

## Synthesis and Structural Features of Boratabenzene Rare-Earth Metal Alkyl Complexes

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A series of solvent-free boratabenzene rare-earth metal alkyl complexes  $(C_5H_5BR)_2LnCH(SiMe_3)_2$  (**9**: R = NEt<sub>2</sub>, Ln = Y; **10**: R = NPh<sub>2</sub>, Ln = Y; **11**: R = CH<sub>3</sub>, Ln = Y; **12**: R = NPh<sub>2</sub>, Ln = Sm; **13**: R = NPh<sub>2</sub>, Ln = Dy; **14**: R = NEt<sub>2</sub>, Ln = Lu; **15**: R = NPh<sub>2</sub>, Ln = Lu; **16**: R = Me, Ln = Lu) were synthesized. The solid-state structures of **10**, **13**, and **15** were determined by single-crystal X-ray diffraction. The crystal structures of **10**, **13**, and **15** feature highly unsymmetrical coordination of the alkyl ligands and short Ln–C(alkyl) distances. The diamagnetic yttrium and lutetium alkyl complexes, **9–11** and **14–16**, were characterized by (<sup>1</sup>H, <sup>13</sup>C, <sup>11</sup>B) NMR spectroscopy. The Ln–C<sub>α</sub>H<sub>α</sub> (<sup>1</sup>H NMR: δ 0.68–0.99 ppm) and Ln–C<sub>α</sub>H<sub>α</sub> (<sup>13</sup>C NMR: δ 33.9–39.1 ppm) resonances of these boratabenzene rare-earth metal alkyl complexes are rather downfield in comparison with those of the bis-Cp rare-earth metal alkyl complexes. <sup>89</sup>Y NMR spectra of the boratabenzene yttrium alkyl complexes **9–11** and the Cp complex  $(C_5H_4Me)_2YCH(SiMe_3)_2$  were recorded. The <sup>89</sup>Y NMR chemical shifts for **9**, **10**, and **11** are 176.1, 170.0, and 162.2 ppm, respectively, which are significantly downfield in comparison with that of  $(C_5H_4Me)_2YCH(SiMe_3)_2$  (44.0 ppm).

### Introduction

Among the organometallic complexes of rare-earth metals, the alkyl species are of particular interest, as they provide highly reactive Ln–C bonds. In general, these complexes are more reactive for chemical transformations than their chloride and amide counterparts. On the other hand, they are usually less stable and more difficult to synthesize, especially the coordinatively unsaturated ones. The most widely investigated rare-earth metal alkyl complexes are those bearing Cp-type

ligands.<sup>1</sup> To further explore the chemistry of the rare-earth metal complexes, ancillary ligands other than Cp and Cp derivatives recently have been introduced.<sup>2</sup>

Boratabenzenes are heterocyclic, 6π-electron, aromatic anions that have been introduced into organometallic chemistry as counterparts of Cp ligands.<sup>3</sup> Recent reports have described an increasing number of organometallic complexes of transition metals bearing boratabenzenes.<sup>4</sup> On the other hand, there have been only a few examples of boratabenzene derivatives of rare-earth metals, and the corresponding rare-earth metal alkyl complexes have not been isolated.<sup>5</sup> Recently, we reported several borotabenzene divalent rare-earth metal complexes<sup>6</sup> and trivalent yttrium chlorides and amides.<sup>7</sup> We now have prepared a series of boratabenzene rare-earth metal chlorides and alkyls. Herein we report these results.

### Results and Discussion

**Synthesis and Crystal Structures of Boratabenzene Rare-Earth Metal Chlorides.** Yttrium chlorides  $[(C_5H_5BNEt_2)_2YCl]_2$  (**1**),<sup>7</sup>  $[(C_5H_5BNPh_2)_2YCl]_2$  (**2**),<sup>7</sup> and  $[(C_5H_5BCH_3)_2YCl]_2$  (**3**)<sup>8</sup>

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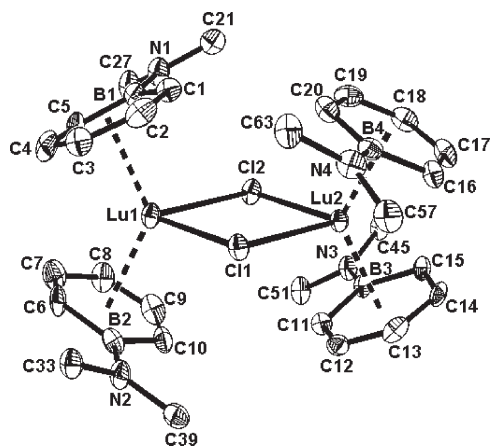
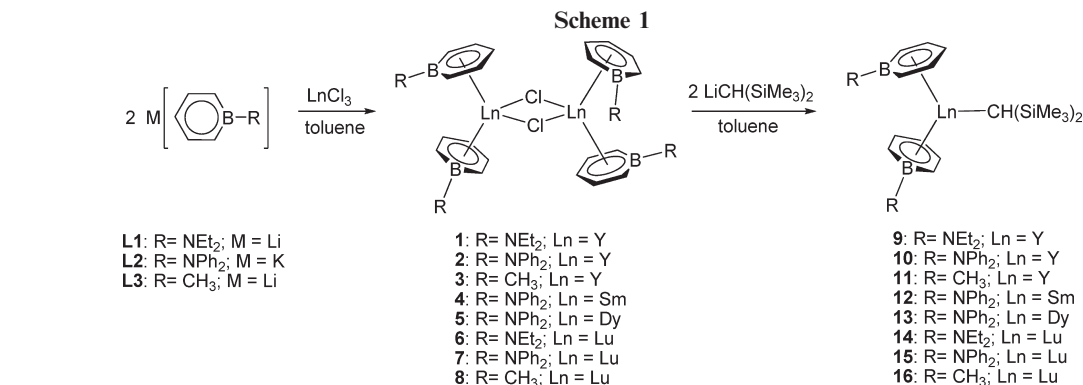
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**Figure 1.** Molecular structure of **7** with thermal ellipsoids at the 30% probability level (the phenyl group is represented by one carbon atom, and the toluene molecule in the lattice is not included). Hydrogen atoms are omitted for clarity.

were prepared according to the procedures reported. Salt elimination reactions of Li[C<sub>5</sub>H<sub>5</sub>BNEt<sub>2</sub>], K[C<sub>5</sub>H<sub>5</sub>BNPh<sub>2</sub>], and Li[C<sub>5</sub>H<sub>5</sub>BCH<sub>3</sub>] with anhydrous SmCl<sub>3</sub>, DyCl<sub>3</sub>, and LuCl<sub>3</sub> in toluene provided the desired boratabenzene rare-earth metal chlorides [(C<sub>5</sub>H<sub>5</sub>BR)<sub>2</sub>LnCl]<sub>2</sub> (**4**: R = NPh<sub>2</sub>, Ln = Sm; **5**: R = NPh<sub>2</sub>, Ln = Dy; **6**: R = NEt<sub>2</sub>, Ln = Lu; **7**: R = NPh<sub>2</sub>, Ln = Lu; **8**: R = Me, Ln = Lu) in 44–62% yield (Scheme 1). Single crystals of **7** were grown from a toluene solution and characterized by X-ray diffraction (Figure 1). Selected bond lengths and angles are given in Table 1. Similar to its yttrium analogue **2**, **7** adopts a dimeric structure. The average distances from the Lu ion to the B atom and C atoms at the 1,5 positions of the boratabenzene ring are 2.844(15), 2.717(15), and 2.705(15) Å, respectively, which are longer than those from the Lu ion to carbon atoms at the 2, 3, and 4 positions of the boratabenzene ring (2.665(14), 2.608(14), and 2.661(15) Å, respectively), indicating a slippage of the Lu ion away from the B atom to give an intermediate ( $\eta^5 \rightarrow \eta^3$ ) coordination mode as observed in other boratabenzene metal complexes.<sup>4,5</sup>

**Synthesis and Crystal Structures of Boratabenzene Rare-Earth Metal Alkyl Complexes.** Salt elimination reactions of the boratabenzene rare-earth metal chlorides (**1**–**8**) with 2 equiv of LiCH(SiMe<sub>3</sub>)<sub>2</sub> in toluene gave the corresponding boratabenzene rare-earth metal alkyl complexes (C<sub>5</sub>H<sub>5</sub>BR)<sub>2</sub>LnCH(SiMe<sub>3</sub>)<sub>2</sub>

