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

Xiufang Wang, Xuebing Leng and Yaofeng Chen*

Four mono(boratabenzene) rare-earth metal dialkyl complexes, [(3,5-Me2-C5H3BR)Ln(CH2SiMe3)2(THF)] (1: R = NEt2, Ln = Sc; 2: R = NEt2, Ln = Lu; 3: R = Ph, Ln = Sc; 4: R = Ph, Ln = Lu), were synthesized efficiently via a one-pot strategy with Li[3,5-Me2-C5H3BR] (R = NEt2, Ph), LnCl3(THF) (Ln = Sc, x = 3; Ln = Lu, x = 0), and LiCH2SiMe3. 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 (ΔG‡ ≈ 71 kJ mol⁻¹) is higher than that of phenylboratabenzene in 3 (ΔG‡ ≈ 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, and have been widely used in organic and polymer synthesis. 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. Boratabenzene is a heterocyclic, 6r-electron aromatic anion that has been introduced into organometallic chemistry as an isoelectronic analogue of the well-known cyclopentadienide anion (Cp). A large number of transition-metal complexes bearing boratabenzenes, in particular the derivatives of Group 4, 6, and 8 metals, have been reported. 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. 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, bis(boratabenzene) divalent rare-earth metal complexes, ansa-heteroborabenzene divalent ytterbium, and amidino-boratabenzene trivalent rare-earth metal complexes, some of which show interesting activities. 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-Me2-C5H3BR]⁺ (R = NEt2, Ph). Li[3,5-Me2-C5H3BNEt2] (LiL1) and Li [3,5-Me2-C5H3BPh] (LiL2) were prepared by a modified procedure (Scheme 1) reported by Herberich and co-workers. 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, with electrophilic reaction. Further transformations were also conducted, and the corresponding products are shown in the Supporting Information.
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 ScCl3(THF)3 in THF-d8 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 LiCH2SiMe3, the desired mono(boratabenzene) scandium dialkyl complex ([3,5-Me2-C5H3BNEt2]Sc(CH2SiMe3)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-Me2-C5H3BR)LnCl3(THF)] (2: R = NEt2, Ln = Lu; 3: R = Ph, Ln = Sc; 4: R = Ph, Ln = Lu) was synthesized by reactions between LiL1 (or LiL2), LnCl3(THF), (Ln = Sc, x = 3; Ln = Lu, x = 0) and LiCH2SiMe3 in THF at ambient temperature in 86–94% yields (Scheme 2). Attempts to prepare the yttrium analogues by reactions of LiCH2SiMe3 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 −CH2SiMe3 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 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 −CH2SiMe3 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 [C5Me5Sc(CH2SiMe3)2(THF)] (2.493(3) Å).† It is also noteworthy that the bonding situation in 1 is rather different from that in the amidino-boratabenzene scandium dialkyl complex [(C2H5BN(Pr)C(H)N(Pr))Sc(CH2SiMe3)2(THF)],11 where the scandium ion is far from the −CH2SiMe3 groups. The average Sc−C (boratabenzene) bond length in 1 is 2.579(3) Å, and Sc−C (boratabenzene) bond length in 1 is much shorter than that in [(C2H5BN(Pr)C(H)N(Pr))Sc(CH2SiMe3)2(THF)] (1.512(3) Å). The trigonal-planar geometry around the nitrogen atom (N−Sc−N = 111.5(2)°) and the shorter Sc−N−Sc ability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Sc−C (boratabenzene) distances are significantly shorter B−C (boratabenzene) bond lengths in 1 and 2.

The rotation barriers of boratabenzene in the mono(boratabenzene) rare-earth metal dialkyl complexes 1–4 are shown in Table 1. The rotation barriers of boratabenzene are affected by the substituents on the boron atom. For example, the $^1$H NMR spectra of the scandium complexes 1 and 3 in toluene-d8 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−CH2SiMe3 respectively. Increasing the temperature of a solution of 1 from 25 to 85 °C results in broadening and coalescence of the Sc−C(boratabenzene) resonances followed by sharpening of the resulting coalesced peak (Fig. 2). The coalescence temperature (ca. 348 K) and the ∆δ for the individual $^1$H NMR resonances due to Sc−CH2SiMe3 groups (ca. 69 Hz) have been used to estimate a ∆G‡ value of ca. 71 kJ mol$^{-1}$ for the rotation of the diethylamino-substituted boratabenzene.14 For 3, the Sc−CH2SiMe3 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 ∆δ (ca. 42 Hz) gives a ∆G‡ value of 75 kJ mol$^{-1}$.
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 \([\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]\).\(^{15,16}\) The above synthesized mono(boratabenzene) rare-earth metal dialkyl complexes, in combination with \([\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]\) and \(\text{Bu_3Al}\), 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 \([\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]\) was low, if \(\text{Bu_3Al}\) was not added (Table 1, entries 1 and 4). However, when five molar ratios of \(\text{Bu_3Al}\) 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-[\(\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]\)-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.\(^{15,16}\) The molecular weights (M\(_w\)) of the resulting polymers are 4.29 \(\times\) 10\(^5\) (M\(_w/M_n = 1.89\)) and 1.65 \(\times\) 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 1  Styrene polymerization catalyzed by monoboratabenzene-Sc-dialkyl/[\(\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]\]/\(\text{Bu_3Al}\) systems.\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Complex</th>
<th>(\text{Bu_3Al}) (eq.)</th>
<th>t (min)</th>
<th>Yield (%)</th>
<th>Activity(^b)</th>
<th>sPS(^c) (%)</th>
<th>aPS(^d) (%)</th>
<th>M(_w) (10(^3))</th>
<th>M(_n) (10(^3))</th>
<th>M(_w/M_n)</th>
<th>(T_m) (^{f}) (°C)</th>
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<tr>
<td>1(^e)</td>
<td>1</td>
<td>0</td>
<td>30</td>
<td>Trace</td>
<td>—</td>
<td>—</td>
<td>—</td>
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<td>—</td>
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<tr>
<td>2</td>
<td>1</td>
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<td>95</td>
<td>1944</td>
<td>96</td>
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<td>3</td>
<td>68</td>
<td>1409</td>
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<td>657</td>
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<td>99.1</td>
<td>157.5</td>
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<tr>
<td>5</td>
<td>3</td>
<td>5</td>
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<td>97</td>
<td>2051</td>
<td>99</td>
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<td>1.74</td>
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<td>74.4</td>
<td>129.8</td>
<td>1.74</td>
<td>267</td>
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\(^a\) Polymerization conditions: Sc complex (18 \(\mu\)mol), 26 °C, Sc complex-[\(\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_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-butane under reflux. \(^d\) Percentage of polymers that are soluble in 2-butane 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-butane under reflux. 

