

# Chemistry of C-Trimethylsilyl-Substituted Heterocarboranes. 33. Synthesis of Mixed-Ligand Metallacarboranes of Yttrium and Lanthanides Derived from Open $\eta^5$ -Pentadiene and $C_2B_4$ -Carborane: A Synthetic and Structural Investigation

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The reactions of *nido*-2-R-3-(Me<sub>3</sub>Si)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> (R = Me<sub>3</sub>Si, **1**; R = Me, **2**) with [ $\eta^5$ -2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>]<sub>3</sub>M in a molar ratio of 1:1, in toluene at elevated temperature (70 °C), produced mixed-ligand dimeric lanthanacarboranes of the type [ $(\eta^5$ -2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>)( $\eta^5$ -2-R-3-(Me<sub>3</sub>Si)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>)M]<sub>2</sub> (**3**, M = Y, R = Me<sub>3</sub>Si; **4**, M = Y, R = Me; **5**, M = Gd, R = Me<sub>3</sub>Si; **6**, M = Gd, R = Me; **7**, M = Tb, R = SiMe<sub>3</sub>; **8**, M = Tb, R = Me; **9**, M = Dy, R = Me<sub>3</sub>Si; **10**, M = Dy, R = Me; **11**, M = Ho, R = Me<sub>3</sub>Si; **12**, M = Ho, R = Me; **13**, M = Er, R = Me<sub>3</sub>Si; **14**, M = Er, R = Me; **15**, M = Tm, R = SiMe<sub>3</sub>; **16**, M = Tm, R = Me; **17**, M = Lu, R = Me<sub>3</sub>Si; **18**, M = Lu, R = Me) as crystalline solids in 75–88% yields. All the compounds were characterized by IR spectroscopy and elemental analyses. While the diamagnetic species **3**, **4**, **17**, and **18** were characterized by <sup>1</sup>H, <sup>13</sup>C, and <sup>11</sup>B NMR spectroscopy, compounds **3–8**, **10**, **12–14**, and **18** were also characterized by single-crystal X-ray diffraction analyses. On the basis of the reactivity pattern and isolated products, an intramolecular H-transfer reaction mechanism is proposed for the formation of these species.

## Introduction

The cyclopentadienyl ([R<sub>5</sub>C<sub>5</sub>]<sup>−</sup>) and various pentadienyl ([R<sub>2</sub>C<sub>5</sub>H<sub>5</sub>]<sup>−</sup>) monoanions and the *nido*-carborane dianions, [*nido*-R<sub>2</sub>C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>]<sup>2−</sup> and [*nido*-R<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>]<sup>2−</sup>, are all similar in that they are six-electron donor ligands in which the metal-binding electrons are typically delocalized in  $\pi$ -type orbitals above a planar five-atom face. The analogy between [R<sub>5</sub>C<sub>5</sub>]<sup>−</sup> and the *nido*-carboranes was first recognized over 40 years ago by Hawthorne.<sup>1</sup> This similarity was demonstrated shortly thereafter by the syntheses of Fe(C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub><sup>2−</sup> and Fe(C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub><sup>−</sup>, analogues of ferrocene,<sup>2</sup> and the mixed-ligand sandwich complex (C<sub>5</sub>H<sub>5</sub>)Fe(C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>).<sup>3</sup> Since then a number of mixed-ligand, half- and full-sandwich metallacarborane complexes have been described.<sup>4</sup> In the same way, a number of so-called “open metallocenes”, where the pentadienyl group replaces one or more cyclopentadienyl ligands, have been synthesized and characterized.<sup>5</sup> The pentadienyls have been shown to be similar to their cyclic analogues in some respects, but possess a unique chemistry that has led to a number of unusual compounds, such

as the metallabenzenes<sup>6</sup> and their  $\pi$ -complexes.<sup>7</sup> On the other hand, there seems to be little information available regarding the syntheses, structures, and reactivities of mixed open pentadienyl/carborane metal complexes. This is especially true for the f-block metals. In order to gain information on these interesting and potentially useful complexes, we initiated a study of the syntheses and structures of some ( $\eta^5$ -2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>)( $\eta^5$ -2,3-(SiMe<sub>3</sub>)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>)Ln complexes, a preliminary report of which has appeared in a recent communication (Ln = Tb and Er).<sup>8</sup> We have extended this study to other lanthanide and yttrium metals, and herein, we report the detailed study of these compounds.

## Experimental Section

**Materials.** Toluene and *n*-hexane were dried over NaH or Na/benzophenone and doubly distilled before use. The synthesis of *nido*-2-R-3-(Me<sub>3</sub>Si)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> (R = Me<sub>3</sub>Si, **1**; R = Me, **2**) followed the published procedure.<sup>9</sup> YCl<sub>3</sub>, GdCl<sub>3</sub>, TbCl<sub>3</sub>, DyCl<sub>3</sub>, HoCl<sub>3</sub>, ErCl<sub>3</sub>, and LuCl<sub>3</sub> were purchased from Aldrich and were degassed in vacuo at 130 °C for 24 h prior to use. The synthesis of

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**Table 1. Analytical Data for Compounds 3 to 18**

no.	compound formula	carbon		hydrogen	
		calculated	found	calculated	found
3	C <sub>30</sub> H <sub>66</sub> B <sub>8</sub> Si <sub>4</sub> Y <sub>2</sub>	44.84	44.46	8.28	8.43
4	C <sub>26</sub> H <sub>54</sub> B <sub>8</sub> Si <sub>2</sub> Y <sub>2</sub>	45.44	45.64	7.92	8.13
5	C <sub>30</sub> H <sub>66</sub> B <sub>8</sub> Si <sub>4</sub> Gd <sub>2</sub>	38.32	38.01	7.08	7.24
6	C <sub>26</sub> H <sub>54</sub> B <sub>8</sub> Si <sub>2</sub> Gd <sub>2</sub>	37.90	37.10	6.61	7.13
7	C <sub>30</sub> H <sub>66</sub> B <sub>8</sub> Si <sub>4</sub> Tb <sub>2</sub>	38.19	38.40	7.05	7.43
8	C <sub>26</sub> H <sub>54</sub> B <sub>8</sub> Si <sub>2</sub> Tb <sub>2</sub>	37.75	38.07	6.58	6.48
9	C <sub>30</sub> H <sub>66</sub> B <sub>8</sub> Si <sub>4</sub> Dy <sub>2</sub>	38.19	38.40	7.05	7.43
10	C <sub>26</sub> H <sub>54</sub> B <sub>8</sub> Si <sub>2</sub> Dy <sub>2</sub>	37.43	37.40	6.52	6.43
11	C <sub>30</sub> H <sub>66</sub> B <sub>8</sub> Si <sub>4</sub> Ho <sub>2</sub>	37.71	37.43	6.96	6.87
12	C <sub>26</sub> H <sub>54</sub> B <sub>8</sub> Si <sub>2</sub> Ho <sub>2</sub>	37.21	37.33	6.49	6.54
13	C <sub>30</sub> H <sub>66</sub> B <sub>8</sub> Si <sub>4</sub> Er <sub>2</sub>	37.53	37.65	6.93	6.75
14	C <sub>26</sub> H <sub>54</sub> B <sub>8</sub> Si <sub>2</sub> Er <sub>2</sub>	37.00	36.96	6.45	6.08
15	C <sub>30</sub> H <sub>66</sub> B <sub>8</sub> Si <sub>4</sub> Tm <sub>2</sub>	37.40	37.31	6.90	7.13
16	C <sub>26</sub> H <sub>54</sub> B <sub>8</sub> Si <sub>2</sub> Tm <sub>2</sub>	36.86	36.70	6.42	5.95
17	C <sub>30</sub> H <sub>66</sub> B <sub>8</sub> Si <sub>4</sub> Lu <sub>2</sub>	36.93	36.78	6.82	6.71
18	C <sub>26</sub> H <sub>54</sub> B <sub>8</sub> Si <sub>2</sub> Lu <sub>2</sub>	36.34	36.26	6.33	6.19

( $\eta^5$ -2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>)K,<sup>8</sup> and its subsequent conversion to ( $\eta^5$ -2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>Ln,<sup>10</sup> followed literature procedures.

**Spectroscopic Procedures.** <sup>1</sup>H, <sup>11</sup>B, and <sup>13</sup>C NMR spectra were recorded on a Bruker Fourier-transform multinuclear NMR spectrometer at 200, 64.2, and 50.3 MHz, respectively. Infrared spectra were recorded on a Perkin-Elmer Model 1600 FT-IR spectrophotometer and Nicolet Magna 550 FT-IR spectrophotometer. Elemental analyses were determined in house at Northern Illinois University using a Perkin-Elmer 2400 CHN elemental analyzer.

**Synthetic Procedures.** All experiments were carried out in 100 mL Pyrex glass round-bottom flasks, equipped with magnetic stirring bars and high-vacuum Teflon valves. After their initial purifications, nonvolatile substances were manipulated in either a drybox or a glove bag, under an atmosphere of dry nitrogen. All known compounds among the products were identified by comparing their IR and/or <sup>1</sup>H NMR spectra with those of authentic samples.

**Syntheses of Mixed-Ligand Metallacarboranes.** All compounds (3–18) were prepared using the same general procedure and reaction times. Therefore, only the synthesis of [( $\eta^5$ -2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>)( $\eta^5$ -2,3-(Me<sub>3</sub>Si)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>)Y]<sub>2</sub> (3) will be described in detail. The amounts, yields, descriptions, and spectral data for compounds 4–18 will then follow. In all cases the Ln(C<sub>7</sub>H<sub>11</sub>)<sub>3</sub> product was isolated, but only in the case of Ln = Y and Lu was any attempt made to characterize the compounds; in all other cases the Ln(C<sub>7</sub>H<sub>11</sub>)<sub>3</sub> was immediately redissolved in toluene preparatory to reaction with the carborane. Table 1 lists the analytical data for compounds 3–18.