**Table 1.** Selected Bond Lengths (Å) and Angles (deg) for **7** (toluene)

Bond Lengths			
Lu1–B1	2.849(15)	Lu2–C14	2.666(14)
Lu1–C1	2.730(15)	Lu2–C15	2.696(13)
Lu1–C2	2.669(16)	Lu2–B4	2.852(13)
Lu1–C3	2.620(14)	Lu2–C16	2.713(13)
Lu1–C4	2.666(16)	Lu2–C17	2.661(15)
Lu1–C5	2.671(14)	Lu2–C18	2.610(13)
Lu1–B2	2.836(15)	Lu2–C19	2.652(13)
Lu1–C6	2.685(16)	Lu2–C20	2.716(14)
Lu1–C7	2.670(16)	Lu1–C11	2.649(4)
Lu1–C8	2.604(15)	Lu1–C12	2.640(4)
Lu1–C9	2.661(15)	Lu2–C11	2.626(4)
Lu1–C10	2.739(16)	Lu2–C12	2.620(4)
Lu2–B3	2.841(12)	B1–N1	1.46(2)
Lu2–C11	2.741(12)	B2–N2	1.47(2)
Lu2–C12	2.661(12)	B3–N3	1.427(18)
Lu2–C13	2.600(13)	B4–N4	1.457(19)

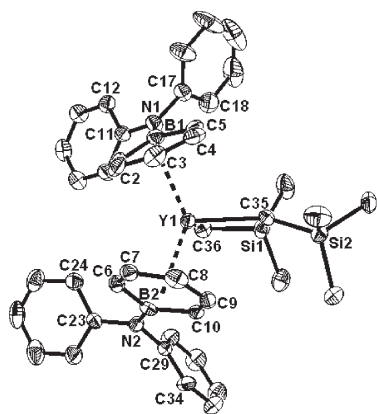
  

Bond Angles			
Cl1–Lu1–Cl2	79.82(12)	$\sum$ N1	359.7
Cl1–Lu2–Cl2	80.62(13)	$\sum$ N2	359.8
Lu1–Cl1–Lu2	99.60(14)	$\sum$ N3	359.9
Lu1–Cl2–Lu2	99.97(14)	$\sum$ N4	359.8

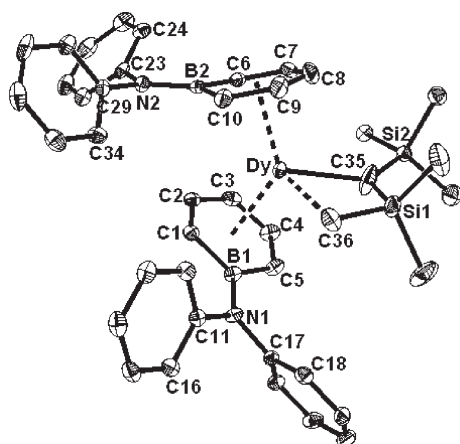
(**9**: R = NEt<sub>2</sub>, Ln = Y; **10**: R = NPh<sub>2</sub>, Ln = Y; **11**: R = CH<sub>3</sub>, Ln = Y; **12**: R = NPh<sub>2</sub>, Ln = Sm; **13**: R = NPh<sub>2</sub>, Ln = Dy; **14**: R = NEt<sub>2</sub>, Ln = Lu; **15**: R = NPh<sub>2</sub>, Ln = Lu; **16**: R = Me, Ln = Lu) in 43–91% yield (Scheme 1). **10**, **12**, **13**, and **15** are solid, while the others are oily products. These boratabenzene rare-earth metal alkyl complexes are quite stable at room temperature, and the VT <sup>1</sup>H NMR spectra of the yttrium alkyl complexes **9**, **10**, and **11** in toluene-*d*<sub>8</sub> show there is no significant decomposition even when the temperature is raised to 110 °C (VT <sup>1</sup>H NMR spectra were provided in the Supporting Information). Single crystals of **10**, **13**, and **15** were grown from hexane solutions and characterized by X-ray diffraction (Figures 2–4). Selected bond lengths and angles are given in Table 2. **10**, **13**, and **15** are all monomers and exhibit bent metallocene-type structures. As observed in the boratabenzene rare-earth metal chlorides, the metal ions in **10**, **13**, and **15** slip away from the B atom to give an intermediate ( $\eta^5 \rightarrow \eta^3$ ) coordination mode. The average Ln–C(ring) bond lengths in **10** (Y), **13** (Dy), and **15** (Lu) are 2.73, 2.73, and 2.67 Å, respectively, which are longer than those in the Cp complexes (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>YCH(SiMe<sub>3</sub>)<sub>2</sub> (2.67 Å),<sup>9</sup> (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>YCH<sub>3</sub>(THF) (2.66 Å),<sup>10</sup> [(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>YCH<sub>3</sub>]<sub>2</sub> (2.66 Å),<sup>11</sup>

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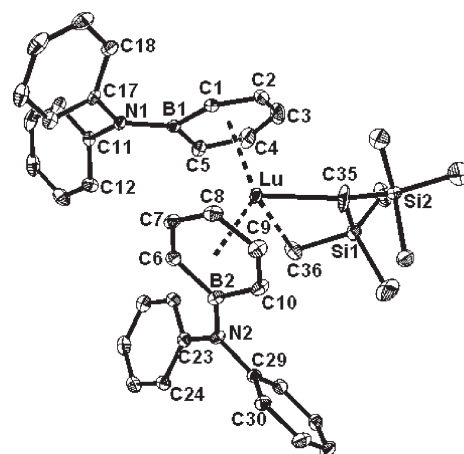


**Figure 2.** Molecular structure of **10** with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.



**Figure 3.** Molecular structure of **13** with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

and  $(\text{C}_5\text{H}_5)_2\text{LuCH}_2\text{SiMe}_3(\text{THF})$  (2.61 Å).<sup>12</sup> In addition, the ring centroid–Ln–ring centroid angles in the boratabenzene rare-earth metal alkyl complexes (131.3° in **10**, 130.1° in **13**, and 130.6° in **15**) are smaller than those in the Cp complexes<sup>13</sup>  $(\text{C}_5\text{Me}_5)_2\text{YCH}(\text{SiMe}_3)_2$  (134.4°),<sup>9</sup>  $(\text{C}_5\text{Me}_5)_2\text{NdCH}(\text{SiMe}_3)_2$  (134.4°),<sup>14</sup> and  $(\text{C}_5\text{Me}_5)_2\text{CeCH}(\text{SiMe}_3)_2$  (134.0°).<sup>15</sup> Thus the boratabenzene rare-earth metal alkyl complexes have a more open coordinative sphere than their Cp analogues. The most interesting structural feature of **10**, **13**, and **15** is the coordination mode of  $-\text{CH}(\text{SiMe}_3)_2$ . The Ln–C35 distances, 2.391(4) Å (**10**), 2.363(4) Å (**13**), and 2.324(4) Å (**15**), are significantly shorter than that in  $(\text{C}_5\text{Me}_5)_2\text{YCH}(\text{SiMe}_3)_2$



**Figure 4.** Molecular structure of **15** with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for **10**, **13**, and **15**

	<b>10</b> (Ln = Y)	<b>13</b> (Ln = Dy)	<b>15</b> (Ln = Lu)
Bond Lengths			
Ln–C1	2.824(4)	2.817(3)	2.734(4)
Ln–C2	2.735(5)	2.739(3)	2.671(4)
Ln–C3	2.628(6)	2.649(3)	2.629(5)
Ln–C4	2.682(5)	2.711(3)	2.608(4)
Ln–C5	2.814(5)	2.785(3)	2.673(4)
Ln–C6	2.823(4)	2.737(3)	2.761(3)
Ln–C7	2.742(5)	2.671(4)	2.674(4)
Ln–C8	2.635(5)	2.670(4)	2.597(4)
Ln–C9	2.654(5)	2.724(4)	2.648(4)
Ln–C10	2.737(4)	2.798(3)	2.730(4)
Ln–C35	2.391(4)	2.363(4)	2.324(4)
Ln–C36	2.775(4)	2.819(3)	2.830(4)
Ln–B1	3.036(5)	2.951(4)	2.941(4)
Ln–B2	2.972(5)	3.001(4)	2.920(4)
B1–N1	1.436(7)	1.461(4)	1.445(5)
B2–N2	1.410(7)	1.441(4)	1.456(5)
Bond Angles			
ΣN1	359.2	360.0	359.5
ΣN2	359.6	359.6	360.0
Si1–C35–Si2	119.8(2)	129.1(3)	120.2(3)
		121.3(3)	129.2(3)
Ln–C35–Si1	96.35(19)	98.27(18)	98.4(2)
Ln–C35–Si2	134.9(2)	130.1(2)	138.4(3)
		139.6(3)	131.4(2)

