the fact that the aminoboratabenzene is a better electron donor than the phenyl-substituted one.

Recently, mono-Cp rare-earth metal dialkyl complexes were found to be the efficient catalysts for styrene polymerization upon activation with $[Ph_3C][B(C_6F_5)_4]$.[15,16] The above synthesized mono(boratabenzene) rare-earth metal dialkyl complexes, in combination with $[Ph_3C][B(C_6F_5)_4]$ and $^iBu_3Al$, were investigated for styrene polymerization. The two scandium complexes **1** and **3** show high catalytic activities for styrene polymerization (Table 1), while the two lutetium alkyls **2** and **4** only give a trace of polymers under the same conditions. The styrene polymerization activity of the combined system of mono(boratabenzene) scandium dialkyl complexes with $[Ph_3C]$-$[B(C_6F_5)_4]$ was low, if $^iBu_3Al$ was not added (Table 1, entries 1 and 4). However, when five molar ratios of $^iBu_3Al$ were used, activities up to 1944 and 2061 kg PS mol^{-1} Sc h^{-1} were achieved for **1** and **3**, respectively (Table 1, entries 2 and 5). Although the rare-earth metal dialkyl-$[Ph_3C][B(C_6F_5)_4]$-AlR_3 ternary cationic catalytic systems have been extensively used for olefin coordination polymerization, the elucidation of the effects of AlR_3 in the reaction remains a challenge.[15b,17] The molecular weights (M_w) of the resulting polymers are 4.29×10^5 (M_w/M_n = 1.89) and 1.65×10^5 (M_w/M_n = 1.74), respectively. The molecular weights of the polymers decrease as the aluminate-to-scandium dialkyl ratio increase, while the M_w/M_n values are almost the same (Table 2, entries 3 and 6). All the resulting polymers are highly syndiotactic and have high melting points (*ca.* 267 °C).

Table 2 Crystallographic data and refinement for complexes **1** and **2**

Complex	**1**	**2**
Empirical formula	$C_{23}H_{49}BNOScSi_2$	$C_{23}H_{49}BLuNOSi_2$
Formula weight	467.58	597.59
Colour	Yellow	Yellow
Crystal system	Monoclinic	Monoclinic
Space group	$P2(1)/n$	$P2(1)/n$
a/Å	10.945(2)	10.9985(9)
b/Å	13.877(3)	14.0655(11)
c/Å	19.505(4)	19.6993(15)
α/°	90.00	90.00
β/°	91.922(4)	91.8000(10)
γ/°	90.00	90.00
Volume/Å^3	2960.9(11)	3046.0(4)
Z	4	4
Density (calculated)/g cm^{-3}	1.049	1.303
F(000)	1024	1224
Θ range/°	1.80 to 27.56	1.78 to 27.00
Reflections collected	19 868	21 338
Unique reflections	6792	6608
Unique reflections ($I > 2\sigma(I)$)	4446	5621
Parameters	272	272
Goodness of fit	1.024	1.028
Final R indices [$I > 2\sigma(I)$]	0.0573, 0.1214	0.0190, 0.0420
$\Delta\rho_{max,\ min}$/e Å^{-3}	0.701, −0.337	0.918, −0.565

Table 1 Styrene polymerization catalyzed by monoboratabenzene-Sc-dialkyl/$[Ph_3C][(C_6F_5)_4]$/$^iBu_3Al$ systems.[a]

Entry	Complex	$^iBu_3Al$ (eq.)	t (min)	Yield (%)	Activity[b]	sPS[c] (%)	aPS[d] (%)	M_n [e] (10^3)	M_w [e] (10^3)	M_w/M_n	T_m [f] (°C)
1[g]	**1**	0	30	Trace	—	—	—	—	—	—	—
2	**1**	5	3	95	1944	96	4	227.2	429.4	1.89	267
3	**1**	10	3	68	1409	95	5	172.6	347.6	2.01	268
4	**3**	0	8	85	657	99	1	99.1	157.5	1.59	267
5	**3**	5	3	97	2061	99	1	95.0	164.8	1.74	265
6	**3**	10	3	85	1737	98	2	74.4	129.8	1.74	267

[a] Polymerization conditions: Sc complex (18 μmol), 26 °C, Sc complex–$[Ph_3C][(C_6F_5)_4]$ (1 : 1 mol/mol), monomer–Sc complex (1000 : 1 mol/mol), toluene–monomer (7 : 1 v/v). [b] kg PS mol^{-1} Sc h^{-1}. [c] Percentage of polymers that are insoluble in 2-butanone under reflux. [d] Percentage of polymers that are soluble in 2-butanone under reflux. [e] Determined by gel permeation chromatography (GPC) relative to the polystyrene standards. [f] Differential scanning calorimetry (DSC) analysis of the polymers that are insoluble in 2-butanone under reflux. [g] Monomer–Sc complex (500 : 1 mol/mol).

