

# Synthesis and Structural Characterization of Hydroxyethyl- and Alkoxyethyl-*o*-Carboranes and Their Alkali and Rare Earth Metal Complexes

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Facile and practical syntheses of 1,2-(HOCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (**1**), its derivatives 1,2-(ROCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (R = CH<sub>3</sub> (**2**), CH<sub>2</sub>Ph (**4**)), and 1-(CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>)-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> (**3**) were reported. Treatment of **1** with excess K metal in THF gave, after fractional crystallization from acetone containing 18-crown-6 ether, two complexes, [*nido*-(HOCH<sub>2</sub>CH<sub>2</sub>)(OCH<sub>2</sub>CH<sub>2</sub>)C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>]{K(18-crown-6)}<sub>n</sub> (**5**) and [*nido*-(HOCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]{K(18-crown-6)}<sub>n</sub> (**6**) in a molar ratio of 1:2. Reaction of **2** with MeOK in methanol afforded, after treatment with Me<sub>3</sub>NHCl, [Me<sub>3</sub>NH][*nido*-(CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] (**7**). **2** reacted with excess Na metal in THF to yield [ $\eta^6$ -[(CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>]Na]{Na(THF)}<sub>n</sub> (**8**). Interactions of **2** with LnCl<sub>3</sub> in the presence of excess Li or Na metal gave, after recrystallization from a mixture of different solvents, half-sandwich *closo*-metallacarboranes [ $\eta^7$ -[(CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>]Er]{Na(CH<sub>3</sub>CN)<sub>2</sub>}<sub>2</sub> (**9**) and [ $\eta^7$ -[(CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>]Y]{Li(THF)<sub>3</sub>}<sub>2</sub> (**10**). Complexes [[ $\eta^7$ -(CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>]Er(THF)]{Na(CH<sub>3</sub>CN)(THF)}<sub>2</sub><sub>n</sub> (**11**) and [[ $\eta^7$ -(CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>]Y(THF)]{Na(THF)<sub>3</sub>}<sub>2</sub> (**12**) were prepared in a similar manner from the monosubstituted *o*-carborane **3**, LnCl<sub>3</sub>, and excess Na in THF. These complexes were characterized by various spectroscopic data, elemental analyses, and X-ray diffraction studies. Structural studies show that the Lewis base-functionalized sidearms have some effects on the coordination environments of the central metal atom through intramolecular interactions between the donor atoms of the sidearms and Lewis acidic metal ions, but do not change the gross structures of the 13-vertex lanthanacarboranes.

## Introduction

Carboranes containing organic functional groups are useful as multifunctional molecules for material science<sup>1</sup> and as boron carriers for boron neutron capture therapy.<sup>2</sup> Those with Lewis base functionalities tethered to the cage carbon atoms can be the precursors to interesting ligands for both d- and f-block metal atoms, particularly with regard to the possibility of either simultaneous or competitive  $\sigma$ -(substituent) and  $\pi$ -(carborane) ligation. Furthermore, the functionalized side chain could temporarily and reversibly coordinate to a metal ion, while stabilizing highly reactive, electronically and sterically unsaturated complexes. In fact, a number of metallacarboranes containing alkylamido pendent groups have been reported.<sup>3</sup> These complexes show interesting structural features and reactivity patterns.<sup>3</sup> In sharp contrast, the chemistry of metallacarboranes with ap-

pendent ether moieties is largely unexplored<sup>4</sup> due partially to the difficulties in the synthesis of ligands.<sup>5</sup>

As a part of our ongoing research on structure/reactivity relationships of lanthanacarboranes,<sup>6</sup> we are interested in substituent effects, particularly those with Lewis base functionalities. With this in mind, we have developed a method of high-yield synthesis of alkoxyethyl-*o*-carboranes. In this contribution, we report on the synthesis and structural characterization of hydroxyethyl- and alkoxyethyl-*o*-carboranes and their alkali and rare earth metal complexes.

## Experimental Section

**General Procedures.** All experiments were performed under an atmosphere of dry dinitrogen with the rigid exclusion

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(1) (a) Yang, X.; Jiang, W.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1992**, *114*, 9719. (b) Müller, J.; Base, K.; Magnera, T. F.; Michl, J. *J. Am. Chem. Soc.* **1992**, *114*, 9721. (c) Chizhevsky, I. T.; Johnson, S. E.; Knobler, C. B.; Gomez, F. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1993**, *115*, 6981. (d) Zinn, A. A.; Zheng, Z.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1996**, *118*, 70.