[( $\eta^5$ -2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>)( $\eta^5$ -2,3-(Me<sub>3</sub>Si)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>)Y]<sub>2</sub> (3). Dry THF (40 mL) was condensed in vacuo into a reaction flask containing 0.50 g (2.6 mmol) of anhydrous YCl<sub>3</sub>, and the resulting heterogeneous mixture was stirred overnight. The mixture was then cooled to -78 °C, and a 9.85 mL THF solution of K(2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>) (7.7 mmol, 0.78 M) was added slowly into the flask with constant stirring. This mixture was slowly warmed to room temperature and stirred for 72 h at this temperature, during which time the heterogeneous reaction mixture turned yellow. This mixture was then filtered to remove KCl to collect a clear filtrate. The solvent was removed slowly from the filtrate to obtain a yellow solid, identified by NMR as Y(C<sub>7</sub>H<sub>11</sub>)<sub>3</sub> [<sup>1</sup>H NMR (*d*<sub>8</sub>-toluene, 25 °C, relative to external Me<sub>4</sub>Si)  $\delta$ : 1.87 (s, 6H, CH<sub>3</sub> in 2,4-C<sub>7</sub>H<sub>11</sub>), 3.12 (m, br, 2H, CH<sub>2</sub> in 2,4-C<sub>7</sub>H<sub>11</sub>), 3.70 (s, 2H, CH<sub>2</sub> in 2,4-C<sub>7</sub>H<sub>11</sub>), 4.30 (m, br, 1H, CH in 2,4-C<sub>7</sub>H<sub>11</sub>) ppm. <sup>13</sup>C NMR (*d*<sub>8</sub>-toluene, 25 °C, relative to external Me<sub>4</sub>Si)  $\delta$ : 29.45 [CH<sub>3</sub> on 2,4-C<sub>7</sub>H<sub>11</sub>], 79.68 [CH<sub>2</sub> on 2,4-C<sub>7</sub>H<sub>11</sub>], 90.57 [CH on 2,4-C<sub>7</sub>H<sub>11</sub>], 148.05 [C on 2,4-

C<sub>7</sub>H<sub>11</sub>] ppm]. The solid was redissolved in 50 mL of anhydrous toluene, and 0.56 g (2.6 mmol) of *nido*-2,3-(SiMe<sub>3</sub>)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> (1) in 20 mL of anhydrous toluene was slowly added at room temperature with constant stirring. After complete addition, the resulting mixture was heated to 70 °C for 24 h, during which time the mixture turned yellow. The solvent was then removed in vacuo to collect a yellow solid, which was repeatedly washed with hexane and then recrystallized from anhydrous toluene to collect orange crystals, identified as [( $\eta^5$ -2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>)( $\eta^5$ -2,3-(Me<sub>3</sub>Si)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>)Y]<sub>2</sub> (3), in 86% yield (0.88 g, 1.1 mmol). IR (cm<sup>-1</sup>, KBr pellet): 2958(s), 2901(s), 2550(s), 2371(s). NMR data for complex 3: <sup>1</sup>H NMR (*d*<sub>8</sub>-toluene, at 25 °C, relative to external Me<sub>4</sub>Si)  $\delta$ : 0.44 (s, 9H, SiCH<sub>3</sub>), 1.19 (br, s, 6H, CH<sub>3</sub> in 2,4-C<sub>7</sub>H<sub>11</sub>), 3.27 (br, s, 2H, CH<sub>2</sub> in 2,4-C<sub>7</sub>H<sub>11</sub>), 4.33 (br, s, 2H, CH<sub>2</sub> in 2,4-C<sub>7</sub>H<sub>11</sub>), 4.78 (br, s, CH in 2,4-C<sub>7</sub>H<sub>11</sub>) ppm. <sup>13</sup>C NMR (*d*<sub>8</sub>-toluene, at 25 °C, relative to external Me<sub>4</sub>Si)  $\delta$ : 0.43 [CH<sub>3</sub>-Si], 26.53 [CH<sub>3</sub> on 2,4-C<sub>7</sub>H<sub>11</sub>], 63.0 [C-cage], 94.02 [CH<sub>2</sub> on 2,4-C<sub>7</sub>H<sub>11</sub>], 116.05 [CH on 2,4-C<sub>7</sub>H<sub>11</sub>], 146.82 [C on 2,4-C<sub>7</sub>H<sub>11</sub>] ppm. <sup>11</sup>B NMR (*d*<sub>8</sub>-toluene, 25 °C, relative to external BF<sub>3</sub>·OEt<sub>2</sub>)  $\delta$ : -27.0 (1B, <sup>1</sup>J<sub>BH</sub> = 165.7 Hz), +25.7 (3B) ppm.

[( $\eta^5$ -2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>)( $\eta^5$ -2-Me-3-(SiMe<sub>3</sub>)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>)Y]<sub>2</sub> (4). A previously weighed sample of anhydrous YCl<sub>3</sub> (0.50 g, 2.6 mmol) was reacted with K(2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>) (9.85 mL, 7.7 mmol, 0.78 M solution in THF) to obtain ( $\eta^5$ -2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>Y as a yellow solid. Then, this solid was redissolved in toluene and was allowed to react with *nido*-2-Me-3-(SiMe<sub>3</sub>)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> (2) (0.42 g, 2.6 mmol) to give a crystalline, orange solid, identified as [( $\eta^5$ -2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>)( $\eta^5$ -2-Me-3-(SiMe<sub>3</sub>)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>)Y]<sub>2</sub> (4) (0.74 g, 1.1 mmol; yield 85%). NMR data for complex 4: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, at 25 °C, relative to external Me<sub>4</sub>Si)  $\delta$ : 0.32 - 0.57 (br, s, 4H, BH), 0.48 (s, 3H, CH<sub>3</sub>-cage), 1.01 (t, 9H, SiCH<sub>3</sub>), 1.36 (s, 6H, CH<sub>3</sub> in 2,4-C<sub>7</sub>H<sub>11</sub>), 1.66-1.99 (m, 2H, CH<sub>2</sub> in 2,4-C<sub>7</sub>H<sub>11</sub>), 5.01-5.13 (m, 2H, CH<sub>2</sub> in 2,4-C<sub>7</sub>H<sub>11</sub>), 5.69-5.88 (m, 1H, CH in 2,4-C<sub>7</sub>H<sub>11</sub>) ppm. <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, at 25 °C, relative to external Me<sub>4</sub>Si)  $\delta$ : 13.97 [CH<sub>3</sub>-Si], 22.77 [CH<sub>3</sub>-cage], 34.16 [CH<sub>3</sub> on 2,4-C<sub>7</sub>H<sub>11</sub>], 65.82 [C-cage], 71.99 [C-cage], 95.41 [CH<sub>2</sub> on 2,4-C<sub>7</sub>H<sub>11</sub>], 113.92 [CH on 2,4-C<sub>7</sub>H<sub>11</sub>], 142.02 [C on 2,4-C<sub>7</sub>H<sub>11</sub>] ppm. <sup>11</sup>B NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, relative to external BF<sub>3</sub>·OEt<sub>2</sub>)  $\delta$ : -48.47 (1B, <sup>1</sup>J<sub>BH</sub> = 167.84 Hz), -20.12 (1B), -0.56 (1B, <sup>1</sup>J<sub>BH</sub> = 118.79 Hz), +27.71 (1B) ppm.

[( $\eta^5$ -2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>)( $\eta^5$ -2,3-(Me<sub>3</sub>Si)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>)Gd]<sub>2</sub> (5). Gadolinium(III) chloride, GdCl<sub>3</sub> (0.50 g, 1.9 mmol), was first reacted with K(2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>) (7.31 mL, 5.7 mmol, 0.78 M solution in THF) and then *nido*-2,3-(SiMe<sub>3</sub>)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> (1) (0.42 g, 1.9 mmol) to give orange crystals, identified as [( $\eta^5$ -2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>)( $\eta^5$ -2,3-(SiMe<sub>3</sub>)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>)Gd]<sub>2</sub> (5) (0.73 g, 0.77 mmol; yield 82%). IR (cm<sup>-1</sup>, KBr pellet): 2958 (s), 2901 (s), 2550 (s), 2371(s) [ $\nu$ (B-H)].

[( $\eta^5$ -2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>)( $\eta^5$ -2-Me-3-(Me<sub>3</sub>Si)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>)Gd]<sub>2</sub> (6). Gadolinium(III) chloride, GdCl<sub>3</sub> (0.50 g, 1.9 mmol), was first reacted with K(2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>) (7.31 mL, 5.7 mmol, 0.78 M solution in THF) and then *nido*-2-Me-3-(SiMe<sub>3</sub>)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> (2) (0.422 g, 2.6 mmol) to give an orange powder, identified as [( $\eta^5$ -2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>)( $\eta^5$ -2-Me-3-(SiMe<sub>3</sub>)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>)Gd]<sub>2</sub> (6) (0.80 g, 0.97 mmol; yield 51%). Mp: >250 °C. IR (cm<sup>-1</sup>, KBr pellet): 2950 (s), 2901 (s), 2448 (s), 2330 (s) [ $\nu$ (B-H)].

[( $\eta^5$ -2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>)( $\eta^5$ -2,3-(Me<sub>3</sub>Si)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>)Tb]<sub>2</sub> (7). Terbium(III) chloride, TbCl<sub>3</sub> (0.50 g, 1.9 mmol), was first reacted with K(2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>) (7.31 mL, 5.7 mmol, 0.78 M solution in THF) and then *nido*-2,3-(SiMe<sub>3</sub>)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> (1) (0.42 g, 1.9 mmol) to give yellow crystals, identified as [( $\eta^5$ -2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>)( $\eta^5$ -2,3-(SiMe<sub>3</sub>)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>)Tb]<sub>2</sub> (7) (0.68 g, 0.72 mmol; yield 76%; mp 105-106 °C (dec)). IR (cm<sup>-1</sup>, KBr pellet): 2590 (s), 2554 (s), 2540 (s), 2371 (w), [ $\nu$ (B-H)].

[( $\eta^5$ -2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>)( $\eta^5$ -2-Me-3-(Me<sub>3</sub>Si)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>)Tb]<sub>2</sub> (8). Terbium(III) chloride, TbCl<sub>3</sub> (0.50 g, 1.9 mmol), was first reacted with K(2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>) (7.23 mL, 5.6 mmol, 0.78 M solution in THF) and *nido*-2-Me-3-(SiMe<sub>3</sub>)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> (2) (0.31 g, 1.9 mmol) to give yellow crystals, identified as [( $\eta^5$ -2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>)( $\eta^5$ -2-Me-

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3-(SiMe<sub>3</sub>)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>/Tb)<sub>2</sub> (**8**) (0.63 g, 0.76 mmol; yield 80%). IR (cm<sup>-1</sup>, KBr pellet): 2558 (vs), 2450 (s, s), 2365 (br, s), 2303 (w) [ $\nu$ (B-H)].

$[(\eta^5\text{-}2,4\text{-}(\text{Me})_2\text{C}_5\text{H}_5)(\eta^5\text{-}2,3\text{-}(\text{Me}_3\text{Si})_2\text{-}2,3\text{-}\text{C}_2\text{B}_4\text{H}_4)\text{Dy}]_2$  (**9**). Dysprosium(III) chloride, DyCl<sub>3</sub> (0.50 g, 1.9 mmol), was first reacted with K(2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>) (7.15 mL, 5.6 mmol, 0.78 M solution in THF) and then *nido*-2,3-(SiMe<sub>3</sub>)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> (**1**) (0.41 g, 1.9 mmol) to give an off-white solid, identified as  $[(\eta^5\text{-}2,4\text{-}(\text{Me})_2\text{C}_5\text{H}_5)(\eta^5\text{-}2,3\text{-}(\text{SiMe}_3)_2\text{-}2,3\text{-}\text{C}_2\text{B}_4\text{H}_4)\text{Dy}]_2$  (**9**) (0.67 g, 0.70 mmol; yield 76%). IR (cm<sup>-1</sup>, KBr pellet): 2546 (vs), 2376 (br, s) [ $\nu$ (B-H)].