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Conclusions

In summary, the synthesis of mono(boratabenzene) rare-earth metal dialkyl complexes was achieved by using multi-substituted boratabenzene ligands. One-pot reactions of boratabenzene lithiums, rare-earth metal chlorides, and $LiCH_2SiMe_3$ provided [(3,5-Me_2-C_5H_3BR)Ln(CH_2SiMe_3)$_2$ (THF)] (**1**: R = NEt_2, Ln = Sc; **2**: R = NEt_2, Ln = Lu; **3**: R = Ph, Ln = Sc; **4**: R = Ph, Ln = Lu) in high yields. Single-crystal X-ray diffraction analysis of **1** and **2** showed that the complexes have a three-legged piano-stool geometry, which is similar to their Cp analogues; however, the Ln–boratabenzene distances are significantly longer than the Ln–Cp ones as the boratabenzene is a poorer electron donor in comparison with Cp. The rotation barriers of boratabenzene in the mono(boratabenzene) rare-earth metal alkyls are influenced by the substituents on the boron atom. Complex **1** displays a higher rotation barrier than complex **3**, which is consistent with the fact that the aminoboratabenzene is a better electron donor than the phenyl-substituted one due to the strong π-interaction between boron and nitrogen. The mono(boratabenzene) scandium dialkyl complexes, activated with [Ph_3C][B(C_6F_5)$_4$] and $^iBu_3Al$, act as good catalyst systems for syndiotactic styrene polymerization.

Experimental

General procedures

All operations were carried out under an atmosphere of argon using Schlenk techniques or in a nitrogen filled glovebox. Toluene, hexane, THF, C_6D_6, THF-d_8 and toluene-d_8 were dried over the Na/K alloy, transferred under vacuum, and stored in the glovebox. Dichlorophenylborane was purchased from Aldrich and used as received. Diethylaminoboron dichloride[18] and $LiCH_2SiMe_3$[19] were synthesized according to the literature procedures. 1-(Diethylamino)-5-methyl-3-methylene-1,2,3,6-tetrahydro-borinine and 1-phenyl-3,5-dimethyl-1,6-dihydroborinine were prepared by using the procedure reported by Herberich and co-workers with the dipotassium salt of 2,4-dimethyl-1,3-pentadiene and diethylaminoboron dichloride (or dichlorophenylborane) as the reactants.[12] ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer at 400 MHz and 100 MHz, respectively. ^{11}B NMR spectra were recorded on a Bruker DXP 400 MHz spectrometer at 128 MHz. Variable-temperature ^{1}H NMR spectra were recorded on an Agilent 600 MHz spectrometer. All chemical shifts were reported in δ units with references to the residual solvent resonance of the deuterated solvents for proton and carbon chemical shifts, and to external $BF_3{\cdot}OEt_2$ for boron chemical shifts. Gel permeation chromatographic (GPC) analysis was performed on a Waters high temperature GPC 2000 at 135 °C. 1,2,4-Trichlorobenzene was used as the eluent, and the system was calibrated using polystyrene standards. Differential scanning calorimetry (DSC) measurements were performed on a Perkin-Elmer Pyris 1 instrument under a nitrogen atmosphere. For the elimination of the thermal history, the samples were heated to 300 °C at 20 °C min^{-1}, and then cooled to 40 °C at 20 °C min^{-1}. In the second runs, the samples were heated to 300 °C at 10 °C min^{-1}, and the melting points recorded were reported. Elemental analysis was performed at the Analytical Laboratory of Shanghai Institute of Organic Chemistry.