(2) (a) Soloway, A. H.; Fairchild, R. G. *Cancer Res.* **1990**, *50*, 1061. (b) Yamamoto, Y. *Pure Appl. Chem.* **1991**, *63*, 423. (c) Hawthorne, M. F. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 950. (d) Soloway, A. H.; Tjarks, W.; Barnum, B. A.; Rong, F.-G.; Barth, R. F.; Codogni, I. M.; Wilson, J. G. *Chem. Rev.* **1998**, *98*, 1515.

(3) (a) Lee, J.-D.; Baek, C.-K.; Ko, J.; Park, K.; Cho, S.; Min, S.-K.; Kang, S. O. *Organometallics* **1999**, *18*, 2189. (b) Zhu, Y.; Vyakaranam, K.; Maguire, J. A.; Quintana, W.; Teixidor, F.; Viñas, C.; Hosmane, N. S. *Inorg. Chem. Comm.* **2001**, *4*, 486. (c) Kim, D.-H.; Won, J. H.; Kim, S.-J.; Ko, J.; Kim, S. H.; Cho, S.; Kang, S. O. *Organometallics* **2001**, *20*, 4298. (d) Park, J.-S.; Kim, D.-H.; Kim, S.-J.; Ko, J.; Kim, S. H.; Cho, S.; Lee, C.-H.; Kang, S. O. *Organometallics* **2001**, *20*, 4483. (e) Park, J.-S.; Kim, D.-H.; Ko, J.; Kim, S. H.; Cho, S.; Lee, C.-H.; Kang, S. O. *Organometallics* **2001**, *20*, 4632. (f) Lee, J.-D.; Lee, Y.-J.; Jeong, H.-J.; Lee, J. S.; Lee, C.-H.; Ko, J.; Kang, S. O. *Organometallics* **2003**, *22*, 445. (g) Lee, Y.-J.; Lee, J.-D.; Ko, J.; Kim, S.-H.; Kang, S. O. *Chem. Commun.* **2003**, 1364.

(4) Shaw, K. F.; Reid, B. D.; Welch, A. J. *J. Organomet. Chem.* **1994**, *482*, 207.

(5) Shaw, K. F.; Welch, A. J. *Polyhedron* **1992**, *11*, 157.

(6) Xie, Z. *Acc. Chem. Res.* **2003**, *36*, 1.

of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. All organic solvents (except CH<sub>3</sub>CN) were refluxed over sodium benzophenone ketyl for several days and freshly distilled prior to use. CH<sub>3</sub>CN was refluxed over CaH<sub>2</sub> for several days and distilled immediately prior to use. All chemicals were purchased from either Aldrich or Acros Chemical Co. and used as received unless otherwise noted. Infrared spectra were obtained from KBr pellets prepared in the glovebox on a Perkin-Elmer 1600 Fourier transform spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker DPX 300 spectrometer at 300.13 and 75.47 MHz, respectively. <sup>11</sup>B NMR spectra were recorded on a Varian Inova 400 spectrometer at 128.32 MHz. All chemical shifts are reported in  $\delta$  units with references to the residual protons of the deuterated solvents for proton and carbon chemical shifts and to external BF<sub>3</sub>·OEt<sub>2</sub> (0.00 ppm) for boron chemical shifts. Elemental analyses were performed by MEDAC Ltd., Brunel University, Middlesex, U.K.