Table 2  Crystallographic data and refinement for complexes 1 and 2

<table>
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<tr>
<th>Complex</th>
<th>Empirical formula</th>
<th>Formula weight</th>
<th>Colour</th>
<th>Crystal system</th>
<th>Crystal system</th>
<th>Space group</th>
<th>Z</th>
<th>Volume/Å(^3)</th>
<th>α/°</th>
<th>β/°</th>
<th>γ/°</th>
<th>F(000)</th>
<th>D(\text{calculated})/g cm(^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C(<em>23)H(</em>{49})NO(_2)ScSi(_2)</td>
<td>467.58</td>
<td>Yellow</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>P2(_1)1/n</td>
<td>1</td>
<td>2960.9(11)</td>
<td>90.00</td>
<td>91.80</td>
<td>90.00</td>
<td>1024</td>
<td>1.049</td>
</tr>
<tr>
<td>2</td>
<td>C(<em>23)H(</em>{49})NO(_2)LuSi(_2)</td>
<td>597.59</td>
<td>Yellow</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>P2(_1)1/n</td>
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<td>3046.0(4)</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
<td>1224</td>
<td>1.303</td>
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</table>

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).
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$_2$SiMe$_3$ provided [(3,5-Me$_2$C$_5$H$_3$Br)Ln(CH$_2$SiMe$_3$)$_2$] (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 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$_3$C][B(C$_6$F$_5$)$_4$] and Bu$_3$Al, 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$_6$D$_{6}$, 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 and LiCH$_2$SiMe$_3$ were synthesized according to the literature procedures.

A THF solution of 1 was added to a solution of Li[3,5-Me$_2$C$_5$H$_3$BPh] (0.55 mmol in 5 mL of THF) at 0 °C under a nitrogen atmosphere, and the reaction mixture was stirred for 15 min at room temperature. The volatiles were removed under vacuum, and the residue was extracted with 4 × 2 mL of hexane. The extracts were dried over MgSO$_4$ and the solvents were removed under vacuum to give Li[3,5-Me$_2$C$_5$H$_3$BNEt$_2$] (100 mg, 0.55 mmol) as a pale yellow solid (530 mg, 38% yield).

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$_6$D$_{6}$, 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 and LiCH$_2$SiMe$_3$ were synthesized according to the literature procedures. A THF solution of 1 was added to a solution of Li[3,5-Me$_2$C$_5$H$_3$BPh] (0.55 mmol in 5 mL of THF) at 0 °C under a nitrogen atmosphere, and the reaction mixture was stirred for 15 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).

A THF solution of Li[3,5-Me$_2$C$_5$H$_3$BNEt$_2$] (100 mg, 0.55 mmol in 4 mL of THF) was added to ScCl$_3$ (THF)$_2$ (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). A THF solution of Li[3,5-Me$_2$C$_5$H$_3$BNEt$_2$] (100 mg, 0.55 mmol in 4 mL of THF) was added to ScCl$_3$ (THF)$_2$ (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).
2.36 (s, 6H, 3-/5-Cδ)

6.08 (t, 4H, THF)

minute, and then the reaction mixture was stirred at room temperature for one hour.

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 F2 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.

Acknowledgements

This work was supported by the State Key Basic Research & Development Program (grant no. 2011CB808705), the National Natural Science Foundation of China (grant no. 21272256, 21132002, 21325210 and 21421091), and the CASSAFE International Partnership Program for Creative Research Teams.

Notes and references


14 \[ \Delta G^\circ = aT^c \Delta (9.972 + \log(T_c/\Delta \delta)) \], \(a\) is a constant of 1.914 \times 10^{-2} \text{kJ mol}^{-1}, \(T_c(K)\) is the coalescence temperature, and \(\Delta \delta \text{(Hz)}\) is the frequency difference of the coalescing signals.