Li[3,5-Me_2-$C_5H_3BNEt_2$]. 2.5 M BuLi solution in hexane (3.1 mL, 7.75 mmol) was added to diisopropylamine (0.95 g, 9.34 mmol) in 10 mL of THF at 0 °C. After stirring at 0 °C for 30 min, the reaction mixture was warmed to room temperature and stirred for 1 h. This formed LDA solution was cooled to −70 °C, and 1-(diethylamino)-5-methyl-3-methylene-1,2,3,6-tetrahydro-borinine (1.38 g, 7.79 mmol) in 10 mL of THF was added dropwise. After stirring at −70 °C for 2 h, the reaction mixture was warmed to room temperature and stirred overnight to give a red solution. The volatiles of the solution were removed under vacuum, the residue was washed with 4 × 7 mL of hexane and dried under vacuum to give Li[3,5-Me_2-$C_5H_3BNEt_2$] as a pale yellow solid (530 mg, 38% yield). ^{1}H NMR (400 MHz, THF-d_8, 25 °C): δ (ppm) 5.14 (s, 2H, 2-/6-*H*), 5.12 (s, 1H, 4-*H*), 3.05 (q, $^3J_{H-H}$ = 6.8 Hz, 4H, NCH_2CH$_3$), 2.03 (s, 6H, 3-/5-CH_3), 1.00 (t, $^3J_{H-H}$ = 6.8 Hz, 6H, NCH$_2$CH_3). ^{13}C NMR (100 MHz, THF-d_8, 25 °C): δ (ppm) 142.2, 107.3 (br), 101.6 (boratabenzene-*C*), 43.6 (N*C*H$_2$CH$_3$), 25.7 (3-/5-*C*H$_3$), 16.3 (NCH$_2$*C*H$_3$). ^{11}B NMR (128 MHz, THF-d_8, 25 °C): δ (ppm) 30.4.

Li[3,5-Me_2-C_5H_3BPh]. Following the procedure described for Li[3,5-Me_2-$C_5H_3BNEt_2$], reaction of 2.5 M BuLi solution in hexane (1.7 mL, 4.25 mmol) with diisopropylamine (0.42 g, 4.15 mmol) in 10 mL of THF gave a LDA solution, which subsequently reacted with 1-phenyl-3,5-dimethyl-1,6-dihydroborinine (0.63 g, 3.46 mmol) to give Li[3,5-Me_2-C_5H_3BPh] as a pale yellow solid (525 mg, 81% yield). ^{1}H NMR (400 MHz, THF-d_8, 25 °C): δ (ppm) 7.72 (d, $^3J_{H-H}$ = 7.6 Hz, 2H, Ph-*H*), 7.08 (t, $^3J_{H-H}$ = 7.4 Hz, 2H, Ph-*H*), 6.93 (t, $^3J_{H-H}$ = 8.0 Hz, 1H, Ph-*H*), 6.21 (s, 2H, 2-/6-*H*), 5.64 (s, 1H, 4-*H*), 2.08 (s, 6H, 3-/5-CH_3). ^{13}C NMR (100 MHz, THF-d_8, 25 °C): δ (ppm) 150.8 (br), 141.3, 132.8, 126.8, 124.4, 121.4 (br), 113.0 (Ph-*C* and boratabenzene-*C*), 25.5 (3-/5-*C*H$_3$). ^{11}B NMR (128 MHz, THF-d_8, 25 °C): δ (ppm) 33.0.

[(3,5-Me_2-$C_5H_3BNEt_2$)Sc(CH_2SiMe_3)$_2$(THF)] (1). A THF solution of Li[3,5-Me_2-$C_5H_3BNEt_2$] (100 mg, 0.55 mmol in 4 mL of THF) was added to $ScCl_3(THF)_3$ (201 mg, 0.55 mmol) in 5 mL of THF. After stirring for 15 min at room temperature, the solution of LiCH($SiMe_3$)$_2$ (103 mg, 1.09 mmol in 2 mL of THF) was added, and the reaction mixture was stirred for 10 min at room temperature. The volatiles were removed under vacuum, and the residue was extracted with 4 × 2 mL of hexane. Evaporation of the yellow extract under vacuum gave **1** as a yellow solid (255 mg, 99% yield). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ (ppm) 6.13 (s, 1H, 4-*H*), 5.61 (s, 2H, 2-/6-*H*), 3.68 (m, 4H, THF), 3.23 (br, 2H, NCH_2CH$_3$), 3.02 (br, 2H, NCH_2CH$_3$), 2.16 (s, 6H, 3-/5-CH_3), 1.23 (m, 4H, THF), 1.11 (t, $^3J_{H-H}$ = 6.8 Hz, 6H, NCH$_2$CH_3), 0.30 (s, 18H, Si*Me*$_3$), −0.02 (d, $^2J_{H-H}$ = 10.4 Hz, 2H, CH_2SiMe$_3$), −0.15 (d, $^2J_{H-H}$ = 10.4 Hz, 2H, CH_2SiMe$_3$). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ (ppm) 150.5, 114.7 (br), 106.3 (boratabenzene-*C*), 72.0 (THF), 44.4 (br), 43.0 (*C*H$_2$SiMe$_3$ and N*C*H$_2$CH$_3$), 26.5, 25.0, 16.0 (3-/5-*C*H$_3$, THF and NCH$_2$*C*H$_3$),