**Preparation of 1,2-(HOCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (1).** A 1.60 M solution of *n*-BuLi in *n*-hexane (12.5 mL, 20.0 mmol) was added dropwise to a solution of *o*-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> (1.44 g, 10.0 mmol) in a dry toluene/Et<sub>2</sub>O mixture (2:1, 30 mL) with stirring at 0 °C. The mixture was allowed to warm to room temperature and stirred for 30 min. The solution was then cooled to 0 °C, and a solution of ethylene oxide (0.88 g, 20.0 mmol) in toluene/Et<sub>2</sub>O (2:1, 10 mL) was added with stirring. The reaction mixture was stirred at room temperature overnight and then quenched with 50 mL of water. The organic layer was separated, and the aqueous layer was extracted with Et<sub>2</sub>O (30 mL × 2). The combined organic portions were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Removal of the solvents gave a white solid that was washed with *n*-hexane (10 mL × 2) and dried under vacuum to afford **1** as a white powder (2.14 g, 92%). Recrystallization from dichloromethane yielded colorless crystals. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>):  $\delta$  4.05 (t, *J* = 5.0 Hz, 2H, CH<sub>2</sub>CH<sub>2</sub>OH), 3.72 (dt, *J* = 5.0 and 6.9 Hz, 4H, CH<sub>2</sub>CH<sub>2</sub>OH), 2.57 (t, *J* = 6.9 Hz, 4H, CH<sub>2</sub>CH<sub>2</sub>OH). <sup>13</sup>C NMR (acetone-*d*<sub>6</sub>):  $\delta$  79.7 (cage C), 61.5 (CH<sub>2</sub>CH<sub>2</sub>OH), 38.4 (CH<sub>2</sub>CH<sub>2</sub>OH). <sup>11</sup>B NMR (acetone-*d*<sub>6</sub>):  $\delta$  -4.7 (2B), -10.4 (8B). IR (KBr, cm<sup>-1</sup>):  $\nu$  3236 (vs), 2950 (w), 2585 (vs), 1455 (m), 1416 (m), 1352 (m), 1064 (vs), 731 (m). Anal. Calcd for C<sub>6</sub>H<sub>20</sub>B<sub>10</sub>O<sub>2</sub>: C, 31.02; H, 8.68. Found: C, 31.02; H, 8.91.

**Preparation of 1,2-(CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (2).** A 1.60 M solution of *n*-BuLi in *n*-hexane (12.5 mL, 20.0 mmol) was added dropwise to a solution of 1,2-(HOCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (**1**; 2.32 g, 10.0 mmol) in a dry toluene/Et<sub>2</sub>O mixture (2:1, 30 mL) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 30 min. The solution was then cooled to 0 °C, and a solution of iodomethane (3.55 g, 25.0 mmol) in toluene/Et<sub>2</sub>O (2:1, 10 mL) was slowly added with stirring. The reaction mixture was stirred overnight and then quenched with 30 mL of water. The organic layer was separated, and the aqueous layer was extracted with ether (30 mL × 2). The combined organic portions were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Removal of the solvents gave a colorless oil that became a white solid at -4 °C (2.16 g, 83%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  3.49 (t, *J* = 6.9 Hz, 4H, CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.32 (s, 6H, CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 2.50 (t, *J* = 6.9 Hz, 4H, CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  70.7 (CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 58.6 (CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 34.9 (CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>); the cage carbon atoms were not observed. <sup>11</sup>B NMR (CDCl<sub>3</sub>):  $\delta$  -4.2 (2B), -10.2 (8B). IR (KBr, cm<sup>-1</sup>):  $\nu$  2931 (m), 2879 (m), 2578 (vs), 1454 (m), 1352 (m), 1120 (vs). MS (FAB): 260 with correct isotope distribution.

**Preparation of 1,2-(CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (2) and 1-(CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>)-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> (3).** A 1.60 M solution of *n*-BuLi in *n*-hexane (12.5 mL, 20.0 mmol) was added dropwise to a solution of *o*-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> (1.44 g, 10.0 mmol) in a dry toluene/Et<sub>2</sub>O mixture (2:1, 30 mL) with stirring at 0 °C. The mixture was allowed to warm to room temperature and stirred for 30 min. The solution was then cooled to 0 °C, and a solution of chloroethyl methyl ether (2.36 g, 25.0 mmol) in toluene/Et<sub>2</sub>O