$[(\eta^5\text{-}2,4\text{-}(\text{Me})_2\text{C}_5\text{H}_5)(\eta^5\text{-}2\text{-}\text{Me}\text{-}3\text{-}(\text{Me}_3\text{Si})\text{-}2,3\text{-}\text{C}_2\text{B}_4\text{H}_4)\text{Dy}]_2$  (**10**). Dysprosium(III) chloride, DyCl<sub>3</sub> (0.50 g, 1.9 mmol), was first reacted with K(2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>) (7.15 mL, 5.6 mmol, 0.78 M solution in THF) and then *nido*-2-Me-3-(SiMe<sub>3</sub>)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> (**2**) (0.30 g, 1.9 mmol) to give an off-white solid, identified as  $[(\eta^5\text{-}2,4\text{-}(\text{Me})_2\text{C}_5\text{H}_5)(\eta^5\text{-}2,3\text{-}(\text{SiMe}_3)_2\text{-}2,3\text{-}\text{C}_2\text{B}_4\text{H}_4)\text{Dy}]_2$  (**10**) (0.60 g, 0.72 mmol; yield 77%). IR (cm<sup>-1</sup>, KBr pellet): 2557 (vs), 2498 (s), 2365 (br, s), 2034 (w) [ $\nu$ (B-H)].

$[(\eta^5\text{-}2,4\text{-}(\text{Me})_2\text{C}_5\text{H}_5)(\eta^5\text{-}2,3\text{-}(\text{Me}_3\text{Si})_2\text{-}2,3\text{-}\text{C}_2\text{B}_4\text{H}_4)\text{Ho}]_2$  (**11**). Holmium(III) chloride, HoCl<sub>3</sub> (0.50 g, 1.8 mmol), was first reacted with K(2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>) (7.08 mL, 5.5 mmol, 0.78 M solution in THF) and then *nido*-2,3-(SiMe<sub>3</sub>)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> (**1**) (0.40 g, 1.8 mmol) to give orange crystals, identified as  $[(\eta^5\text{-}2,4\text{-}(\text{Me})_2\text{C}_5\text{H}_5)(\eta^5\text{-}2,3\text{-}(\text{SiMe}_3)_2\text{-}2,3\text{-}\text{C}_2\text{B}_4\text{H}_4)\text{Ho}]_2$  (**11**) (0.77 g, 0.81 mmol; yield 88%). IR (cm<sup>-1</sup>, KBr pellet): 2544 (s), 2361 (br, s), 2309 (s, w) [ $\nu$ (B-H)].

$[(\eta^5\text{-}2,4\text{-}(\text{Me})_2\text{C}_5\text{H}_5)(\eta^5\text{-}2\text{-}\text{Me}\text{-}3\text{-}(\text{Me}_3\text{Si})\text{-}2,3\text{-}\text{C}_2\text{B}_4\text{H}_4)\text{Ho}]_2$  (**12**). Holmium(III) chloride, HoCl<sub>3</sub> (0.50 g, 1.8 mmol), was first reacted with K(2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>) (7.08 mL, 5.5 mmol, 0.78 M solution in THF) and then *nido*-2-Me-3-(SiMe<sub>3</sub>)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> (**2**) (0.30 g, 1.8 mmol) to give orange crystals, identified as  $[(\eta^5\text{-}2,4\text{-}(\text{Me})_2\text{C}_5\text{H}_5)(\eta^5\text{-}2,3\text{-}(\text{SiMe}_3)_2\text{-}2,3\text{-}\text{C}_2\text{B}_4\text{H}_4)\text{Ho}]_2$  (**12**) (0.63 g, 0.75 mmol; yield 82%). IR (cm<sup>-1</sup>, KBr pellet): 2558 (s), 2498 (s), 2367 (s), 2309 (w) [ $\nu$ (B-H)].

$[(\eta^5\text{-}2,4\text{-}(\text{Me})_2\text{C}_5\text{H}_5)(\eta^5\text{-}2,3\text{-}(\text{Me}_3\text{Si})_2\text{-}2,3\text{-}\text{C}_2\text{B}_4\text{H}_4)\text{Er}]_2$  (**13**). Erbium(III) chloride, ErCl<sub>3</sub> (0.50 g, 1.8 mmol), was first reacted with K(2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>) (7.00 mL, 5.5 mmol, 0.78 M solution in THF) and then *nido*-2,3-(SiMe<sub>3</sub>)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> (**1**) (0.40 g, 1.8 mmol) to give pale orange crystals, identified as  $[(\eta^5\text{-}2,4\text{-}(\text{Me})_2\text{C}_5\text{H}_5)(\eta^5\text{-}2,3\text{-}(\text{SiMe}_3)_2\text{-}2,3\text{-}\text{C}_2\text{B}_4\text{H}_4)\text{Er}]_2$  (**13**) (0.72 g, 0.75 mmol; yield 82%; mp 80–82 °C (dec)). IR (cm<sup>-1</sup>, KBr pellet): 2587 (s), 2542 (s), 2362 (s), 2290 (w) [ $\nu$ (B-H)].

$[(\eta^5\text{-}2,4\text{-}(\text{Me})_2\text{C}_5\text{H}_5)(\eta^5\text{-}2\text{-}\text{Me}\text{-}3\text{-}(\text{Me}_3\text{Si})\text{-}2,3\text{-}\text{C}_2\text{B}_4\text{H}_4)\text{Er}]_2$  (**14**). Erbium(III) chloride, ErCl<sub>3</sub> (0.50 g, 1.8 mmol), was first reacted with K(2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>) (7.00 mL, 5.5 mmol, 0.78 M solution in THF) and then *nido*-2-Me-3-(SiMe<sub>3</sub>)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> (**2**) (0.30 g, 1.8 mmol) to give pale orange crystals, identified as  $[(\eta^5\text{-}2,4\text{-}(\text{Me})_2\text{C}_5\text{H}_5)(\eta^5\text{-}2\text{-}\text{Me}\text{-}3\text{-}(\text{SiMe}_3)_2\text{-}2,3\text{-}\text{C}_2\text{B}_4\text{H}_4)\text{Er}]_2$  (**14**) (0.63 g, 0.75 mmol; yield 82%). IR (cm<sup>-1</sup>, KBr pellet): 2559 (vs), 2498 (vs), 2374 (s), 2358 (s), 2309 (w) [ $\nu$ (B-H)].

$[(\eta^5\text{-}2,4\text{-}(\text{Me})_2\text{C}_5\text{H}_5)(\eta^5\text{-}2,3\text{-}(\text{Me}_3\text{Si})_2\text{-}2,3\text{-}\text{C}_2\text{B}_4\text{H}_4)\text{Tm}]_2$  (**15**). Thulium(III) chloride, TmCl<sub>3</sub> (0.50 g, 1.8 mmol), was first reacted with K(2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>) (7.00 mL, 5.5 mmol, 0.78 M solution in THF) and then *nido*-2,3-(SiMe<sub>3</sub>)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> (**1**) (0.426 g, 1.8 mmol) to give orange crystals, identified as  $[(\eta^5\text{-}2,4\text{-}(\text{Me})_2\text{C}_5\text{H}_5)(\eta^5\text{-}2,3\text{-}(\text{SiMe}_3)_2\text{-}2,3\text{-}\text{C}_2\text{B}_4\text{H}_4)\text{Tm}]_2$  (**15**) (0.956 g; yield 54%). Mp > 250 °C. IR (cm<sup>-1</sup>, KBr pellets): 2859 (br, s), 2673 (w), 2360 (s) 2300 [ $\nu$ (B-H)].

$[(\eta^5\text{-}2,4\text{-}(\text{Me})_2\text{C}_5\text{H}_5)(\eta^5\text{-}2\text{-}\text{Me}\text{-}3\text{-}(\text{Me}_3\text{Si})\text{-}2,3\text{-}\text{C}_2\text{B}_4\text{H}_4)\text{Tm}]_2$  (**16**). Thulium(III) chloride, TmCl<sub>3</sub> (0.50 g, 1.8 mmol), was first reacted with K(2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>) (7.00 mL, 5.5 mmol, 0.78 M solution in THF) and then *nido*-2-Me-3-(SiMe<sub>3</sub>)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> (**2**) (0.296 g, 1.81 mmol) to give an orange powder, identified as  $[(\eta^5\text{-}2,4\text{-}(\text{Me})_2\text{C}_5\text{H}_5)(\eta^5\text{-}2\text{-}\text{Me}\text{-}3\text{-}(\text{SiMe}_3)_2\text{-}2,3\text{-}\text{C}_2\text{B}_4\text{H}_4)\text{Tm}]_2$  (**16**) (1.20 g, 1.41 mmol; yield 78%). Mp: 210–115 °C. IR (cm<sup>-1</sup>, KBr pellet): 2559 (vs), 2374 (s), 2485 (s), 2335 (w) [ $\nu$ (B-H)].

$[(\eta^5\text{-}2,4\text{-}(\text{Me})_2\text{C}_5\text{H}_5)(\eta^5\text{-}2,3\text{-}(\text{Me}_3\text{Si})_2\text{-}2,3\text{-}\text{C}_2\text{B}_4\text{H}_4)\text{Lu}]_2$  (**17**). Lutetium(III) chloride, LuCl<sub>3</sub> (0.50 g, 1.8 mmol), was reacted with K(2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>) (6.85 mL, 5.3 mmol, 0.78 M solution in THF) to give a dark red solid  $\{\text{Lu}[\text{C}_7\text{H}_{11}]_3\}$ , which was isolated and characterized by NMR spectra. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, relative to external Me<sub>4</sub>Si)  $\delta$ : 1.96 (s, 6H, CH<sub>3</sub> in 2,4-C<sub>7</sub>H<sub>11</sub>), 3.74–3.82 (m, br, 2H, CH<sub>2</sub> in 2,4-C<sub>7</sub>H<sub>11</sub>), 4.52 (s, 1H, CH in 2,4-C<sub>7</sub>H<sub>11</sub>), 4.52–5.04 (m, br, 2H, CH<sub>2</sub> in 2,4-C<sub>7</sub>H<sub>11</sub>) ppm. <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, relative to external Me<sub>4</sub>Si)  $\delta$ : 28.37 [CH<sub>3</sub> on 2,4-C<sub>7</sub>H<sub>11</sub>], 80.71 [CH<sub>2</sub> on 2,4-C<sub>7</sub>H<sub>11</sub>], 90.21 [CH on 2,4-C<sub>7</sub>H<sub>11</sub>], 148.25 [C on 2,4-C<sub>7</sub>H<sub>11</sub>] ppm. The compound was then reacted with *nido*-2,3-(SiMe<sub>3</sub>)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> (**1**) (0.39 g, 1.78 mmol) to give orange crystals, identified as  $[(\eta^5\text{-}2,4\text{-}(\text{Me})_2\text{C}_5\text{H}_5)(\eta^5\text{-}2,3\text{-}(\text{SiMe}_3)_2\text{-}2,3\text{-}\text{C}_2\text{B}_4\text{H}_4)\text{Lu}]_2$  (**17**) (0.65 g, 0.67 mmol; yield 75%). Mp: 238 °C (dec). IR (cm<sup>-1</sup>, KBr pellet): 2587 (s, s), 2542 (s, s), 2362 (s, s), 2290 (s, w) [ $\nu$ (B-H)]. NMR data for complex **17**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, at 25 °C, relative to external Me<sub>4</sub>Si)  $\delta$ : BH not observed, 0.47 (s, 9H, SiCH<sub>3</sub>), 1.68–1.91 (br, s, 6H, CH<sub>3</sub> in 2,4-C<sub>7</sub>H<sub>11</sub>), 2.02–2.13 (m, 2H, CH<sub>2</sub> in 2,4-C<sub>7</sub>H<sub>11</sub>), 4.92–5.13 (m, 2H, CH<sub>2</sub> in 2,4-C<sub>7</sub>H<sub>11</sub>), 5.83 (br, s, CH in 2,4-C<sub>7</sub>H<sub>11</sub>) ppm. <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, at 25 °C, relative to external Me<sub>4</sub>Si)  $\delta$ : 2.09 [CH<sub>3</sub>-Si], 26.30 [CH<sub>3</sub> on 2,4-C<sub>7</sub>H<sub>11</sub>], 79.42 [C-cage], 96.01 [CH<sub>2</sub> on 2,4-C<sub>7</sub>H<sub>11</sub>], 115.62 [CH on 2,4-C<sub>7</sub>H<sub>11</sub>], 145.74 [C on 2,4-C<sub>7</sub>H<sub>11</sub>] ppm. <sup>11</sup>B NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, relative to external BF<sub>3</sub>·OEt<sub>2</sub>)  $\delta$ : -20.25 (1B, <sup>1</sup>J<sub>BH</sub> = 158.21 Hz), +29.79 (3B) ppm.