(2.468(7) Å) if the difference in  $\text{Ln}^{3+}$  ionic radii is counted (eight-coordinate ionic radii:  $\text{Y}^{3+}$  (1.019 Å),  $\text{Dy}^{3+}$  (1.027 Å),  $\text{Lu}^{3+}$  (0.977 Å)).<sup>16</sup> The  $-\text{CH}(\text{SiMe}_3)_2$  ligand coordinates to the metal ion in a highly unsymmetrical fashion. A remarkable difference between the two  $\angle\text{Ln}–\text{C}(35)–\text{Si}$  angles was observed, 96.35(19)° and 134.9(2)° in **10**, 98.27(18)° and 130.1(2)° (or 139.6(3)°, one  $\text{SiMe}_3$  group is disordered) in **13**, and 98.4(2)° and 138.4(3)° (or 131.4(2)°, one  $\text{SiMe}_3$  group is disordered) in **15**. Additionally, **10**, **13**, and **15** have very close  $\text{Ln}\cdots\text{C}(36)$  contacts,  $\text{Y}\cdots\text{C}(36)$  (2.775(4) Å),  $\text{Dy}\cdots\text{C}(36)$  (2.819(3) Å), and  $\text{Lu}\cdots\text{C}(36)$  (2.830(4) Å). These contacts are shorter than the sum of the  $\text{CH}_3$  van der Waals radius (2.0 Å)<sup>17</sup> and the eight-coordinate metal ionic radius. The above

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structural features suggested a  $\beta$ -agostic interaction between the electron-deficient metal center and the Si–C bond, as observed in some other coordinatively unsaturated rare-earth metal complexes.<sup>14,18</sup> It is worthy to note that the  $\beta$ -agostic interaction in the boratabenzene yttrium alkyl complex (**10**) is stronger than that in its amide analogue  $(\text{C}_5\text{H}_5\text{BNPh}_2)_2\text{YN}(\text{SiMe}_3)_2$  ( $\text{Y}\cdots\text{C}_\beta = 2.912(7)$  Å and  $\Delta\angle\text{Ln}-\text{C}_\alpha-\text{Si} = 19^\circ$ ).<sup>7</sup> This is because the  $\text{C}_\alpha$  atom of  $-\text{CH}(\text{SiMe}_3)_2$  has no lone electron pair like the N atom of  $-\text{N}(\text{SiMe}_3)_2$  in the amide complex, where the donation of the lone electron pair on the N atom to the metal center partially relieves the electron deficiency of the metal ion.

**NMR Characters of Boratabenzene Rare-Earth Metal Alkyl Complexes.** The chemical shifts of metal nuclei are very sensitive to the small changes in the local environment of the metal.<sup>19</sup> The unique properties of the  $\text{Y}^{3+}$  ion (diamagnetic, 100% natural abundance, and  $I = 1/2$ ) allow  $^{89}\text{Y}$  to be one of only a few isotopes of the rare-earth metals that are amenable to an NMR study.<sup>20</sup> The previous studies have shown that the  $^{89}\text{Y}$  NMR chemical shifts of the metal complexes are greatly influenced by the ligands.<sup>21</sup> The  $^{89}\text{Y}$  NMR chemical shifts move upfield with increased electronegativity and  $\pi$ -donating ability of the ligands. The homo-leptic alkyl complex  $\text{Y}(\text{CH}(\text{SiMe}_3)_2)_3$  has a  $^{89}\text{Y}$  NMR signal at 895 ppm,<sup>21</sup> while that of the tri(1-methylcyclopentadienyl) complex  $((\text{C}_5\text{H}_4\text{Me})_3\text{Y}(\text{THF}))$  appears at  $-371$  ppm.<sup>20</sup> The group contributions of various ligands to  $^{89}\text{Y}$  nuclear shielding have been estimated by Schaverien as the following:  $[\text{C}_5\text{Me}_5]^-$  (ca.  $-100$  ppm) > alkoxides (ca.  $15$  ppm) > aryloxides (ca.  $56$  ppm) > amides (ca.  $190$  ppm) > alkyl (ca.  $300$  ppm).<sup>21</sup> However, the wide application of  $^{89}\text{Y}$  NMR spectroscopy was impaired by its low receptivity ( $0.681$  relative to  $^{13}\text{C}$ ), resonance frequency ( $19.6$  MHz at a magnetic field strength of  $9.36$  T ( $^1\text{H} = 400$  MHz)), and extremely long yttrium nucleus relaxation time ( $T_1$ ), which leads to a very long measurement time.<sup>22</sup> The advantage of  $^{89}\text{Y}$  NMR spectroscopy is also partially offset by the solubility of the yttrium complexes; the deuterated solvents that have coordinating ability to the  $\text{Y}^{3+}$  ion, such as  $\text{THF}-d_8$ , could change the coordination situation of the complexes, especially for the coordinatively unsaturated complexes. The high solubility of the boratabenzene yttrium alkyl complexes **9–11** in the generally noncoordinating solvent  $\text{C}_6\text{D}_6$  makes the  $^{89}\text{Y}$  NMR spectroscopy measurement possible and the  $^{89}\text{Y}$  NMR data informative. To better understand the properties of the boratabenzene yttrium complexes and the difference between the boratabenzene ligand and the Cp ligand,  $^{89}\text{Y}$  NMR spectra of **9–11** and the Cp complex  $(\text{C}_5\text{H}_4\text{Me})_2\text{YCH}(\text{SiMe}_3)_2$  were recorded at  $19.6$  MHz. The  $^{89}\text{Y}$  NMR chemical shifts for **9**, **10**, and **11** are  $176.1$ ,  $170.0$ , and  $162.2$  ppm, respectively, which are significantly downfield in comparison with that for  $(\text{C}_5\text{H}_4\text{Me})_2\text{YCH}(\text{SiMe}_3)_2$  ( $44.0$  ppm). The group contributions of  $[\text{C}_5\text{H}_5\text{BNET}_2]^-$ ,  $[\text{C}_5\text{H}_5\text{BNPh}_2]^-$ , and  $[\text{C}_5\text{H}_5\text{BMe}]^-$  to  $^{89}\text{Y}$  nuclear shielding

are  $-61$ ,  $-64$ , and  $-68$  ppm, respectively. The lower group contribution of the boratabenzene ligand to  $^{89}\text{Y}$  nuclear shielding in comparison with that of the Cp ligand  $[(\text{C}_5\text{H}_4\text{Me})]^-$  ( $-128$  ppm) reveals that the boratabenzene ligand is a poorer  $\pi$ -donor than the Cp ligand.