(2:1, 10 mL) was slowly added with stirring. The reaction mixture was refluxed overnight and then quenched with 30 mL of water. The organic layer was separated, and the aqueous solution was extracted with Et<sub>2</sub>O (20 mL × 2). Removal of the solvents gave the yellow oil. Column chromatographic (SiO<sub>2</sub>, 230–300 mesh) separation using *n*-hexane/ethyl acetate (25:3) as eluant gave **2** (1.26 g, 4.8 mmol, 52%), **3** (0.42 g, 2.1 mmol, 23%), and *o*-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> (0.12 g, 0.8 mmol), respectively. For **3**: <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  3.92 (s, 1H, cage CH), 3.46 (t, *J* = 6.0 Hz, 2H, CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.31 (s, 3H, CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 2.49 (t, *J* = 6.0 Hz, 2H, CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  70.0 (CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 60.1 (cage C), 58.6 (CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 37.4 (CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>). <sup>11</sup>B NMR (CDCl<sub>3</sub>):  $\delta$  -2.4 (1B), -5.9 (1B), -10.1 (2B), -11.2 (2B), -12.5 (2B), -13.2 (2B). IR (KBr, cm<sup>-1</sup>):  $\nu$  2961 (w), 2573 (vs), 1399 (m), 1257 (vs), 1082 (vs), 979 (vs), 819 (vs), 502 (m). MS (FAB): 202 with correct isotope distribution.

**Preparation of 1,2-(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (4).** This compound was prepared as a white solid (at -4 °C) from 1,2-(HOCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (**1**; 2.32 g, 10.0 mmol), *n*-BuLi in *n*-hexane (1.60 M, 12.5 mL, 20.0 mmol), and benzyl bromide (4.27 g, 25.0 mmol) in toluene/Et<sub>2</sub>O using the same procedures reported for **2**: yield 1.77 g (43%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.38 (m, 10H, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>), 4.50 (br s, 4H, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>), 3.83 (t, *J* = 6.9 Hz, 4H, CH<sub>2</sub>CH<sub>2</sub>O), 2.51 (t, *J* = 6.9 Hz, 4H, CH<sub>2</sub>CH<sub>2</sub>O). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  137.4, 129.0, 128.7, 127.8, 73.1 (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>), 68.4 (CH<sub>2</sub>CH<sub>2</sub>O), 34.9 (CH<sub>2</sub>CH<sub>2</sub>O), the cage carbon atoms were not observed. <sup>11</sup>B NMR (CDCl<sub>3</sub>):  $\delta$  -5.1 (2B), -11.5 (8B). IR (KBr, cm<sup>-1</sup>):  $\nu$  3050 (w), 2942 (m), 2894 (m), 2582 (vs), 1422 (m), 1346 (m), 1053 (s), 917 (w), 734 (m), 514 (w). MS (FAB): 412 with correct isotope distribution.