$[(\eta^5\text{-}2,4\text{-}(\text{Me})_2\text{C}_5\text{H}_5)(\eta^5\text{-}2\text{-}\text{Me}\text{-}3\text{-}(\text{Me}_3\text{Si})\text{-}2,3\text{-}\text{C}_2\text{B}_4\text{H}_4)\text{Lu}]_2$  (**18**). The 1.8 mmol sample of  $\{\text{Lu}[\text{C}_7\text{H}_{11}]_3\}$  was then reacted with *nido*-2-Me-3-(SiMe<sub>3</sub>)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> (**2**) (0.29 g, 1.8 mmol) to give orange crystals, identified as  $[(\eta^5\text{-}2,4\text{-}(\text{Me})_2\text{C}_5\text{H}_5)(\eta^5\text{-}2\text{-}\text{Me}\text{-}3\text{-}(\text{SiMe}_3)_2\text{-}2,3\text{-}\text{C}_2\text{B}_4\text{H}_4)\text{Lu}]_2$  (**18**) (0.59 g, 0.69 mmol; yield 78%). Mp: > 250 °C. IR (cm<sup>-1</sup>, KBr pellet): 2560 (vs), 2499 (vs), 2373 (br, s) [ $\nu$ (B-H)]. NMR data for complex **18**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, at 25 °C, relative to external Me<sub>4</sub>Si)  $\delta$ : 0.39–0.57 (br, s, 4H, BH), 0.32 (s, 3H, CH<sub>3</sub>-cage), 0.38 (t, 9H, SiCH<sub>3</sub>), 1.87–1.90 (br, s, 6H, CH<sub>3</sub> in 2,4-C<sub>7</sub>H<sub>11</sub>), 2.23 (m, 2H, CH<sub>2</sub> in 2,4-C<sub>7</sub>H<sub>11</sub>), 5.01–5.13 (m, 2H, CH<sub>2</sub> in 2,4-C<sub>7</sub>H<sub>11</sub>), 5.83 (m, 1H, CH in 2,4-C<sub>7</sub>H<sub>11</sub>) ppm. <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, at 25 °C, relative to external Me<sub>4</sub>Si)  $\delta$ : 0.068 [CH<sub>3</sub>-Si], 23.65 [CH<sub>3</sub>-cage], 31.68 [CH<sub>3</sub> on 2,4-C<sub>7</sub>H<sub>11</sub>], [C-cage] were not observed, 111.47 [CH<sub>2</sub> on 2,4-C<sub>7</sub>H<sub>11</sub>], 114.51 [CH on 2,4-C<sub>7</sub>H<sub>11</sub>], 145.75 [C on 2,4-C<sub>7</sub>H<sub>11</sub>] ppm. <sup>11</sup>B NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, relative to external BF<sub>3</sub>·OEt<sub>2</sub>)  $\delta$ : -49.27 (1B, <sup>1</sup>J<sub>BH</sub> = 167.84 Hz), -0.46 (2B, <sup>1</sup>J<sub>BH</sub> = 108.90 Hz), +13.24 (1B) ppm.

**X-ray Analyses of 3–5, 7, 8, 10–14, and 18.** X-ray-quality crystals of **3–5, 7, 8, 10–14, and 18** were grown from toluene solution by slow evaporation. The crystals were mounted on a Bruker SMART CCD PLATFORM diffractometer under a low-temperature nitrogen stream to collect crystallographic data. The pertinent crystallographic data for **3, 5, 7, 6, and 13** are summarized in Table 2, while crystallographic data for **4, 8, 10, 12, 14, and 18** are summarized in Table 3. Compounds **3, 5, 7, and 13** were found to be isostructural, and their space groups were uniquely determined from systematic absences as *P2<sub>1</sub>/n*. Similar measurements on **4, 8, 10, 12, 14, and 18** were also consistent with the *C2/c* space group. Although compound **6** was chemically isostructural with **4, 8, 10, 12, 14, and 18**, the systematic absences were consistent with *P1̄*. Intensity data for these compounds were collected at 203(±2) K. For each compound, 50 frames were repeated at the end of data collection to monitor crystal decay, and no significant change in intensities was observed. All data, considered as observed [*I* > 2σ(*I*)], were corrected for Lorentz, polarization, and absorption effects (Sheldrick, G. M. *SADABS*, Program for Empirical Absorption Correction of Area Detector Data; University Göttingen: Germany, 2005). Semiempirical absorption corrections were applied for each structure, and the relevant minimum and maximum transmission factors are listed in Table 2 for **3, 5, 7, 6, and 13** and Table 3 for **4, 8, 10, 12, 14, and 18**. All structures were solved by direct methods and refined by full-matrix least-squares techniques

Table 2. Crystallographic Data<sup>a</sup> for Complexes 3, 5, 6, 7, and 13

	3	5	7	6	13
formula	C <sub>15</sub> H <sub>33</sub> B <sub>4</sub> Si <sub>2</sub> Y	C <sub>15</sub> H <sub>33</sub> B <sub>4</sub> GdSi <sub>2</sub>	C <sub>15</sub> H <sub>33</sub> B <sub>4</sub> Si <sub>2</sub> Tb	C <sub>13</sub> H <sub>27</sub> B <sub>4</sub> SiGd	C <sub>15</sub> H <sub>33</sub> B <sub>4</sub> ErSi <sub>2</sub>
fw	401.74	464.04	471.75	477.77	480.09
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 1	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> , Å	15.6185(12)	15.7007(15)	15.686(4)	8.388(2)	15.5736(17)
<i>b</i> , Å	8.4258(7)	8.4042(8)	8.425(2)	11.686(3)	8.4389(9)
<i>c</i> , Å	16.7041(13)	16.8002(16)	16.778(4)	14.244(4)	16.6439(18)
α, deg	90	90	90	72.634(4)	90
β, deg	94.7850(10)	94.898(2)	94.812(4)	73.370(4)	94.683(2)
γ, deg	90	90	90	76.350(4)	90
<i>V</i> , Å <sup>3</sup>	2190.6(3)	2208.7(4)	2209.5(9)	1259.3(5)	2180.1(4)
<i>Z</i>	4	4	4	2	4
<i>D</i> <sub>calcd</sub> , g cm <sup>-3</sup>	1.218	1.414	1.418	2.287	1.463
abs coeff, mm <sup>-1</sup>	2.764	3.104	3.302	6.448	3.952
cryst dimens, mm	0.80 × 0.25 × 0.02	0.50 × 0.12 × 0.12	0.72 × 0.10 × 0.18	0.20 × 0.10 × 0.04	0.52 × 0.10 × 0.08
scan sp in ω; min., max.	1.72, 25.00	1.70, 25.0	1.71, 25.0	1.54, 29.44	1.72, 25.0
<i>T</i> , K	203(2)	203(2)	203(2)	203(2)	203(2)
no. of data collected	15 083	16 071	14 590	11 931	15 521
no. of obsd reflns, <i>I</i> > 2σ( <i>I</i> )	3797	3874	3850	10 451	3828
no. of params refined	233	233	233	413	233
GOF	1.616	1.574	1.335	1.090	1.161
<i>g</i> <sup>c</sup>	0.0003(3)	0.00026(10)	0.00039(11)	0.00000(9)	0.00000(16)
<i>μ</i> <sub>(max, min)</sub> , e /Å <sup>3</sup>	+0.557, -1.506	+0.596, -1.101	+1.568, -0.622	+4.692, -1.948	+1.563, -1.519
<i>R</i> <sub>1</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0940	0.0371	0.0375	0.0684	0.0362
<i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.1805	0.0701	0.0766	0.1978	0.0889

<sup>a</sup> Graphite-monochromatized Mo Kα radiation, λ = 0.71073 Å. <sup>b</sup>*R* = Σ||*F*<sub>o</sub>| - |*F*<sub>c</sub>||/Σ|*F*<sub>o</sub>|, *R*<sub>w</sub> = [Σ*w*(*F*<sub>o</sub><sup>2</sup> - *F*<sub>c</sub><sup>2</sup>)/Σ*w*(*F*<sub>o</sub><sup>2</sup>)<sup>1/2</sup>]. <sup>c</sup>*w* = 1/[σ<sup>2</sup>(*F*<sub>o</sub>) + *g*(*F*<sub>o</sub>)<sup>2</sup>].

Table 3. Crystallographic Data<sup>a</sup> for Complexes 4, 8, 10, 12, 14, and 18

	4	8	10	12	14	18
formula	C <sub>13</sub> H <sub>27</sub> B <sub>4</sub> SiY	C <sub>13</sub> H <sub>27</sub> B <sub>4</sub> SiTb	C <sub>13</sub> H <sub>27</sub> B <sub>4</sub> DySi	C <sub>13</sub> H <sub>27</sub> B <sub>4</sub> HoSi	C <sub>13</sub> H <sub>27</sub> B <sub>4</sub> ErSi	C <sub>13</sub> H <sub>27</sub> B <sub>4</sub> LuSi
fw	343.59	413.60	417.18	419.61	421.94	429.65
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> , Å	18.253(2)	18.324(2)	18.272(3)	18.2086(16)	18.164(3)	17.988(2)
<i>b</i> , Å	12.8793(15)	12.8915(14)	12.886(2)	12.8584(11)	12.869(2)	12.8355(14)
<i>c</i> , Å	16.5441(19)	16.5424(18)	16.553(3)	16.5389(15)	16.553(3)	16.5444(18)
α, deg	90	90	90	90	90	90
β, deg	110.847(2)	110.961(2)	110.903(2)	110.813(1)	110.610(3)	110.297(2)
γ, deg	90	90	90	90	90	90
<i>V</i> , Å <sup>3</sup>	3634.6(7)	3649.2(7)	3641.2(11)	3619.6(6)	3621.8(12)	3582.6(7)
<i>Z</i>	8	8	8	8	8	8
<i>D</i> <sub>calcd</sub> , g cm <sup>-3</sup>	1.256	1.506	1.522	1.540	1.548	1.593
abs coeff, mm <sup>-1</sup>	3.258	3.925	4.153	4.421	4.683	5.561
cryst dimens, mm	0.20 × 0.18 × 0.16	1.00 × 0.60 × 0.60	0.80 × 0.12 × 0.12	0.40 × 0.40 × 0.30	1.20 × 0.60 × 0.60	0.60 × 0.40 × 0.10
scan sp in ω; min., max.	1.98, 25.00	1.98, 25.00	1.98, 25.00	1.98, 25.00	1.98, 25.00	1.99, 25.00
<i>T</i> , K	203(2)	203(2)	203(2)	203(2)	203(2)	203(2)
no. of data collected	13 475	13 159	13 246	13 101	12 264	12 875
no. of obsd reflns, <i>I</i> > 2σ( <i>I</i> )	3209	3219	3209	3197	3156	3156
no. of params refined	200	200	200	200	200	200
GOF	1.263	1.454	1.359	1.286	1.167	1.455
<i>g</i> <sup>c</sup>	0.00000(10)	0.00218(13)	0.00000(4)	0.00028(3)	0.00087(13)	0.00062(7)
<i>μ</i> <sub>(max, min)</sub> , e /Å <sup>3</sup>	+0.545, -0.463	+1.494, -1.823	+0.611, -0.692	+0.675, -0.304	+1.589, -3.867	+1.960, -1.633
<i>R</i> <sub>1</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0436	0.0433	0.0272	0.0188	0.0471	0.0483
<i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0918	0.0977	0.0587	0.0467	0.1280	0.1085