The  $^1\text{H}$  NMR spectra of the diamagnetic yttrium and lutetium alkyl complexes, **9–11** and **14–16**, all show two sets of boratabenzene signals, indicating the boratabenzene rings are magnetically nonequivalent. This is different from that of their amide analogues, where only one set of boratabenzene signals was observed.<sup>7</sup> On the other hand, the Me groups of  $-\text{CH}(\text{SiMe}_3)_2$  in **9–11** and **14–16** are all magnetically equivalent and displayed as one signal, this is opposite of the highly unsymmetrical coordination of  $-\text{CH}(\text{SiMe}_3)_2$  observed in the solid state. The VT  $^1\text{H}$  NMR spectra of the alkyl complexes **9**, **10**, and **11** in toluene- $d_8$  show that the rotation barrier of the metal–alkyl bond is much higher than that of the metal–boratabenzene axis. The  $^{13}\text{C}$  NMR signals for  $\text{Ln}-\text{C}_\alpha\text{H}_\alpha$  of the boratabenzene yttrium and lutetium complexes, **9–11** ( $33.9$ ,  $39.1$ , and  $38.7$  ppm) and **14–16** ( $34.1$ ,  $38.6$ , and  $38.6$  ppm), are downfield in comparison with those of the bis-Cp complexes ( $27.5$  to  $29.3$  ppm) (Table 3). The mono-Cp complexes,  $(\text{C}_5\text{Me}_5)(\text{OAr})\text{YCH}(\text{SiMe}_3)_2$ <sup>21</sup> and  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)-(^i\text{BuN})]\text{LuCH}(\text{SiMe}_3)_2$ ,<sup>23</sup> which bear a  $\sigma$ -donor aryloxy or amide, have corresponding  $^{13}\text{C}$  NMR signals at  $32.0$  and  $44.7$  ppm, respectively, and  $\text{Y}(\text{CH}(\text{SiMe}_3)_2)_3$  has the signal at  $50.0$  ppm. Thus, the downfield shift of  $\text{Ln}-\text{C}_\alpha\text{H}_\alpha$  signals in the boratabenzene complexes is not unexpected and is consistent with the poor  $\pi$ -donating property of the boratabenzene ligand. Interestingly, the  $^1\text{H}$  NMR signals for  $\text{Ln}-\text{C}_\alpha\text{H}_\alpha$  of **9–11** ( $0.79$ ,  $0.68$ , and  $0.95$  ppm) and **14–16** ( $0.92$ ,  $0.74$ , and  $0.99$  ppm) are at significantly lower field not only than those of the bis-Cp complexes ( $-0.59$  to  $0.30$  ppm) but also than those of  $(\text{C}_5\text{Me}_5)(\text{OAr})\text{YCH}(\text{SiMe}_3)_2$  ( $-0.39$  ppm),<sup>21</sup>  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)-(^i\text{BuN})]\text{LuCH}(\text{SiMe}_3)_2$  ( $-1.14$  ppm),<sup>23</sup> and  $\text{Y}(\text{CH}(\text{SiMe}_3)_2)_3$  ( $-0.62$  ppm)<sup>24</sup> (Table 3). To evaluate if the difference in the  $\text{Ln}-\text{C}_\alpha\text{H}_\alpha$  signals between the boratabenzene complexes and the Cp complexes is due to the possible  $\alpha$ -agostic interaction between the  $\text{C}_\alpha-\text{H}_\alpha$  bond and the electron-deficient rare-earth metal ion, the  $\text{C}_\alpha-\text{H}_\alpha$  coupling constants ( $^1J_{\text{C}-\text{H}}$ ) of **9–11**, **15**, and  $(\text{C}_5\text{H}_4\text{Me})_2\text{YCH}(\text{SiMe}_3)_2$  were measured.<sup>25</sup> The small  $\text{C}_\alpha-\text{H}_\alpha$  coupling constants of the boratabenzene complexes (**9**:  $92.2$  Hz, **10**:  $92.3$  Hz, **11**:  $92.2$  Hz, **15**:  $92.3$  Hz) indicate that an  $\alpha$ -agostic interaction between the  $\text{C}_\alpha-\text{H}_\alpha$  bond and the metal ion is possible. However, these  $\text{C}_\alpha-\text{H}_\alpha$  coupling constants are very close to that of  $(\text{C}_5\text{H}_4\text{Me})_2\text{YCH}(\text{SiMe}_3)_2$  ( $94.4$  Hz); thus the  $\alpha$ -agostic interaction is not the main contributor for the extraordinary downfield shift of  $\text{Ln}-\text{C}_\alpha\text{H}_\alpha$  signals in the boratabenzene complexes. The reason for the unusual shift of  $\text{Ln}-\text{C}_\alpha\text{H}_\alpha$  signals in the boratabenzene complexes is unclear at the present stage.

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(25)  $^1J_{\text{C}-\text{H}}$  is commonly used to identify agostic interactions in solution: a signature of an agostic interaction is an unusually low  $^1J_{\text{C}-\text{H}}$  value in the region  $50$ – $100$  Hz,<sup>(a–c)</sup> while a  $^1J_{\text{C}-\text{H}}$  value in the region  $120$ – $130$  Hz means the absence of agostic interaction.<sup>(d,e)</sup> (a) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. (b) Brookhart, M.; Green, M. L. H.; Wong, L. L. *Prog. Inorg. Chem.* **1988**, *36*, 1. (c) Brookhart, M.; Green, M. L. H.; Parkin, G. *Proc. Natl. Acad. Sci. U. S. A.* **2007**, *104*, 6908. (d) Pantazis, D. A.; McGrady, J. E.; Besora, M.; Maseras, F.; Etienne, M. *Organometallics* **2008**, *27*, 1128. (e) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; Wiley: New York, 2001.

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**Table 3.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Signals for  $\text{Ln}-\text{C}_\alpha\text{H}_\alpha$  of 9–11, 14–16, and Other Yttrium and Lutetium Alkyl Complexes

metal ion	complexes	$^1\text{H}$ NMR ( $\delta$ ppm) <sup>a</sup>	$^{13}\text{C}$ NMR ( $\delta$ ppm) <sup>a</sup>	ref
$\text{Y}^{3+}$	$(\text{C}_5\text{H}_5\text{BNEt}_2)_2\text{YCH}(\text{SiMe}_3)_2$ ( <b>9</b> )	0.79	33.88	this work
	$(\text{C}_5\text{H}_5\text{BNPh}_2)_2\text{YCH}(\text{SiMe}_3)_2$ ( <b>10</b> )	0.68	39.06	this work
	$(\text{C}_5\text{H}_5\text{BCH}_3)_2\text{YCH}(\text{SiMe}_3)_2$ ( <b>11</b> )	0.95	38.7	this work
	$(\text{C}_5\text{H}_4\text{Me})_2\text{YCH}(\text{SiMe}_3)_2$	0.30	27.39	this work
	$(\text{C}_5\text{Me}_5)_2\text{YCH}(\text{SiMe}_3)_2$	−0.10	25.19	9
	$[\text{Et}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_5\text{Me}_4)]\text{YCH}(\text{SiMe}_3)_2$	−0.59	29.3 <sup>b</sup>	18b
	$(R,S)\text{-Me}_2\text{Si}(\text{C}_5\text{Me}_4)[(+)\text{-neomenthyl-C}_5\text{H}_3]\text{YCH}(\text{SiMe}_3)_2$	−0.55, −0.56		27
	$(\text{C}_5\text{Me}_5)(\text{OAr})\text{YCH}(\text{SiMe}_3)_2$	−0.39	32.0 <sup>c</sup>	21
	$(2,4,7\text{-Me}_3\text{C}_9\text{H}_4)_2\text{YCH}(\text{SiMe}_3)_2$	0.16	26.03	28
	$(\text{C}_9\text{Me}_7)_2\text{YCH}(\text{SiMe}_3)_2$	−0.37	27.5	29
	$\text{Y}(\text{CH}(\text{SiMe}_3)_2)_3$	−0.62	50.0	24
$\text{Lu}^{3+}$	$(\text{C}_5\text{H}_5\text{BNEt}_2)_2\text{LuCH}(\text{SiMe}_3)_2$ ( <b>14</b> )	0.92	34.1	this work
	$(\text{C}_5\text{H}_5\text{BNPh}_2)_2\text{LuCH}(\text{SiMe}_3)_2$ ( <b>15</b> )	0.74	38.6	this work
	$(\text{C}_5\text{H}_5\text{BCH}_3)_2\text{LuCH}(\text{SiMe}_3)_2$ ( <b>16</b> )	0.99	38.6	this work
	$(\text{C}_5\text{Me}_5)_2\text{LuCH}(\text{SiMe}_3)_2$	−0.02		14
	$[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{LuCH}(\text{SiMe}_3)_2$	−0.411 <sup>b</sup>		30
	$[\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_5\text{Me}_4)]\text{LuCH}(\text{SiMe}_3)_2$	−0.50	29.1	18b
	$[\text{Et}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_5\text{Me}_4)]\text{LuCH}(\text{SiMe}_3)_2$	−0.52		18b
	$(R,S)\text{-Me}_2\text{Si}(\text{C}_5\text{Me}_4)[(+)\text{-neomenthyl-C}_5\text{H}_3]\text{LuCH}(\text{SiMe}_3)_2$	0.06, −0.48	—	27
	$[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(^i\text{BuN})]\text{LuCH}(\text{SiMe}_3)_2$	−1.14	44.7	23

<sup>a</sup> NMR spectra were measured in  $\text{C}_6\text{D}_6$  at 25 °C. <sup>b</sup> NMR spectra were measured in toluene- $d_8$  at 25 °C. <sup>c</sup> NMR spectra were measured in toluene- $d_8$  at −80 °C.