**Preparation of [1,2-(HOCH<sub>2</sub>CH<sub>2</sub>)(OCH<sub>2</sub>CH<sub>2</sub>)C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>]-{K(18-crown-6)}<sub>n</sub> (5) and [1,2-(HOCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]-{K(18-crown-6)}<sub>n</sub> (6).** Finely cut K metal (390 mg, 10.0 mmol) was added to a THF (25 mL) solution of 1,2-(HOCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (**1**; 232 mg, 1.0 mmol), and the mixture was stirred at room temperature for a week. After removal of excess K and solvent, a THF solution (20 mL) of 18-crown-6 (254 mg, 1.0 mmol) was added and stirred for 10 min. Removal of THF and fractional crystallization from acetone in air afforded **5** (172 mg, 0.3 mmol, 30%) and **6** (330 mg, 0.6 mmol, 60%) as colorless crystals, respectively. For **5**: <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>):  $\delta$  4.24 (t, *J* = 5.0 Hz, 1H, CH<sub>2</sub>CH<sub>2</sub>OH), 4.06 (dt, *J* = 5.0 and 5.7 Hz, 2H, CH<sub>2</sub>CH<sub>2</sub>OH), 3.65 (s, 24H, C<sub>12</sub>H<sub>24</sub>O<sub>6</sub>), 3.26 (t, *J* = 5.7 Hz, 2H, CH<sub>2</sub>CH<sub>2</sub>O), 2.34 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>O). <sup>13</sup>C NMR (acetone-*d*<sub>6</sub>):  $\delta$  71.3 (C<sub>12</sub>H<sub>24</sub>O<sub>6</sub>), 68.1 (CH<sub>2</sub>CH<sub>2</sub>OH), 65.3 (CH<sub>2</sub>CH<sub>2</sub>O), 40.5 (CH<sub>2</sub>CH<sub>2</sub>O); the cage carbon atoms were not observed. <sup>11</sup>B NMR (acetone-*d*<sub>6</sub>):  $\delta$  32.0 (1B), 11.7 (1B), 3.1 (2B), -3.1 (1B), -14.9 (1B), -20.0 (1B), -25.7 (1B), -28.6 (1B), -34.0 (1B). IR (KBr, cm<sup>-1</sup>):  $\nu$  3488 (s), 2903 (vs), 2520 (vs), 1465 (m), 1391 (m), 1349 (m), 1105 (vs), 956 (m) 835 (m). Anal. Calcd for C<sub>18</sub>H<sub>43</sub>B<sub>10</sub>KO<sub>8</sub>: C, 40.43; H, 8.11. Found: C, 40.14; H, 7.88. For **6**: <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>):  $\delta$  4.03 (t, *J* = 5.4 Hz, 2H, CH<sub>2</sub>CH<sub>2</sub>OH), 3.74 (dt, *J* = 5.4 and 6.9 Hz, 4H, CH<sub>2</sub>CH<sub>2</sub>OH), 3.66 (s, 24H, C<sub>12</sub>H<sub>24</sub>O<sub>6</sub>), 2.58 (t, *J* = 6.9 Hz, 4H, CH<sub>2</sub>CH<sub>2</sub>OH). <sup>13</sup>C NMR (acetone-*d*<sub>6</sub>):  $\delta$  71.0 (C<sub>12</sub>H<sub>24</sub>O), 63.8 (CH<sub>2</sub>CH<sub>2</sub>OH), 38.9 (CH<sub>2</sub>CH<sub>2</sub>OH); the cage carbon atoms were not observed. <sup>11</sup>B NMR (acetone-*d*<sub>6</sub>):  $\delta$  -9.9 (2B), -11.6 (1B), -17.3 (2B), -18.4 (2B), -33.6 (1B), -36.6 (1B). IR (KBr, cm<sup>-1</sup>):  $\nu$  3549 (s), 2899 (vs), 2519 (vs), 1466 (m), 1351 (m), 1246 (m), 1108 (vs), 959 (m) 838 (m). Anal. Calcd for C<sub>18</sub>H<sub>44</sub>B<sub>9</sub>KO<sub>8</sub>: C, 41.19; H, 8.45. Found: C, 41.25; H, 8.71.

**Preparation of [Me<sub>3</sub>NH][nido-(CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]** (**7**). Distilled CH<sub>3</sub>OH (15 mL) was added to a mixture of 1,2-(CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (**2**; 260 mg, 1.0 mmol) and KOH (224 mg, 4.0 mmol) with stirring at 0 °C. The reaction mixture was warmed to room temperature and then refluxed overnight. After removal of the solvent, water (10 mL) was added. The aqueous solution was neutralized with diluted HCl. Addition of aqueous Me<sub>3</sub>NHCl solution gave a white precipitate. The product was filtered off, washed with water (3 × 5 mL), and dried in a vacuum to give **7** as a white solid (266 mg, 86%). <sup>1</sup>H

NMR (acetone- $d_6$ ):  $\delta$  3.65 (t,  $J = 6.5$  Hz, 4H,  $\text{CH}_2\text{CH}_2\text{OCH}_3$ ), 3.51 (s, 6H,  $\text{CH}_2\text{CH}_2\text{OCH}_3$ ), 3.09 (s, 9H,  $(\text{CH}_3)_3\text{NH}$ ), 2.55 (t,  $J = 6.5$  Hz, 4H,  $\text{CH}_2\text{CH}_2\text{OCH}_3$ ).  $^{13}\text{C}$  NMR (acetone- $d_6$ ):  $\delta$  74.1 (cage C), 64.3 ( $\text{CH}_2\text{CH}_2\text{OCH}_3$ ), 62.0 ( $\text{CH}_2\text{CH}_2\text{OCH}_3$ ), 42.3 ( $(\text{CH}_3)_3\text{NH}$ ), 38.2 ( $\text{CH}_2\text{CH}_2\text{OCH}_3$ ).  $^{11}\text{B}$  NMR (acetone- $d_6$ ):  $\delta$  -9.2 (2B), -10.3 (1B), -17.0 (2B), -18.0 (2B), -33.3 (1B), -36.1 (1B). IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  3615 (br m), 2912 (s), 2535 (s), 1362 (m), 1250 (m), 1112 (s), 960 (m), 851 (m). Anal. Calcd for  $\text{C}_{11}\text{H}_{14}\text{B}_9\text{NO}_2$ : C, 42.66; H, 11.07. Found: C, 42.35; H, 11.15.