<sup>a</sup> Graphite-monochromatized Mo Kα radiation, λ = 0.71073 Å. <sup>b</sup>*R* = Σ||*F*<sub>o</sub>| - |*F*<sub>c</sub>||/Σ|*F*<sub>o</sub>|, *R*<sub>w</sub> = [Σ*w*(*F*<sub>o</sub><sup>2</sup> - *F*<sub>c</sub><sup>2</sup>)/Σ*w*(*F*<sub>o</sub><sup>2</sup>)<sup>1/2</sup>]. <sup>c</sup>*w* = 1/[σ<sup>2</sup>(*F*<sub>o</sub>) + *g*(*F*<sub>o</sub>)<sup>2</sup>].

using the *SHELXTL* suite of programs.<sup>12</sup> All structures were refined on *F*<sup>2</sup> for all reflections.<sup>13</sup> Weighted *wR*<sub>2</sub> and goodness of fit were based on *F*<sup>2</sup>. The observed criterion of *I* > 2.0σ(*I*) was used for the *R*-factor calculation. Full-matrix refinement was performed for each structure. In all of the structures, the non-H atoms were refined anisotropically. The final values of *R* and weighted *wR*<sub>2</sub> are listed in Table 2 and Table 3. For all structures *R*<sub>1</sub> = Σ||*F*<sub>o</sub>| - |*F*<sub>c</sub>||/Σ|*F*<sub>o</sub>|; *wR*<sub>2</sub> = [Σ*w*(*F*<sub>o</sub><sup>2</sup> - *F*<sub>c</sub><sup>2</sup>)/Σ*w*(*F*<sub>o</sub><sup>2</sup>)<sup>1/2</sup>], *w* = [σ<sup>2</sup>(*F*<sub>o</sub><sup>2</sup>) + (*aP*)<sup>2</sup> + *bP*]<sup>-1</sup>. Some selected interatomic distances are listed in Table 4 and Table 5, while selected angles are listed in Tables 6 and 7,

respectively. The detailed crystallographic parameters of all compounds can be seen in the Supporting Information available online.

## Results and Discussion

**Synthesis.** The mixed-ligand dimeric lanthanacarboranes of the type [(η<sup>5</sup>-2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>)(η<sup>5</sup>-2-R-3-(Me<sub>3</sub>Si)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>)Ln]<sub>2</sub> (**3**, M = Y, R = Me<sub>3</sub>Si; **4**, M = Y, R = Me; **5**, M = Gd, R = Me<sub>3</sub>Si; **6**, M = Gd, R = Me; **7**, M = Tb, R = Me<sub>3</sub>Si; **8**, M = Tb, R = Me; **9**, M = Dy, R = Me<sub>3</sub>Si; **10**, M = Dy, R = Me; **11**, M = Ho, R = Me<sub>3</sub>Si; **12**, M = Ho, R = Me; **13**, M = Er, R = Me<sub>3</sub>Si; **14**, M = Er, R = Me; **15**, M = Tm, R = Me<sub>3</sub>Si; **16**, M = Tm, R = Me; **17**, M = Lu, R = Me<sub>3</sub>Si; **18**, M = Lu, R = Me) were prepared as crystalline solids in 50–88% yield

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Table 4. Selected Bond Lengths (Å) for Complexes 3, 5, 7, 6, and 13

bond	3, Ln = Y	5, Ln = Gd	7, Ln = Tb	6, Ln = Gd	13, Ln = Er
Ln–C(1A)	2.645(7)	2.680(5)	2.660(5)	2.66(2)	2.628(5)
Ln–C(2A)	2.631(7)	2.667(4)	2.667(5)	2.61(2)	2.601(5)
Ln–B(3A)	2.680(9)	2.725(5)	2.698(6)	2.72(2)	2.656(6)
Ln–B(4A)	2.728(9)	2.765(6)	2.748(6)	2.81(3)	2.692(6)
Ln–B(5A)	2.679(9)	2.698(6)	2.682(7)	2.75(2)	2.633(6)
Ln–H(3) <sup>a</sup>	2.681(9)	2.698(6)	2.684(7)	2.63(3)	2.659(6)
Ln–H(4) <sup>a</sup>	2.748(9)	2.783(6)	2.777(7)	2.71(3)	2.726(6)
Ln–Cnt(1A) <sup>a,b</sup>	2.305(9)	2.347(6)	2.325(7)	2.36(3)	2.272(6)
Ln–C(11)	2.646(8)	2.685(5)	2.673(6)	2.66(2)	2.628(6)
Ln–C(12)	2.688(8)	2.726(5)	2.712(5)	2.76(2)	2.678(5)
Ln–C(13)	2.632(8)	2.667(5)	2.647(5)	2.72(2)	2.619(5)
Ln–C(14)	2.691(8)	2.729(5)	2.714(5)	2.76(2)	2.664(5)
Ln–C(15)	2.638(9)	2.687(5)	2.671(6)	2.66(2)	2.619(5)
Ln–Cnt(2) <sup>a,c</sup>	2.183(8)	2.230(5)	2.211(6)	2.23(2)	2.162(6)

<sup>a</sup> Calculated data. <sup>b</sup> Cnt(1A) = C<sub>2</sub>B<sub>3</sub> centroid. <sup>c</sup> Cnt(2) = C<sub>5</sub> centroid.

Table 5. Selected Bond Lengths (Å) for Complexes 4, 8, 10, 12, 14, and 18

bond	4, Ln = Y	8, Ln = Tb	10, Ln = Dy	12, Ln = Ho	14, Ln = Er	18, Ln = Lu
Ln–C(1A)	2.627(4)	2.639(6)	2.630(4)	2.613(3)	2.614(7)	2.572(8)
Ln–C(2A)	2.617(4)	2.632(6)	2.615(4)	2.605(3)	2.592(6)	2.563(8)
Ln–B(3A)	2.678(4)	2.690(7)	2.677(5)	2.669(3)	2.645(7)	2.62(1)
Ln–B(4A)	2.727(4)	2.739(8)	2.734(5)	2.716(4)	2.695(8)	2.665(9)
Ln–B(5A)	2.681(4)	2.690(8)	2.684(5)	2.671(4)	2.675(8)	2.62(1)
Ln–H(3) <sup>a</sup>	2.680(4)	2.697(8)	2.681(5)	2.674(5)	2.695(8)	2.64(1)
Ln–H(4) <sup>a</sup>	2.773(4)	2.785(8)	2.748(5)	2.757(5)	2.734(8)	2.72(1)
Ln–Cnt(1A) <sup>a,b</sup>	2.302(4)	2.314(8)	2.305(5)	2.289(5)	2.276(8)	2.23(1)
Ln–C(11)	2.636(4)	2.660(8)	2.647(5)	2.625(4)	2.623(8)	2.58(1)
Ln–C(12)	2.688(4)	2.703(7)	2.687(4)	2.674(3)	2.664(7)	2.636(9)
Ln–C(13)	2.624(4)	2.630(7)	2.621(4)	2.623(3)	2.606(7)	2.597(9)
Ln–C(14)	2.682(4)	2.683(7)	2.685(4)	2.674(3)	2.672(8)	2.639(8)
Ln–C(15)	2.618(4)	2.645(7)	2.631(4)	2.609(3)	2.597(7)	2.577(9)
Ln–Cnt(2) <sup>a,c</sup>	2.171(4)	2.189(7)	2.183(5)	2.164(3)	2.152(7)	2.122(9)

<sup>a</sup> Calculated data. <sup>b</sup> Cnt(1A) = C<sub>2</sub>B<sub>3</sub> centroid. <sup>c</sup> Cnt(2) = C<sub>5</sub> centroid.

via ligand exchange reactions between *nido*-2-R-3-(Me<sub>3</sub>Si)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> (R = Me<sub>3</sub>Si, **1**; R = Me, **2**) and [η<sup>5</sup>-2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>]<sub>3</sub>M in a molar ratio of 1:1 in toluene at elevated temperature (70 °C). A general synthetic procedure is outlined in Scheme 1. The traditional method of synthesizing metallocarboranes has been to first form the dianion of the carborane by reaction with a strong base (BuLi or NaH) and then react the resulting group 1 precursor species with a selective metal halide. Such an approach, especially when dealing with the lanthanides, can lead to complications due to ligand redistribution reactions or reactions with strong base-induced products.<sup>14–18</sup> An alternative approach that has been less used in recent years is to react the neutral carborane with a metal reagent containing ligands that are more basic than the carborane.<sup>19</sup> It is this latter approach that is used in this work. Temperature is very important in these

ligand exchange reactions. The reactions do not take place to any measurable extent when the reaction temperature is below 60 °C. On the other hand, the reactions give low-yield, impure products if the temperature is higher than 100 °C, most likely due to product decompositions; the best temperature for these reactions was found to be 70–85 °C. Reference to Scheme 1 shows that the primary reaction is a proton transfer from the “diprotic” *nido*-2-R-3-(Me<sub>3</sub>Si)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> to two of the [2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>]<sup>−</sup> ligands, with the metal playing somewhat of a passive role. Therefore, it was speculated that the method should be a general one, applicable to any (2,4-(R)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>M compound.<sup>8</sup> The present study shows that this is only partially true. Although the method can be successfully used with yttrium and the later lanthanides (Gd, Tb, Dy, Ho, Er, Tm, Lu), it failed with the earlier lanthanides. The reaction of YbX<sub>3</sub> with K[2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>] gave the reduced Yb<sup>2+</sup> product, which did not further react. It has been observed that YbCl<sub>2</sub> does not react with the monoanionic carborane [C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>]<sup>−</sup>.<sup>18b</sup> All experimental evidence indicates that (η<sup>5</sup>-2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>Ln (La, Ce, Pr, Nd, Sm) could be prepared; indeed, (η<sup>5</sup>-2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>Nd has been structurally characterized.<sup>11a</sup> However, their reactions with *nido*-2-R-3-(Me<sub>3</sub>Si)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> (R = Me<sub>3</sub>Si, **1**; R = Me, **2**) proved unsuccessful. Varying the molar ratio of (η<sup>5</sup>-2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>-Ln to *nido*-2-R-3-(Me<sub>3</sub>Si)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> (R = Me<sub>3</sub>Si, **1**; R = Me, **2**) did not give rise to different products. Differences in the synthetic viability of late and early lanthanocarboranes have been noted in the large cage system, where it was found that the reaction between LnCl<sub>3</sub>(THF)<sub>x</sub> and Na<sub>2</sub>(C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>) gave rise to half-sandwich complexes when Ln = Y, Er, Yb, and Lu,<sup>18b</sup> but