In summary, salt elimination reactions of the solvent-free boratabenzene rare-earth metal chlorides  $[(\text{C}_5\text{H}_5\text{BR})_2\text{LnCl}]_2$  (**1**: R =  $\text{NEt}_2$ , Ln = Y; **2**: R =  $\text{NPh}_2$ , Ln = Y; **3**: R = Me, Ln = Y; **4**: R =  $\text{NPh}_2$ , Ln = Sm; **5**: R =  $\text{NPh}_2$ , Ln = Dy; **6**: R =  $\text{NEt}_2$ , Ln = Lu; **7**: R =  $\text{NPh}_2$ , Ln = Lu; **8**: R = Me, Ln = Lu) with 2 equiv of  $\text{LiCH}(\text{SiMe}_3)_2$  in toluene gave the corresponding boratabenzene rare-earth metal alkyl complexes  $(\text{C}_5\text{H}_5\text{BR})_2\text{-LnCH}(\text{SiMe}_3)_2$  (**9**: R =  $\text{NEt}_2$ , Ln = Y; **10**: R =  $\text{NPh}_2$ , Ln = Y; **11**: R =  $\text{CH}_3$ , Ln = Y; **12**: R =  $\text{NPh}_2$ , Ln = Sm; **13**: R =  $\text{NPh}_2$ , Ln = Dy; **14**: R =  $\text{NEt}_2$ , Ln = Lu; **15**: R =  $\text{NPh}_2$ , Ln = Lu; **16**: R = Me, Ln = Lu). The solid-state structures of **10**, **13**, and **15** show a strong  $\beta$ -agostic interaction between the metal center and the Si– $\text{C}_\beta$  bond of the alkyl ligand. The  $^{89}\text{Y}$  NMR spectra of the yttrium alkyl complexes reveal that the boratabenzene ligand is a poorer  $\pi$ -donor than the Cp ligand. The  $\text{Ln}-\text{C}_\alpha\text{H}_\alpha$  and  $\text{Ln}-\text{C}_\alpha\text{H}_\alpha$  signals of the boratabenzene rare-earth metal alkyl complexes are rather downfield in comparison with those of the bis-Cp rare-earth metal alkyl complexes.

## Experimental Section

**General Procedures.** All operations were carried out under an atmosphere of argon using standard Schlenk techniques or in a nitrogen-filled glovebox. THF was distilled from Na-benzophenone ketyl. Toluene, hexane,  $\text{C}_6\text{D}_6$ , toluene- $d_8$ , and THF- $d_8$  were dried over Na/K alloy, distilled under vacuum, and stored in the glovebox.  $[(\text{C}_5\text{H}_5\text{BNEt}_2)_2\text{YCl}]_2$  (**1**),<sup>7</sup>  $[(\text{C}_5\text{H}_5\text{BNPh}_2)_2\text{YCl}]_2$  (**2**),<sup>7</sup> and  $[(\text{C}_5\text{H}_5\text{BCH}_3)_2\text{YCl}]_2$  (**3**)<sup>8</sup> were prepared according to the procedures reported.  $\text{LiCH}(\text{SiMe}_3)_2$ <sup>26</sup> was synthesized following the literature.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Varian Mercury 300 MHz (or 400 MHz) spectrometer at 300 MHz (or 400 MHz) and 75 MHz (or 100 MHz), respectively.  $^{11}\text{B}$  NMR spectra were recorded on a Bruker DXP 400 MHz spectrometer at 128 MHz.  $^{89}\text{Y}$  NMR spectra were recorded on a Bruker DXP 400 MHz spectrometer at 19.6 MHz. All chemical shifts were reported in  $\delta$  units with references to the residual solvent resonance of the deuterated solvents for proton and carbon chemical shifts, to external  $\text{BF}_3\cdot\text{OEt}_2$  for boron chemical shifts, and to 3 M  $\text{YCl}_3$  in  $\text{D}_2\text{O}$  for yttrium chemical shifts.

Elemental analysis was performed by Analytical Laboratory of Shanghai Institute of Organic Chemistry.

$[(\text{C}_5\text{H}_5\text{BNPh}_2)_2\text{SmCl}]_2$  (**4**). Anhydrous  $\text{SmCl}_3$  (388 mg, 1.51 mmol) and  $\text{K}[\text{C}_5\text{H}_5\text{BNPh}_2]$  (855 mg, 3.02 mmol) were mixed in 65 mL of toluene, and the reaction mixture was stirred for 3 days at 110 °C. The precipitate was removed by centrifugation, and the clear brown solution was evaporated in vacuo to give a brown solid. The solid was washed with  $2 \times 3$  mL of hexane and dried in vacuo to afford **4** as a pale brown solid (631 mg, 62% yield). Anal. Calcd (%) for  $\text{C}_{68}\text{H}_{60}\text{B}_4\text{Cl}_2\text{N}_4\text{Sm}_2$ : C, 60.58; H, 4.49; N, 4.16. Found: C, 60.00; H, 5.01; N, 4.34.

$[(\text{C}_5\text{H}_5\text{BNPh}_2)_2\text{DyCl}]_2$  (**5**). Following the procedure described for **4**, reaction of anhydrous  $\text{DyCl}_3$  (475 mg, 1.77 mmol) and  $\text{K}[\text{C}_5\text{H}_5\text{BNPh}_2]$  (1.00 g, 3.53 mmol) in 70 mL of toluene gave **5** as a yellow solid (618 mg, 51% yield). Anal. Calcd (%) for  $\text{C}_{68}\text{H}_{60}\text{B}_4\text{Cl}_2\text{N}_4\text{Dy}_2$ : C, 59.51; H, 4.41; N, 4.08. Found: C, 59.46; H, 4.59; N, 4.12.

$[(\text{C}_5\text{H}_5\text{BNEt}_2)_2\text{LuCl}]_2$  (**6**). Following the procedure described for **4**, reaction of anhydrous  $\text{LuCl}_3$  (285 mg, 1.01 mmol) and  $\text{Li}[\text{C}_5\text{H}_5\text{BNEt}_2]$  (314 mg, 2.02 mmol) in 50 mL of toluene gave **6** as a yellow solid (285 mg, 56% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  (ppm) 7.36 (dd,  $J = 10.8$  Hz,  $J = 6.8$  Hz, 8H, 3-/5- $H$ ), 6.14 (dd,  $J = 11.2$  Hz,  $J = 1.6$  Hz, 8H, 2-/6- $H$ ), 5.96 (tt,  $J = 6.8$  Hz,  $J = 1.2$  Hz, 4H, 4- $H$ ), 3.38 (m, 8H,  $\text{NCH}_2$ ), 3.13 (m, 8H,  $\text{NCH}_2$ ), 1.15 (t, 24H,  $J = 6.8$  Hz,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) 143.1 (3-/5- $C$ ), 115.0 (2-/6- $C$ ), 99.8 (4- $C$ ), 42.6 ( $\text{NCH}_2$ ), 15.9 ( $\text{CH}_3$ ).  $^{11}\text{B}$  NMR (128 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) 31.7. Anal. Calcd (%) for  $\text{C}_{36}\text{H}_{60}\text{B}_4\text{Cl}_2\text{N}_4\text{Lu}_2$ : C, 42.68; H, 5.97; N, 5.53. Found: C, 41.92; H, 5.97; N, 5.41.