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4.2 (Si*Me*$_3$). ^{11}B NMR (128 MHz, C_6D_6, 25 °C): δ (ppm) 32.7. Anal. calcd (%) for $C_{23}H_{49}BNOScSi_2$: C, 59.08; H, 10.56; N, 3.00. Found: C, 58.58; H, 10.57; N, 2.91.

[(3,5-Me$_2$-C$_5$H$_3$BNEt$_2$)Lu(CH$_2$SiMe$_3$)$_2$(THF)] (2). Following the procedure described for **1**, reaction of Li[3,5-Me$_2$-C$_5$H$_3$BNEt$_2$] (100 mg, 0.55 mmol in 4 mL of THF), $LuCl_3$ (154 mg, 0.55 mmol in 5 mL of THF), and $LiCH_2SiMe_3$ (105 mg, 1.10 mmol in 2 mL of THF) gave **2** as a yellow solid (307 mg, 94% yield). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ (ppm) 6.08 (t, $^4J_{H-H}$ = 2.0 Hz, 1H, 4-*H*), 5.61 (d, $^4J_{H-H}$ = 2.0 Hz, 2H, 2-/6-*H*), 3.57 (br, 4H, THF), 3.21 (br, 2H, NC*H*$_2$CH$_3$), 3.06 (br, 2H, NC*H*$_2$CH$_3$), 2.20 (s, 6H, 3-/5-C*H*$_3$), 1.15 (br, 4H, THF), 1.12 (t, $^3J_{H-H}$ = 7.2 Hz, 6H, NCH$_2$C*H*$_3$), 0.31 (s, 18H, Si*Me*$_3$), −0.73 (s, 4H, C*H*$_2$SiMe$_3$). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ (ppm) 151.4, 113.1 (br), 104.8 (boratabenzene-*C*), 71.6 (THF), 43.0, 40.8 (*C*H$_2$SiMe$_3$ and N*C*H$_2$CH$_3$), 26.1, 24.9, 16.1 (3-/5-*C*H$_3$, THF and NCH$_2$*C*H$_3$), 4.6 (Si*Me*$_3$). ^{11}B NMR (128 MHz, C_6D_6, 25 °C): δ (ppm) 32.9. Anal. calcd (%) for $C_{23}H_{49}BLuNOSi_2$: C, 46.23; H, 8.26; N, 2.34. Found: C, 46.53; H, 8.06; N, 2.27.