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**Table 6. Selected Bond Angles (deg) for Complexes 3, 5, 7, 6, and 13**

3					
C(2)–C(1)–B(5)	112.0(6)	C(14)–C(13)–C(12)	131.6(8)	Cnt(2)–Y(A)–H(3)	96.6(3)
C(1)–C(2)–B(3)	110.1(7)	C(15)–C(14)–C(13)	125.8(8)	Cnt(2)–Y(A)–H(4)	100.1(3)
C(2)–B(3)–B(4)	107.1(7)	Cnt(1A)–Y(A)–H(3)	109.2(3)	Cnt(2)–Y(A)–B(3)	110.2(3)
B(3)–B(4)–B(5)	105.4(7)	Cnt(1A)–Y(A)–H(4)	110.6(3)	Cnt(2)–Y(A)–B(4)	111.7(3)
C(1)–B(5)–B(4)	105.3(7)	Cnt(1A)–Y(A)–B(3)	104.0(3)	Cnt(1A)–Y(A)–Cnt(2)	142.4(4)
C(11)–C(12)–C(13)	127.1(8)	Cnt(1A)–Y(A)–B(4)	104.9(3)		
5					
C(2)–C(1)–B(5)	111.1(4)	C(14)–C(13)–C(12)	131.5(5)	Cnt(2)–Gd(A)–H(3)	96.4(2)
C(1)–C(2)–B(3)	110.6(4)	C(15)–C(14)–C(13)	126.7(5)	Cnt(2)–Gd(A)–H(4)	100.9(2)
C(2)–B(3)–B(4)	106.6(4)	Cnt(1A)–Gd(A)–H(3)	109.5(2)	Cnt(2)–Gd(A)–B(3)	110.2(2)
B(3)–B(4)–B(5)	105.1(4)	Cnt(1A)–Gd(A)–H(4)	110.3(2)	Cnt(2)–Gd(A)–B(4)	112.2(2)
C(1)–B(5)–B(4)	106.5(4)	Cnt(1A)–Gd(A)–B(3)	104.0(2)	Cnt(1A)–Gd(A)–Cnt(2)	142.3(3)
C(11)–C(12)–C(13)	127.2(5)	Cnt(1A)–Gd(A)–B(4)	104.6(2)		
7					
C(2)–C(1)–B(5)	111.7(4)	C(14)–C(13)–C(12)	131.1(5)	Cnt(2)–Tb(A)–H(3)	96.6(2)
C(1)–C(2)–B(3)	109.6(4)	C(15)–C(14)–C(13)	127.2(5)	Cnt(2)–Tb(A)–H(4)	100.4(2)
C(2)–B(3)–B(4)	107.0(4)	Cnt(1A)–Tb(A)–H(3)	109.233	Cnt(2)–Tb(A)–B(3)	110.1(2)
B(3)–B(4)–B(5)	105.3(5)	Cnt(1A)–Tb(A)–H(4)	110.6(2)	Cnt(2)–Tb(A)–B(4)	111.7(2)
C(1)–B(5)–B(4)	106.3(5)	Cnt(1A)–Tb(A)–B(3)	104.1(2)	Cnt(1A)–Tb(A)–Cnt(2)	142.5(3)
C(11)–C(12)–C(13)	127.2(6)	Cnt(1A)–Tb(A)–B(4)	104.9(2)		
6					
C(2)–C(1)–B(5)	110(2)	C(14)–C(13)–C(12)	133.7(19)	Cnt(2)–Gd(A)–H(3)	96.1(3)
C(1)–C(2)–B(3)	108(2)	C(15)–C(14)–C(13)	126(2)	Cnt(2)–Gd(A)–H(4)	101.5(3)
C(2)–B(3)–B(4)	108(2)	Cnt(1A)–Gd(A)–H(3)	109.0(3)	Cnt(2)–Gd(A)–B(3)	110.2(3)
B(3)–B(4)–B(5)	107.5(19)	Cnt(1A)–Gd(A)–H(4)	110.8(3)	Cnt(2)–Gd(A)–B(4)	113.0(3)
C(1)–B(5)–B(4)	106(2)	Cnt(1A)–Gd(A)–B(3)	104.5(3)	Cnt(1A)–Gd(A)–Cnt(2)	141.0(4)
C(11)–C(12)–C(13)	120(2)	Cnt(1A)–Gd(A)–B(4)	105.3(3)		
13					
C(2)–C(1)–B(5)	110.6(4)	C(14)–C(13)–C(12)	131.4(5)	Cnt(2)–Er(A)–H(3)	109.6(2)
C(1)–C(2)–B(3)	110.9(4)	C(15)–C(14)–C(13)	127.2(5)	Cnt(2)–Er(A)–H(4)	110.4(2)
C(2)–B(3)–B(4)	106.6(4)	Cnt(1A)–Er(A)–H(3)	109.6(2)	Cnt(2)–Er(A)–B(3)	109.9(2)
B(3)–B(4)–B(5)	105.2(4)	Cnt(1A)–Er(A)–H(4)	110.4(2)	Cnt(2)–Er(A)–B(4)	111.5(2)
C(1)–B(5)–B(4)	106.5(4)	Cnt(1A)–Er(A)–B(3)	104.2(2)	Cnt(1A)–Er(A)–Cnt(2)	142.6(3)
C(11)–C(12)–C(13)	126.9(5)	Cnt(1A)–Er(A)–B(4)	104.8(2)		

only the full-sandwich lanthanacarboranes could be isolated for the early lanthanides, irrespective of the molar ratio of the reactants.<sup>18a</sup>

It should be noted that neither a 1:1 nor a 1:2 molar ratio mixture of *nido*-2-R-3-(Me<sub>3</sub>Si)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> (R = Me<sub>3</sub>Si, **1**; R = Me, **2**) and ( $\eta^5$ -2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>)K gave any indication of reaction when heated to 70 °C in toluene. This, along with the inability to form any open pentadienyl lanthanacarboranes of the early lanthanides, indicates that the metal plays a fairly active role in the proton-transfer process. The reaction could involve an initial proton transfer between the *nido*-2-R-3-(Me<sub>3</sub>Si)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> and a ( $\eta^5$ -2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>)M to give a neutral 2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>6</sub> and a bis(pentadienyl)lanthanacarborane intermediate, most likely of the type *exo*-( $\eta^5$ -2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>)M(2-R-3-(Me<sub>3</sub>Si)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>5</sub>), where the bis(pentadienyl)lanthanide bridges the two facial borons opposite the bridged hydrogen. The lanthanides {*exo*-( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Er[4,5-( $\mu$ -H)-2,3-(SiMe<sub>3</sub>)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>]}·(THF) and {*exo*-( $\eta^8$ -C<sub>8</sub>H<sub>8</sub>)Gd[4,5-( $\mu$ -H)-2,3-(SiMe<sub>3</sub>)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>]}·2(THF) have been synthesized and were found to have such structures.<sup>20</sup> This intermediate could then undergo an intramolecular proton transfer to give another equivalent of 2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>6</sub> and ( $\eta^5$ -2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>)( $\eta^5$ -2-R-3-(Me<sub>3</sub>Si)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>)M; this sequence is summarized in Scheme 2. It should be emphasized that there is no direct experimental evidence for the existence of the bis(pentadienyl)lanthanacarborane intermediate. However, the mechanism does account for some rather interesting facts about this reaction. First, *nido*-2-R-3-(Me<sub>3</sub>Si)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> is not a strong enough acid by itself to protonate the pentadienyl salt K[2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>]; the added stability

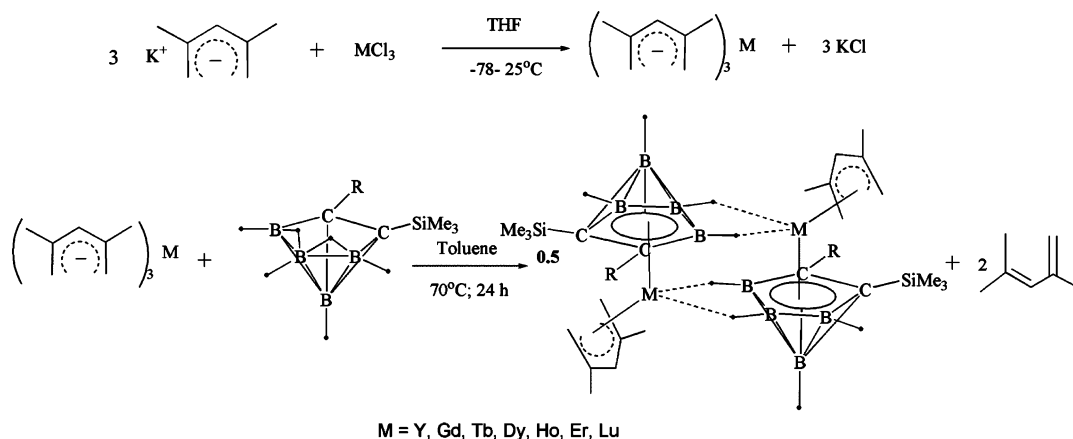
furnished by the formation of the lanthanacarborane intermediate could facilitate such a transfer. It can also help rationalize why the earlier, more ionic ( $\eta^5$ -(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>Ln compounds do not react. For such compounds the intermediate would not be expected to be stable. Irrespective of the mechanism, it is apparent that the metal plays a more active role than would be expected from the net balanced equation.

**Crystal Structures.** Due to the new synthetic strategy used in this study and the possibility of comparing a series of chemically similar lanthanides, the unambiguous structures of compounds **3–8**, **10**, **12–14**, and **18** were determined by X-ray diffraction. The C<sub>(cage)</sub>-bis(trimethylsilyl)-substituted compounds **3**, **5**, **7**, and **13** are isostructural, as are the Me/SiMe<sub>3</sub> ones **4**, **8**, **10**, **12**, **14**, and **18**. Although compound **6** crystallizes in a different space group from the other Me/SiMe<sub>3</sub> lanthanacarborane, its molecular geometry is quite similar; therefore, only a general structure for each lanthanacarborane type is shown in Figures 1 and 2, respectively. Some important bond distances and selected bond angles for **3**, **5**, **7**, **6**, and **13** are listed in Tables 3 and 5, respectively, while the bond distances and angles for complexes **4**, **8**, **10**, **12**, **14**, and **18** are listed in Tables 4 and 6, respectively. Figures 1 and 2 show that these compounds crystallize as dimers of the form [( $\eta^5$ -2,4-(Me)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>)( $\eta^5$ -2-R-3-(Me<sub>3</sub>Si)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>)M]<sub>2</sub> (**3**, M = Y, R = Me<sub>3</sub>Si; **4**, M = Y, R = Me; **5**, M = Gd, R = Me<sub>3</sub>Si; **6**, M = Gd, R = Me; **7**, Ln = Tb, R = Me<sub>3</sub>Si; **8**, M = Tb, R = Me; **10**, M = Dy, R = Me; **12**, M = Ho, R = Me; **13**, M = Er, R = Me<sub>3</sub>Si; **14**, M = Er, R = Me; **18**, M = Lu, R = Me). In all cases, the two ligands seem to be essentially  $\eta^5$ -bonded to the metal. However, a careful inspection of the individual Ln–C distances of the pentadienyl ligands (see Tables 3 and 4) reveals that in all

(20) Wang, J.; Zheng, C.; Maguire, J. A.; Hosmane, N. S. *Organometallics* **2006**, *25*, 000–000.