$[(\text{C}_5\text{H}_5\text{BNPh}_2)_2\text{LuCl}]_2$  (**7**). Following the procedure described for **4**, reaction of anhydrous  $\text{LuCl}_3$  (465 mg, 1.65 mmol) and  $\text{K}[\text{C}_5\text{H}_5\text{BNPh}_2]$  (906 mg, 3.20 mmol) in 70 mL of toluene gave **7** as a yellow solid (495 mg, 44% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) 7.26–7.18 (m, 32H, Ph- $H$ ), 7.05–6.99 (m, 8H, Ph- $H$ ), 6.73 (dd,  $J = 10.8$  Hz,  $J = 6.9$  Hz, 8H, 3-/5- $H$ ), 6.32 (d,  $J = 10.8$  Hz, 8H, 2-/6- $H$ ), 5.71 (t,  $J = 6.9$  Hz, 4H, 4- $H$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 149.3 (Ph- $C$ ), 143.2 (3-/5- $C$ ), 128.8 (Ph- $C$ ), 127.4 (Ph- $C$ ), 123.8 (Ph- $C$ ), 118.6 (2-/6- $C$ ), 101.6 (4- $C$ ).  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 33.9. Anal. Calcd (%) for  $\text{C}_{68}\text{H}_{60}\text{B}_4\text{Cl}_2\text{N}_4\text{Lu}_2$ : C, 58.45; H, 4.33; N, 4.01. Found: C, 57.63; H, 4.85; N, 4.07.

$[(\text{C}_5\text{H}_5\text{BCH}_3)_2\text{LuCl}]_2$  (**8**). Following the procedure described for **4**, reaction of anhydrous  $\text{LuCl}_3$  (503 mg, 1.79 mmol) and  $\text{Li}[\text{C}_5\text{H}_5\text{BCH}_3]$  (350 mg, 3.57 mmol) in 70 mL of toluene gave **8** as a pale yellow solid (392 mg, 56% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) 7.34 (dd,  $J = 10.5$  Hz,  $J = 7.2$  Hz, 8H, 3-/5- $H$ ),

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6.84 (d,  $J = 9.3$  Hz, 8H, 2-/6-*H*), 6.24 (t,  $J = 7.2$  Hz, 4H, 4-*H*), 1.15 (s, 12H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) 142.0 (3-/5-*C*), 132.5 (2-/6-*C*), 110.7 (4-*C*), 6.1 ( $\text{CH}_3$ ).  $^{11}\text{B}$  NMR (128 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) 42.6. Anal. Calcd (%) for  $\text{C}_{24}\text{H}_{32}\text{B}_4\text{Cl}_2\text{Lu}_2$ : C, 36.74; H, 4.11. Found: C, 36.77; H, 4.67.

( $\text{C}_5\text{H}_5\text{BN}(\text{Et})_2$ ) $_2\text{YCH}(\text{SiMe}_3)_2$  (**9**). A toluene solution of  $\text{LiCH}(\text{SiMe}_3)_2$  (79.1 mg, 0.475 mmol in 4 mL of toluene) was added to  $[(\text{C}_5\text{H}_5\text{BN}(\text{Et})_2)_2\text{YCl}]_2$  (200 mg, 0.238 mmol) in 3 mL of toluene. After stirring for 40 min at room temperature, the mixture was filtrated. Evaporation of the yellow filtrate in vacuo left an orange oil, which was extracted by  $2 \times 2$  mL of hexane. Removal of the solvent of the extract gave **9** as an orange oil (235 mg, 91% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) 7.21 (dd,  $J = 11.1$  Hz,  $J = 6.8$  Hz, 2H, 3-/5-*H*), 7.08 (dd,  $J = 11.1$  Hz,  $J = 6.8$  Hz, 2H, 3-/5-*H*), 6.16 (t,  $J = 6.8$  Hz, 1H, 4-*H*), 5.96 (d,  $J = 11.1$  Hz, 2H, 2-/6-*H*), 5.79 (m, 3H, 4-*H* and 2-/6-*H*), 3.27 (m, 4H,  $\text{NCH}_2$ ), 2.97 (m, 4H,  $\text{NCH}_2$ ), 1.07 (t, 12H,  $J = 7.2$  Hz,  $\text{CH}_3$ ), 0.79 (d,  $J_{\text{Y-H}} = 3.0$  Hz, 1H,  $\text{YCH}$ ), 0.15 (s, 18H,  $\text{Si}(\text{CH}_3)_3$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) 141.6 (3-/5-*C*), 141.5 (3-/5-*C*), 117.6 (2-/6-*C*), 114.9 (2-/6-*C*), 101.7 (4-*C*), 101.5 (4-*C*), 43.4 ( $\text{NCH}_2$ ), 42.8 ( $\text{NCH}_2$ ), 33.9 (d,  $J_{\text{Y-C}} = 29.8$  Hz,  $\text{YCH}$ ), 16.1 ( $\text{CH}_3$ ), 15.8 ( $\text{CH}_3$ ), 3.7 ( $\text{Si}(\text{CH}_3)_3$ ).  $^{11}\text{B}$  NMR (128 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) 33.1.  $^{89}\text{Y}$  NMR (19.6 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) 176.1. Anal. Calcd (%) for  $\text{C}_{25}\text{H}_{49}\text{B}_2\text{N}_2\text{Si}_2\text{Y}$ : C, 55.16; H, 9.07; N, 5.15. Found: C, 54.77; H, 9.88; N, 5.24.

( $\text{C}_5\text{H}_5\text{BN}(\text{Ph})_2$ ) $_2\text{YCH}(\text{SiMe}_3)_2$  (**10**). A toluene solution of  $\text{LiCH}(\text{SiMe}_3)_2$  (48.3 mg, 0.290 mmol in 3 mL of toluene) was added to  $[(\text{C}_5\text{H}_5\text{BN}(\text{Ph})_2)_2\text{YCl}]_2$  (155 mg, 0.126 mmol) in 3 mL of toluene. After stirring for 10 h at room temperature, the mixture was filtrated. Evaporation of the yellow filtrate in vacuo left an orange oil, which was extracted by  $5 \times 3$  mL of hexane. The combined yellow extraction was concentrated to ca. 4 mL and kept at room temperature overnight to give **10** as orange crystals. Crystallization of the concentrated mother liquor afforded a second crop of **10** (122 mg in total, 66% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) 7.27 (dd,  $J = 10.8$  Hz,  $J = 6.9$  Hz, 2H, 3-/5-*H*), 7.24–7.14 (m, 18H, Ph-*H* and 3-/5-*H*), 7.00–6.94 (m, 4H, Ph-*H*), 6.38 (d,  $J = 9.6$  Hz, 2H, 2-/6-*H*), 6.29 (d,  $J = 9.6$  Hz, 2H, 2-/6-*H*), 6.17 (t,  $J = 6.9$  Hz, 1H, 4-*H*), 5.88 (t,  $J = 6.9$  Hz, 1H, 4-*H*), 0.68 (d,  $J_{\text{Y-H}} = 3$  Hz, 1H,  $\text{YCH}$ ), 0.077 (s, 18H,  $\text{Si}(\text{CH}_3)_3$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) 149.9 (Ph-*C*), 149.9 (Ph-*C*), 142.1 (3-/5-*C*), 141.2 (3-/5-*C*), 129.4 (Ph-*C*), 129.3 (Ph-*C*), 127.2 (Ph-*C*), 127.0 (Ph-*C*), 124.0 (Ph-*C*), 123.9 (Ph-*C*), 120.6 (2-/6-*C*), 119.0 (2-/6-*C*), 105.0 (4-*C*), 104.9 (4-*C*), 39.1 (d,  $J_{\text{Y-C}} = 29.8$  Hz,  $\text{YCH}$ ), 3.5 ( $\text{Si}(\text{CH}_3)_3$ ).  $^{11}\text{B}$  NMR (128 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) 34.1.  $^{89}\text{Y}$  NMR (19.6 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) 170.0. Anal. Calcd (%) for  $\text{C}_{41}\text{H}_{49}\text{B}_2\text{N}_2\text{Si}_2\text{Y}$ : C, 66.86; H, 6.71; N, 3.80. Found: C, 66.25; H, 6.79; N, 3.74.