[(3,5-Me$_2$-C$_5$H$_3$BPh)Sc(CH$_2$SiMe$_3$)$_2$(THF)] (3). Following the procedure described for **1**, reaction of Li[3,5-Me$_2$-C$_5$H$_3$BPh] (79 mg, 0.42 mmol in 4 mL of THF), $ScCl_3(THF)_3$ (154 mg, 0.42 mmol in 5 mL of THF) and $LiCH_2SiMe_3$ (79 mg, 0.84 mmol in 2 mL of THF) gave **3** as a yellow solid (170 mg, 86% yield). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ (ppm) 7.96 (dd, $^3J_{H-H}$ = 8.0 Hz, $^4J_{H-H}$ = 1.6 Hz, 2H, Ph-*H*), 7.32 (t, $^3J_{H-H}$ = 6.8 Hz, 2H, Ph-*H*), 7.23 (tt, $^3J_{H-H}$ = 7.2 Hz, $^4J_{H-H}$ = 1.6 Hz, 1H, Ph-*H*), 6.83 (s, 2H, 2-/6-*H*), 6.78 (s, 1H, 4-*H*), 3.36 (br, 4H, THF), 2.36 (s, 6H, 3-/5-C*H*$_3$), 0.88 (br, 4H, THF), 0.25 (s, 18H, Si*Me*$_3$), −0.10 (s, 4H, C*H*$_2$SiMe$_3$). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ (ppm) 150.5, 132.9, 128.3, 128.2, 127.9, 127.5 (br), 117.5 (Ph-*C* and boratabenzene-*C*), 72.0 (THF), 47.9 (br, *C*H$_2$SiMe$_3$), 26.4 (3-/5-*C*H$_3$), 24.5 (THF), 4.1 (Si*Me*$_3$). ^{11}B NMR (128 MHz, C_6D_6, 25 °C): δ (ppm) 36.7. Anal. calcd (%) for $C_{25}H_{44}BOScSi_2$: C, 63.54; H, 9.39. Found: C, 62.87; H, 9.13.

[(3,5-Me$_2$-C$_5$H$_3$BPh)Lu(CH$_2$SiMe$_3$)$_2$(THF)] (4). Following the procedure described for **1**, reaction of Li[3,5-Me$_2$-C$_5$H$_3$BPh] (80 mg, 0.43 mmol in 4 mL of THF), $LuCl_3$ (120 mg, 0.43 mmol in 5 mL of THF) and $LiCH_2SiMe_3$ (80 mg, 0.85 mmol in 2 mL of THF) gave **4** as a yellow solid (220 mg, 86% yield). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ (ppm) 8.00 (dd, $^3J_{H-H}$ = 8.0 Hz, $^4J_{H-H}$ = 1.2 Hz, 2H, Ph-*H*), 7.33 (t, $^3J_{H-H}$ = 6.8 Hz, 2H, Ph-*H*), 7.23 (tt, $^3J_{H-H}$ = 7.2 Hz, $^4J_{H-H}$ = 1.2 Hz, 1H, Ph-*H*), 6.86 (s, 2H, 2-/6-*H*), 6.71 (s, 1H, 4-*H*), 3.24 (br, 4H, THF), 2.38 (s, 6H, 3-/5-C*H*$_3$), 0.91 (br, 4H, THF), 0.28 (s, 18H, Si*Me*$_3$), −0.78 (br, 4H, C*H*$_2$SiMe$_3$). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ (ppm) 150.8, 133.0, 128.2, 128.0, 127.0, 116.5 (Ph-*C* and boratabenzene-*C*), 71.0 (THF), 43.1 (*C*H$_2$SiMe$_3$), 26.0, 24.6 (3-/5-*C*H$_3$ and THF), 4.5 (Si*Me*$_3$). ^{11}B NMR (128 MHz, C_6D_6, 25 °C): δ (ppm) 37.0. Anal. calcd (%) for $C_{25}H_{44}BLuOSi_2$: C, 49.83; H, 7.36. Found: C, 49.32; H, 7.39.

A typical procedure for styrene polymerization. The mono (boratabenzene) scandium dialkyl complex (18 μmol) and [Ph$_3$C][B(C$_6$F$_5$)$_4$] (18 μmol) were mixed in toluene. The above reaction mixture was stirred at room temperature for one minute, and then ^{i}Bu$_3$Al (90 μmol) and styrene (1.87 g, 18 mmol) were added under vigorous stirring. The reaction solution became very viscous after several minutes, and the polymerization was quenched with 2 mL of acidic methanol. The reaction mixture was poured into 50 mL of methanol to precipitate the polymer. The resulting polymer was isolated, washed with methanol, and dried under vacuum for one day to a constant weight.

X-ray crystallography

Single crystals of **1** and **2** were grown from hexane solutions. Suitable single crystals were mounted under a nitrogen atmosphere on a glass fiber, and data collection was performed on a Bruker APEX2 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 133(2) K. The SMART program package was used to determine the unit cell parameters. The absorption correction was applied using SADABS. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were placed at calculated positions and included in the structure calculations. All calculations were carried out using the SHELXL-97 and SHELXL-2014 programs. The software used is given in ref. 20. Crystallographic data and refinement for **1** and **2** are listed in Table 2.

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