Table 7. Selected Bond Angles (deg) for Complexes 4, 8, 10, 12, 14, and 18

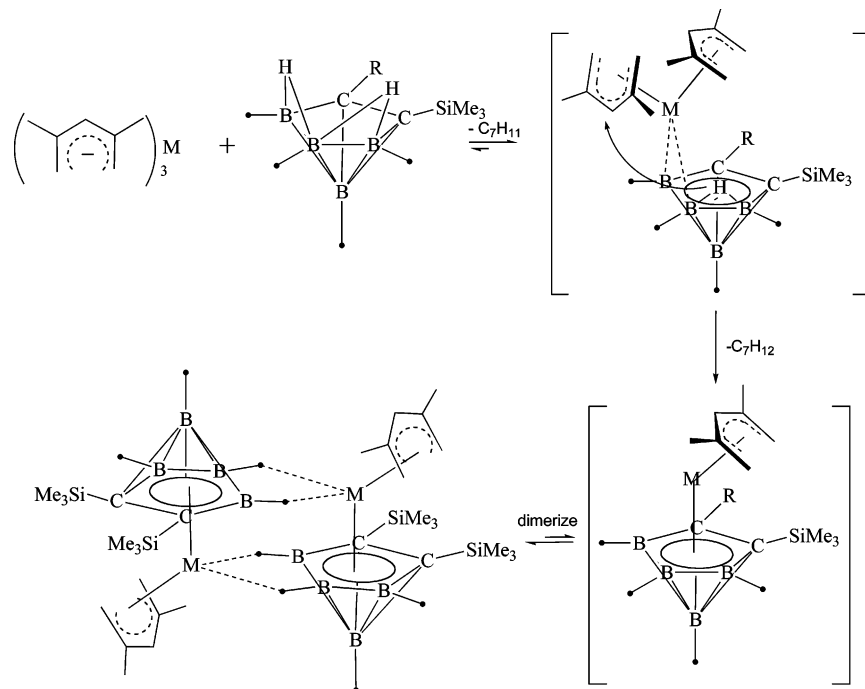
4					
C(2)–C(1)–B(5)	113.0(3)	C(14)–C(13)–C(12)	131.1(4)	Cnt(2)–Y(A)–H(3)	98.9(2)
C(1)–C(2)–B(3)	110.3(3)	C(15)–C(14)–C(13)	127.1(4)	Cnt(2)–Y(A)–H(4)	99.7(2)
C(2)–B(3)–B(4)	106.6(3)	Cnt(1A)–Y(A)–H(3)	111.7(2)	Cnt(2)–Y(A)–B(3)	112.8(2)
B(3)–B(4)–B(5)	105.0(3)	Cnt(1A)–Y(A)–H(4)	112.7(2)	Cnt(2)–Y(A)–B(4)	112.8(2)
C(1)–B(5)–B(4)	105.1(3)	Cnt(1A)–Y(A)–B(3)	106.2(2)	Cnt(1A)–Y(A)–Cnt(2)	138.4(3)
C(11)–C(12)–C(13)	127.0(4)	Cnt(1A)–Y(A)–B(4)	107.0(2)		
8					
C(2)–C(1)–B(5)	113.1(6)	C(14)–C(13)–C(12)	130.7(8)	Cnt(2)–Tb(A)–H(3)	99.1(3)
C(1)–C(2)–B(3)	110.4(5)	C(15)–C(14)–C(13)	128.3(7)	Cnt(2)–Tb(A)–H(4)	100.0(3)
C(2)–B(3)–B(4)	106.8(6)	Cnt(1A)–Tb(A)–H(3)	111.8(3)	Cnt(2)–Tb(A)–B(3)	113.0(3)
B(3)–B(4)–B(5)	104.6(6)	Cnt(1A)–Tb(A)–H(4)	112.6(3)	Cnt(2)–Tb(A)–B(4)	113.1(3)
C(1)–B(5)–B(4)	105.1(6)	Cnt(1A)–Tb(A)–B(3)	106.3(3)	Cnt(1A)–Tb(A)–Cnt(2)	138.1(4)
C(11)–C(12)–C(13)	127.0(8)	Cnt(1A)–Tb(A)–B(4)	107.0(3)		
10					
C(2)–C(1)–B(5)	113.0(4)	C(14)–C(13)–C(12)	131.1(5)	Cnt(2)–Dy(A)–H(3)	96.6(2)
C(1)–C(2)–B(3)	110.5(4)	C(15)–C(14)–C(13)	127.3(5)	Cnt(2)–Dy(A)–H(4)	100.1(2)
C(2)–B(3)–B(4)	106.7(4)	Cnt(1A)–Dy(A)–H(3)	109.2(2)	Cnt(2)–Dy(A)–B(3)	110.2(2)
B(3)–B(4)–B(5)	104.6(4)	Cnt(1A)–Dy(A)–H(4)	110.6(2)	Cnt(2)–Dy(A)–B(4)	111.7(2)
C(1)–B(5)–B(4)	105.1(4)	Cnt(1A)–Dy(A)–B(3)	104.0(2)	Cnt(1A)–Dy(A)–Cnt(2)	142.4(3)
C(11)–C(12)–C(13)	127.1(5)	Cnt(1A)–Dy(A)–B(4)	104.9(2)		
12					
C(2)–C(1)–B(5)	113.3(3)	C(14)–C(13)–C(12)	130.7(4)	Cnt(2)–Ho(A)–H(3)	98.7(1)
C(1)–C(2)–B(3)	110.2(3)	C(15)–C(14)–C(13)	127.3(3)	Cnt(2)–Ho(A)–H(4)	99.5(1)
C(2)–B(3)–B(4)	106.7(3)	Cnt(1A)–Ho(A)–H(3)	111.7(1)	Cnt(2)–Ho(A)–B(3)	106.2(1)
B(3)–B(4)–B(5)	104.9(3)	Cnt(1A)–Ho(A)–H(4)	112.7(1)	Cnt(2)–Ho(A)–B(4)	106.9(1)
C(1)–B(5)–B(4)	104.9(3)	Cnt(1A)–Ho(A)–B(3)	106.2(1)	Cnt(1A)–Ho(A)–Cnt(2)	138.5(2)
C(11)–C(12)–C(13)	127.4(4)	Cnt(1A)–Ho(A)–B(4)	107.0(1)		
14					
C(2)–C(1)–B(5)	113.9(6)	C(14)–C(13)–C(12)	131.3(8)	Cnt(2)–Er(A)–H(3)	98.7(3)
C(1)–C(2)–B(3)	109.3(6)	C(15)–C(14)–C(13)	126.4(8)	Cnt(2)–Er(A)–H(4)	99.5(3)
C(2)–B(3)–B(4)	108.3(6)	Cnt(1A)–Er(A)–H(3)	111.7(3)	Cnt(2)–Er(A)–B(3)	112.6(3)
B(3)–B(4)–B(5)	104.4(6)	Cnt(1A)–Er(A)–H(4)	112.5(3)	Cnt(2)–Er(A)–B(4)	112.6(3)
C(1)–B(5)–B(4)	104.0(6)	Cnt(1A)–Er(A)–B(3)	106.2(3)	Cnt(1A)–Er(A)–Cnt(2)	138.6(4)
C(11)–C(12)–C(13)	128.0(8)	Cnt(1A)–Er(A)–B(4)	107.0(3)		
18					
C(2)–C(1)–B(5)	113.9(6)	C(14)–C(13)–C(12)	131.3(8)	Cnt(2)–Lu(A)–H(3)	97.9(3)
C(1)–C(2)–B(3)	109.3(6)	C(15)–C(14)–C(13)	126.4(8)	Cnt(2)–Lu(A)–H(4)	98.0(3)
C(2)–B(3)–B(4)	108.3(6)	Cnt(1A)–Lu(A)–H(3)	111.6(3)	Cnt(2)–Lu(A)–B(3)	111.7(3)
B(3)–B(4)–B(5)	104.4(6)	Cnt(1A)–Lu(A)–H(4)	111.9(3)	Cnt(2)–Lu(A)–B(4)	111.4(3)
C(1)–B(5)–B(4)	104.0(6)	Cnt(1A)–Lu(A)–B(3)	106.2(3)	Cnt(1A)–Lu(A)–Cnt(2)	139.6(4)
C(11)–C(12)–C(13)	128.0(8)	Cnt(1A)–Lu(A)–B(4)	107.1(3)		

Scheme 1. Synthesis of the Mixed-Ligand Dimeric Metallacarboranes  $[(\eta^5\text{-}2,4\text{-(Me)}_2\text{C}_5\text{H}_5)(\eta^5\text{-}2\text{-R-}3\text{-(SiMe}_3\text{)-}2,3\text{-C}_2\text{B}_4\text{H}_4)\text{Ln}]_2$  (Ln = lanthanide, R = SiMe<sub>3</sub>, Me)

compounds the Ln–C(12,14) distances are slightly longer than the other three Ln–C distances, indicating a slight folding along the C(12)–C(14) axis (the C11–C14 and C12–C15 dihedral angles are 8.2° and 8.5°, respectively, in **7** and 7.7° and 7.0°, respectively, in **13**). Such a bond distance discrepancy was noted in the  $(2,4\text{-(Me)}_2\text{C}_5\text{H}_5)_3\text{Nd}$  complex and attributed to the differences in the charge densities on the carbons coupled with an essentially ionic Nd–ligand bonding.<sup>11a</sup> The  $(\eta^5\text{-}2,4\text{-}$

$(\text{Me})_2\text{C}_5\text{H}_5)(\eta^5\text{-}2\text{-R-}3\text{-(Me}_3\text{Si)-}2,3\text{-C}_2\text{B}_4\text{H}_4)\text{M}$  complexes are front-to-back oriented in a dimer so that each M(III) ion is  $\eta^2$ -bonded to a neighboring carborane. At least as measured by the calculated Ln–H distances (see Tables 3 and 4), the Ln–H–B bonds are relatively strong. Such dimer formation is quite common in the lanthanacarboranes.<sup>16</sup> The Ln–C<sub>2</sub>B<sub>3</sub>(centroid, Cnt1A) distances are 2.305 Å (Y), 2.347 Å (Gd), 2.325 Å (Tb), and 2.272 Å (Er) for **3**, **5**, **7**, and **13**, respectively, and 2.302 Å