( $\text{C}_5\text{H}_5\text{BCH}_3$ ) $_2\text{YCH}(\text{SiMe}_3)_2$  (**11**). A toluene solution of  $\text{LiCH}(\text{SiMe}_3)_2$  (51.6 mg, 0.310 mmol in 3 mL of toluene) was added to  $[(\text{C}_5\text{H}_5\text{BCH}_3)_2\text{YCl}]_2$  (95.0 mg, 0.155 mmol) in 2 mL of toluene at  $-65^\circ\text{C}$  with stirring. The reaction mixture was gradually warmed to room temperature. The reaction mixture was filtered, and evaporation of the yellow filtrate in vacuo gave a brown oil. The oil was extracted by  $3 \times 1.5$  mL of hexane, the extract was concentrated to approximately 1 mL, and the residue was stored at  $-30^\circ\text{C}$  overnight. Some white precipitate that had formed was removed. Removal of the solvent gave **11** as a brown oil (80 mg, 60% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) 7.26 (dd,  $J = 10.4$  Hz,  $J = 6.8$  Hz, 2H, 3-/5-*H*), 7.06 (dd,  $J = 10.4$  Hz,  $J = 7.0$  Hz, 2H, 3-/5-*H*), 6.63 (dd,  $J = 10.4$  Hz,  $J = 1.6$  Hz, 2H, 2-/6-*H*), 6.61 (dd,  $J = 10.4$  Hz,  $J = 1.6$  Hz, 2H, 2-/6-*H*),

6.50 (tt,  $J = 7.2$  Hz,  $J = 1.6$  Hz, 1H, 4-*H*), 6.27 (tt,  $J = 6.8$  Hz,  $J = 1.6$  Hz, 1H, 4-*H*), 1.00 (s, 3H,  $\text{BCH}_3$ ), 0.98 (s, 3H,  $\text{BCH}_3$ ), 0.95 (d,  $J_{\text{Y-H}} = 2.8$  Hz, 1H,  $\text{YCH}$ ), 0.031 (s, 18H,  $\text{Si}(\text{CH}_3)_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) 139.6 (3-/5-*C*), 139.6 (3-/5-*C*), 134.4 (2-/6-*C*), 133.1 (2-/6-*C*), 112.4 (4-*C*), 112.2 (4-*C*), 38.7 (d,  $J_{\text{Y-C}} = 29.7$  Hz,  $\text{YCH}$ ), 6.00 ( $\text{BCH}_3$ ), 3.5 ( $\text{Si}(\text{CH}_3)_3$ ).  $^{11}\text{B}$  NMR (128 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) 42.6.  $^{89}\text{Y}$  NMR (19.6 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) 162.2. A satisfactory elemental analysis result for **11** could not be obtained. There are small amounts of impurities, which show some signals at 0–0.4 ppm in the  $^1\text{H}$  NMR spectrum. As **11** is an oil, the impurities could not be removed by recrystallization. The NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{11}\text{B}$ ,  $^{89}\text{Y}$ ) spectra of the complex are provided in the Supporting Information.

( $\text{C}_5\text{H}_5\text{BN}(\text{Ph})_2$ ) $_2\text{SmCH}(\text{SiMe}_3)_2$  (**12**). Following the procedure described for **10**, reaction of  $\text{LiCH}(\text{SiMe}_3)_2$  (27.6 mg, 0.166 mmol in 2 mL of toluene) and  $[(\text{C}_5\text{H}_5\text{BN}(\text{Ph})_2)_2\text{SmCl}]_2$  (102 mg, 0.0757 mmol in 2 mL of toluene) gave **12** as dark red crystals (52 mg, 43% yield). Anal. Calcd (%) for  $\text{C}_{41}\text{H}_{49}\text{B}_2\text{N}_2\text{Si}_2\text{Sm}$ : C, 61.71; H, 6.19; N, 3.51. Found: C, 60.95; H, 6.06; N, 3.77.

( $\text{C}_5\text{H}_5\text{BN}(\text{Ph})_2$ ) $_2\text{DyCH}(\text{SiMe}_3)_2$  (**13**). Following the procedure described for **10**, reaction of  $\text{LiCH}(\text{SiMe}_3)_2$  (36.3 mg, 0.218 mmol in 2.5 mL of toluene) and  $[(\text{C}_5\text{H}_5\text{BN}(\text{Ph})_2)_2\text{DyCl}]_2$  (150 mg, 0.109 mmol in 3 mL of toluene) gave **13** as red crystals (90 mg, 51% yield). Anal. Calcd (%) for  $\text{C}_{41}\text{H}_{49}\text{B}_2\text{N}_2\text{Si}_2\text{Dy}$ : C, 60.78; H, 6.10; N, 3.46. Found: C, 59.85; H, 6.11; N, 3.52.

( $\text{C}_5\text{H}_5\text{BN}(\text{Et})_2$ ) $_2\text{LuCH}(\text{SiMe}_3)_2$  (**14**). A toluene solution of  $\text{LiCH}(\text{SiMe}_3)_2$  (26.3 mg, 0.158 mmol in 2 mL of toluene) was added to  $[(\text{C}_5\text{H}_5\text{BN}(\text{Et})_2)_2\text{LuCl}]_2$  (80 mg, 0.079 mmol) in 2 mL of toluene at  $-30^\circ\text{C}$  with stirring. The reaction mixture was gradually warmed to room temperature and filtered. Evaporation of the yellow filtrate in vacuo left an orange oil, which was extracted with  $3 \times 1.5$  mL of hexane. The extract was concentrated to approximately 1 mL, and the residue was stored at  $-30^\circ\text{C}$  overnight. Some white precipitate that had formed was removed. Removal of the solvent gave **14** as an orange oil (89 mg, 89% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) 6.98 (dd,  $J = 11.2$  Hz,  $J = 6.8$  Hz, 2H, 3-/5-*H*), 6.91 (dd,  $J = 11.2$  Hz,  $J = 6.4$  Hz, 2H, 3-/5-*H*), 6.36 (tt,  $J = 6.8$  Hz,  $J = 1.6$  Hz, 1H, 4-*H*), 5.90 (tt,  $J = 6.8$  Hz,  $J = 1.6$  Hz, 1H, 4-*H*), 5.84 (dd,  $J = 11.2$  Hz,  $J = 1.2$  Hz, 2H, 2-/6-*H*), 5.56 (dd,  $J = 11.2$  Hz,  $J = 1.2$  Hz, 2H, 2-/6-*H*), 3.37 (m,  $J = 7.2$  Hz, 2H,  $\text{NCH}_2$ ), 3.26 (m,  $J = 7.2$  Hz, 2H,  $\text{NCH}_2$ ), 2.98 (m, 4H,  $\text{NCH}_2$ ), 1.10 (t,  $J = 7.2$  Hz, 6H,  $\text{CH}_3$ ), 1.09 (t,  $J = 7.2$  Hz, 6H,  $\text{CH}_3$ ), 0.92 (s, 1H,  $\text{LuCH}$ ), 0.12 (s, 18H,  $\text{Si}(\text{CH}_3)_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) 141.6 (3-/5-*C*), 140.8 (3-/5-*C*), 116.6 (2-/6-*C*), 111.8 (2-/6-*C*), 101.4 (4-*C*), 101.1 (4-*C*), 43.5 ( $\text{NCH}_2$ ), 42.8 ( $\text{NCH}_2$ ), 34.1 ( $\text{LuCH}$ ), 16.2 ( $\text{CH}_3$ ), 15.7 ( $\text{CH}_3$ ), 4.4 ( $\text{Si}(\text{CH}_3)_3$ ).  $^{11}\text{B}$  NMR (128 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) 33.4. A satisfactory elemental analysis result for **14** could not be obtained. There are small amounts of impurities, which show some signals at 0–0.4 ppm in the  $^1\text{H}$  NMR spectrum. As **14** is an oil, the impurities could not be removed by recrystallization. The NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{11}\text{B}$ ) spectra of the complex are provided in the Supporting Information.

( $\text{C}_5\text{H}_5\text{BN}(\text{Ph})_2$ ) $_2\text{LuCH}(\text{SiMe}_3)_2$  (**15**). Following the procedure described for **10**, reaction of  $\text{LiCH}(\text{SiMe}_3)_2$  (39.9 mg, 0.240 mmol in 3 mL of toluene) and  $[(\text{C}_5\text{H}_5\text{BN}(\text{Ph})_2)_2\text{LuCl}]_2$  (146 mg, 0.104 mmol in 3 mL of toluene) gave **15** as orange crystals (102 mg, 59% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) 7.25–7.15 (m, 18H, Ph-*H* and 3-/5-*H*), 7.11 (dd,  $J = 10.5$  Hz,  $J = 6.6$  Hz, 2H, 3-/5-*H*), 7.00–6.94 (m, 4H, Ph-*H*), 6.33 (d,  $J = 9.9$  Hz, 2H, 2-/6-*H*), 6.26 (t,  $J = 6.9$  Hz, 1H, 4-*H*), 6.19 (d,  $J = 10.2$  Hz, 2H, 2-/6-*H*), 5.92 (t,  $J = 6.9$  Hz, 1H, 4-*H*), 0.74 (s, 1H,  $\text{LuCH}$ ), 0.081 (s, 18H,  $\text{Si}(\text{CH}_3)_3$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) 149.9 (Ph-*C*), 149.8 (Ph-*C*), 142.1 (3-/5-*C*), 141.1 (3-/5-*C*), 129.5 (Ph-*C*), 129.3 (Ph-*C*), 127.4 (Ph-*C*), 127.3 (Ph-*C*), 124.0 (Ph-*C*), 123.9 (Ph-*C*), 119.4 (2-/6-*C*), 116.8 (2-/6-*C*), 104.2 (4-*C*), 104.1 (4-*C*), 38.6 ( $\text{LuCH}$ ), 4.1 ( $\text{Si}(\text{CH}_3)_3$ ).  $^{11}\text{B}$  NMR (128 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) 34.3. Anal. Calcd (%) for  $\text{C}_{41}\text{H}_{49}\text{B}_2\text{N}_2\text{Si}_2\text{Lu}$ : C, 59.86; H, 6.00; N, 3.41. Found: C, 59.48; H, 6.31; N, 3.38.

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**Table 4.** Crystallographic Data and Refinement for **7**·(toluene), **10**, **13**, and **15**

	<b>7</b> ·(toluene)	<b>10</b>	<b>13</b>	<b>15</b>
formula	C <sub>75</sub> H <sub>68</sub> B <sub>4</sub> Cl <sub>2</sub> Lu <sub>2</sub> N <sub>4</sub>	C <sub>41</sub> H <sub>49</sub> B <sub>2</sub> N <sub>2</sub> Si <sub>2</sub> Y	C <sub>41</sub> H <sub>49</sub> B <sub>2</sub> N <sub>2</sub> Si <sub>2</sub> Dy	C <sub>41</sub> H <sub>49</sub> B <sub>2</sub> N <sub>2</sub> Si <sub>2</sub> Lu
fw	1489.41	736.53	808.11	820.58
color	yellow	yellow	orange	yellow
cryst syst	monoclinic	monoclinic	orthorhombic	orthorhombic
space group	<i>Pn</i>	<i>P2</i> (1)/ <i>c</i>	<i>P2</i> (1)2(1)2(1)	<i>P2</i> (1)2(1)2(1)
<i>a</i> , Å	11.7871(8)	11.3673(14)	8.6490(3)	8.6296(6)
<i>b</i> , Å	11.8143(8)	11.0027(13)	17.8750(5)	17.7256(12)
<i>c</i> , Å	24.2512(16)	31.775(4)	25.3892(8)	25.2551(18)
β, deg	100.8960(10)	97.492(2)	90.00	90.00
<i>V</i> , Å <sup>3</sup>	3316.2(4)	3940.3(8)	3925.2(2)	3863.1(5)
<i>Z</i>	2	4	4	4
<i>D</i> <sub>calcd</sub> , g/cm <sup>3</sup>	1.492	1.242	1.367	1.411
<i>F</i> (000)	1484	1544	1644	1664
θ range, deg	1.71 to 26.00	1.96 to 25.50	1.60 to 25.01	1.40 to 25.01
no. of reflns collected	17 878	20 200	45 609	44 487
no. of unique reflns	11 422	7332	6881	6785
no. of obsd reflns ( <i>I</i> > 2σ( <i>I</i> ))	8622	3343	6769	6687
no. of params	775	440	471	469
goodness of fit	1.013	0.871	1.128	1.059
final <i>R</i> , <i>R</i> <sub>w</sub> ( <i>I</i> > 2σ( <i>I</i> ))	0.0852, 0.2042	0.0558, 0.0949	0.0216, 0.0544	0.0225, 0.0589
Δρ <sub>max,min</sub> , e Å <sup>-3</sup>	2.644, −2.835	0.505, −0.695	0.772, −0.522	1.010, −0.715

(C<sub>5</sub>H<sub>5</sub>BCH<sub>3</sub>)<sub>2</sub>LuCH(SiMe<sub>3</sub>)<sub>2</sub> (**16**). Following the procedure described for **11**, reaction of LiCH(SiMe<sub>3</sub>)<sub>2</sub> (42.4 mg, 0.255 mmol in 3 mL of toluene) and [(C<sub>5</sub>H<sub>5</sub>BCH<sub>3</sub>)<sub>2</sub>LuCl]<sub>2</sub> (100 mg, 0.127 mmol in 3 mL of toluene) gave **16** as a red oil (70 mg, 53% yield). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ (ppm) 7.11 (dd, *J* = 10.5 Hz, *J* = 7.2 Hz, 2H, 3-/5-*H*), 6.93 (dd, *J* = 7.2 Hz, 2H, 3-/5-*H*), 6.64 (t, *J* = 7.2 Hz, 1H, 4-*H*), 6.50 (d, *J* = 11.1 Hz, 2H, 2-/6-*H*), 6.46 (d, *J* = 10.8 Hz, 2H, 2-/6-*H*), 6.38 (t, *J* = 6.9 Hz, 1H, 4-*H*), 1.12 (s, 3H, BCH<sub>3</sub>), 1.11 (s, 3H, BCH<sub>3</sub>), 0.99 (s, 1H, LuCH), 0.057 (s, 18H, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>): δ (ppm) 139.8 (3-/5-*C*), 139.4 (3-/5-*C*), 133.1 (2-/6-*C*), 131.0 (2-/6-*C*), 112.0 (4-*C*), 111.4 (4-*C*), 38.6 (LuCH), 6.4 (br s, BCH<sub>3</sub>), 4.1 (Si(CH<sub>3</sub>)<sub>3</sub>). <sup>11</sup>B NMR (128 MHz, C<sub>6</sub>D<sub>6</sub>): δ (ppm) 42.8. A satisfactory elemental analysis result for **16** could not be obtained. There are small amounts of impurities, which show some signals at 0–0.4 ppm in the <sup>1</sup>H NMR spectrum. As **16** is an oil, the impurities could not be removed by recrystallization. The NMR (<sup>1</sup>H, <sup>13</sup>C, <sup>11</sup>B) spectra of the complex are provided in the Supporting Information.

**X-ray Crystallography.** Suitable single crystals of **7**·(toluene), **10**, **13**, and **15** were sealed in thin-walled glass capillaries. Data collection of **7**·(toluene) and **10** was performed at 20 °C on a Bruker SMART diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). 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*<sup>2</sup> by full-matrix least-squares techniques with anisotropic thermal para-

meters for non-hydrogen atoms. Hydrogen atoms were placed at calculated positions and were included in the structure calculation. All calculations were carried out using the SHELXL-97 program.

Data collection of **13** and **15** was performed at −100 °C on a Bruker SMART APEXII diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The SMART program package was used to determine the unit-cell parameters. The absorption correction was applied using APEX2 software package. The structures were solved by direct methods and refined on *F*<sup>2</sup> by full-matrix least-squares. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were refined with isotropic parameters at calculated positions without further refinement. All calculations were carried out using the SHELXL-97 program.

Crystallographic data and refinement for **7**·(toluene), **10**, **13**, and **15** are listed in Table 4.

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**Supporting Information Available:** NMR (<sup>1</sup>H, <sup>13</sup>C, <sup>11</sup>B, <sup>89</sup>Y) spectra of **6**–**11** and **14**–**16** and CIF files giving X-ray crystallographic data for **7**·(toluene), **10**, **13**, and **15**. This material is available free of charge via the Internet at <http://pubs.acs.org>.