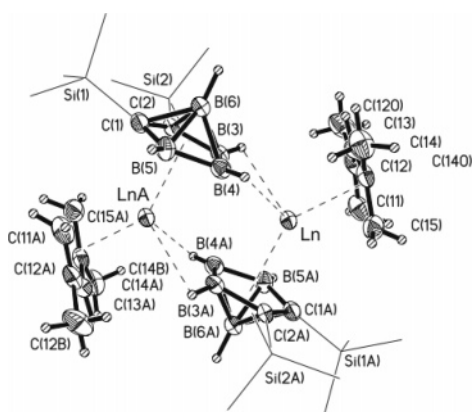
**Scheme 2. Proposed Mechanism of the Ligand Exchange Reactions for the Synthesis of Mixed-Ligand Dimeric Metallocarboranes**



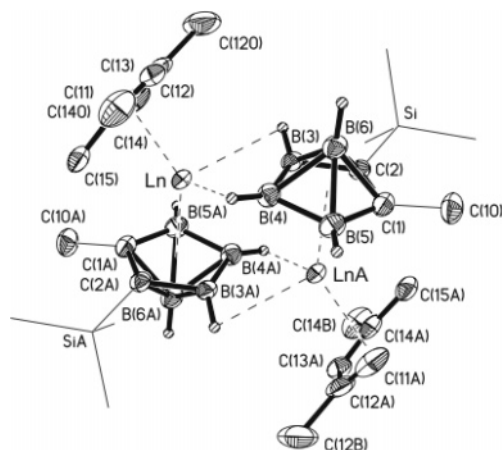
(Y), 2.363 Å (Gd), 2.314 Å (Tb), 2.305 Å (Dy), 2.289 Å (Ho), 2.276 Å (Er), and 2.233 Å (Lu) for **4**, **6**, **8**, **10**, **12**, **14**, and **18**, respectively, which parallel the change in the ionic radii of the metals.<sup>21</sup> For the same metal, these Ln–Cnt(1A) distances are slightly smaller than those found in the half-sandwich trinuclear carborane cluster  $\{[\eta^5\text{-}1\text{-Ln-}2,3\text{-}(\text{SiMe}_3)_2\text{-}2,3\text{-C}_2\text{B}_4\text{H}_4]_3\{[\mu\text{-}1\text{-Li-}2,3\text{-}(\text{SiMe}_3)_2\text{-}2,3\text{-C}_2\text{B}_4\text{H}_4]_3(\mu_3\text{-OMe})\}[\mu\text{-Li-(C}_4\text{H}_8\text{O})]_3(\mu_3\text{-O})\}$ <sup>17</sup> and those found in the  $[1\text{-Cl-}1\text{-}(\mu\text{-Cl-}2,2',3,3'\text{-}(\text{SiMe}_3)_4\text{-}5,6\text{-}[(\mu\text{-H})_2\text{-Li(TMEDA)-}4,4'\text{-}5'\text{-}[(\mu\text{-H})_3\text{Li(TMEDA)]-}1,1'\text{-}commo\text{-Ln}(2,3\text{-C}_2\text{B}_4\text{H}_4)_2]^- \text{anion.}^{22}$  The data in Tables 3 and 4 show that the Ln–Cnt(2) distances, while being slightly smaller than those of the Ln–Cnt(1A), also vary as the ionic radii of the lanthanides vary. As with most full- and mixed-sandwich lanthanacarboranes, the complexes are bent, with a second carborane ligand  $\eta^2$ -bonded to the metal in a dimer.<sup>16</sup> The Cnt(1A)–Ln–Cnt(2) angles in the  $C_{(\text{cage})}$ -bis(trimethylsilyl)-substituted carboranes are all essentially the same, ranging from 142.3° for **5** (Gd) to 142.6° for **13** (Er), while those of the Me/

SiMe carboranes show a bit more variation, varying from a low of 138.1° for **8** (Tb) to a high of 142.4° for **10** (Dy).

**Spectroscopy and Analysis.** All compounds were also characterized by IR spectroscopy and elemental analyses. The results of these analyses are consistent with the crystal structures. The IR spectra of the lanthanacarboranes all exhibit well-resolved multiple terminal B–H stretching vibrations in the 2270–2590  $\text{cm}^{-1}$  range. Such fine structures of B–H stretching bands have been previously observed in other *closo*- and *commo*-lanthanacarboranes and lithiacarboranes when M–H–B bridging interactions are present.<sup>16,22,23</sup> Because of the strong paramagnetism of complexes **5**–**16**, no useful NMR spectra could be obtained. However, the diamagnetic yttrium (**3** and **4**) and lutetium (**17** and **18**) complexes gave interpretable NMR data. In addition, the NMR spectra of the precursors,  $\text{Y}(\text{C}_7\text{H}_{11})_3$  and  $\text{Lu}(\text{C}_7\text{H}_{11})_3$ , were also obtained. Their <sup>13</sup>C NMR spectra show CH<sub>3</sub> resonances at  $\delta = 29.45$  and 28.37 ppm, CH<sub>2</sub> at  $\delta$



**Figure 1.** Molecular structure of  $[(\eta^5\text{-}2,4\text{-}(\text{Me})_2\text{C}_5\text{H}_5)(\eta^5\text{-}2,3\text{-}(\text{Me}_3\text{Si})_2\text{-C}_2\text{B}_4\text{H}_4)\text{M}]_2$  (**3**, M = Y; **5**, M = Gd; **7**, M = Tb; **13**, M = Er) with the thermal ellipsoids drawn at the 50% probability level. The *exo*-polyhedral SiMe<sub>3</sub> groups were drawn with thinner lines for clarity.



**Figure 2.** Perspective view of  $[(\eta^5\text{-}2,4\text{-}(\text{Me})_2\text{C}_5\text{H}_5)(\eta^5\text{-}2\text{-Me-}3\text{-}(\text{Me}_3\text{Si})\text{-C}_2\text{B}_4\text{H}_4)\text{M}]_2$  (**4**, M = Y; **6**, M = Gd; **8**, M = Tb; **10**, M = Dy; **12**, M = Ho; **14**, M = Er; **18**, M = Lu) with the thermal ellipsoids drawn at the 50% probability level. The *exo*-polyhedral SiMe<sub>3</sub> groups were drawn with thinner lines for clarity.



= 79.68 and 80.71 ppm, CH at  $\delta = 90.57$  and 90.21 ppm, and C resonances at  $\delta = 148.05$  and 148.25 ppm for  $Y(C_7H_{11})_3$  and  $Lu(C_7H_{11})_3$ , respectively. This is of interest in that the  $Lu(C_7H_{11})_3$   $^{13}C$  NMR spectrum found in this work is essentially identical to that reported by Schumann and Dietrich for the lutetium compound whose solid-state structure was found to be  $Lu(\eta^3-C_7H_{11})(\eta^5-C_7H_{11})_2$ .<sup>24</sup> Zielinski and co-workers reported an even more complex product, obtained in low yield, from the reaction of  $LuCl_3$  and  $KC_7H_{11}$ ,  $(\eta^5-C_7H_{11})Lu(\eta^5:\eta^3-(CH_3)C_5H_5-CH_2CH_2CH(CH_3)C_3H_3(CH_3))$ .<sup>25</sup> The  $^{13}C$  NMR resonances assigned to the  $\eta^5-C_7H_{11}$  ligand agrees well with that found in this work. It seems that the reaction of  $LuCl_3$  and  $KC_7H_{11}$  leads to a mixture of products. However, this does not seem to affect their ability to act as precursors in syntheses of the lutetacarboranes **17** and **18**.

The  $^1H$  NMR spectrum of **3** showed a resonance at  $\delta = 0.44$  due to the  $SiCH_3$  protons, plus resonances at  $\delta$  1.19, 3.27, 4.33, and 4.78 ppm assigned to the protons in the  $[2,4-C_7H_{11}]^-$  ligand. These latter resonances agreed quite well with those found for  $Y(C_7H_{11})_3$ . The B–H resonances were not observed. In the same way, the  $^{13}C$  NMR spectra of **3** showed resonances similar to those found in  $Y(C_7H_{11})_3$  at  $\delta = 26.5$ , 94.0, 116.0, and 146.8 ppm. In addition, resonances were found at  $\delta$  0.43 and 63.0 ppm, assigned to the  $SiCH_3$  and cage carbons, respectively. The  $^{11}B$  NMR spectrum of **3** shows two peaks in a 3:1 peak area ratio at  $\delta = 25.7$  ppm, due to the overlap of the basal borons, and a well-resolved doublet at  $\delta = -27.0$  ppm assigned to the apical boron. While all three types of boron should be doublets due to the presence of the cage hydrogens, the broadness of the two downfield resonances could prevent their resolution. In case of **4**, the  $^1H$  NMR spectrum showed four broad singlets at  $\delta = 3.12$ , 3.43, 4.17, and 4.48 ppm due to the  $CH_2$  groups of 2,4- $C_7H_{11}$ , a singlet at  $\delta = 4.79$  ppm due to the  $CH$  group of 2,4- $C_7H_{11}$ , and a singlet peak at 2.12 for the  $CH_3$  group of 2,4-

$C_7H_{11}$ . A singlet at  $\delta = 0.35$  ppm that was assigned to the  $CH_3$  proton of the  $SiMe_3$  group and a singlet at 2.32 ppm for  $CH_3$  that is connected to the cage were observed. The separation of proton signals of  $CH_2$  groups of 2,4- $C_7H_{11}$  is due to the different chemical environment of these protons. The  $^{13}C$  NMR spectrum shows the presence of 2,4- $C_7H_{11}$  molecules at  $\delta = 26.5$ , 94.0, 126.8, and 152.0 ppm, plus a quartet due to the  $CH_3$  carbon of the  $SiMe_3$  groups at  $\delta = 0.43$  ppm, respectively. The cage carbons were present at 116.0 and 121.0 ppm in the spectra. Similarly, the  $^{11}B$  NMR spectrum of **4** shows a broad peak at  $\delta = 27.0$  ppm and a well-resolved doublet at  $\delta = -20.3$  ppm (apical B) in a 3:1 ratio.  $^1H$ ,  $^{11}B$ , and  $^{13}C$  NMR spectra of **17** are quite similar to those of **3**, while those of **18** are comparable with **4**, except for small differences in the chemical shifts (see the details in the Experimental Section).

## Conclusions

A highly efficient synthesis of novel mixed-ligand dimeric lanthanacarboranes of the type  $[(\eta^5-2,4-(Me)_2C_5H_5)(\eta^5-2-R-3-(Me_3Si)-2,3-C_2B_4H_4)Ln]_2$  ( $Ln = Y, Gd, Tb, Dy, Ho, Er, Tm, Lu$ ;  $R = SiMe_3, Me$ ) was developed via ligand exchange reactions between *nido*-2-R-3-( $Me_3Si$ )-2,3- $C_2B_4H_6$  ( $R = Me_3Si$ , **1**;  $R = Me$ , **2**) and  $[\eta^5-2,4-(Me)_2C_5H_5]_3Ln$ . The analogous early lanthanide ( $Ln = La-Eu$ ) complexes could not be made under the conditions employed in the present work.

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**Supporting Information Available:** Tables of crystallographic data, including fractional coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates of complexes **3–5**, **7**, **8**, **10–14**, and **18**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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