**Preparation of  $[\{\eta^7\text{-}[(\text{CH}_3\text{OCH}_2\text{CH}_2)_2\text{C}_2\text{B}_{10}\text{H}_{10}]\text{Na}\}\{\text{Na}(\text{THF})\}_3]_n$  (**8**).** Finely cut Na metal (230 mg, 10.0 mmol) was added to a THF (25 mL) solution of 1,2- $(\text{CH}_3\text{OCH}_2\text{CH}_2)_2$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$  (**2**; 260 mg, 1.0 mmol), and the mixture was stirred at room temperature for a week. After removal of excess Na, the clear pale yellow solution was concentrated to about 10 mL, and toluene (about 10 mL) was added. **8** was isolated as colorless crystals after this solution stood at room temperature for 3 days (196 mg, 52%).  $^1\text{H}$  NMR (pyridine- $d_5$ ):  $\delta$  3.91 (br s, 4H,  $\text{CH}_2\text{CH}_2\text{OCH}_3$ ), 3.64 (m, 4H, THF), 3.27 (s, 6H,  $\text{CH}_2\text{CH}_2\text{OCH}_3$ ), 3.10 (br s, 4H,  $\text{CH}_2\text{CH}_2\text{OCH}_3$ ), 1.58 (m, 4H, THF).  $^{13}\text{C}$  NMR (pyridine- $d_5$ ):  $\delta$  75.4 ( $\text{CH}_2\text{CH}_2\text{OCH}_3$ ), 67.2 (THF), 57.1 ( $\text{CH}_2\text{CH}_2\text{OCH}_3$ ), 43.2 ( $\text{CH}_2\text{CH}_2\text{OCH}_3$ ), 25.1 (THF); the cage carbon atoms were not observed.  $^{11}\text{B}$  NMR (pyridine- $d_5$ ):  $\delta$  -2.4 (3B), -5.2 (3B), -11.1 (2B), -23.7 (2B). IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  2929 (vs), 2882 (vs), 2577 (vs), 2504 (vs), 2426 (vs), 1453 (s), 1112 (vs), 1058 (vs), 906 (m), 734 (w). Anal. Calcd for  $\text{C}_{12}\text{H}_{32}\text{B}_{10}\text{Na}_2\text{O}_3$ : C, 38.08; H, 8.52. Found: C, 38.43; H, 8.29.

**Preparation of  $[\{\eta^7\text{-}[(\text{CH}_3\text{OCH}_2\text{CH}_2)_2\text{C}_2\text{B}_{10}\text{H}_{10}]\text{Er}\}\{\text{Na}(\text{CH}_3\text{CN})\}_2]_n$  (**9**).** Finely cut Na metal (230 mg, 10.0 mmol) was added to a THF (10 mL) solution of **2** (260 mg, 1.0 mmol), and the mixture was stirred at room temperature for 2 days.  $\text{ErCl}_3$  (274 mg, 1.0 mmol) was then added, and the reaction mixture was stirred at room temperature for 4 days. The precipitate and excess Na metal were filtered off and washed with THF (5 mL  $\times$  3). Removal of the solvent gave a pink solid that was extracted with  $\text{CH}_3\text{CN}$  (10 mL  $\times$  2). The resulting solutions were combined and concentrated to about 10 mL, and toluene (about 7 mL) was added. **9** was isolated as pink crystals after this solution stood at room temperature overnight (186 mg, 35%).  $^1\text{H}$  NMR (pyridine- $d_5$ ):  $\delta$  1.82 (s,  $\text{CH}_3\text{-CN}$ ), and other broad, unresolved peaks.  $^{13}\text{C}$  NMR (pyridine- $d_5$ ):  $\delta$  116.8 ( $\text{CH}_3\text{CN}$ ), 30.9, 22.0, 13.4 ( $\text{CH}_2\text{CH}_2\text{OCH}_3$ ), 0.3 ( $\text{CH}_3\text{CN}$ ).  $^{11}\text{B}$  NMR (pyridine- $d_5$ ): many broad, unresolved resonances. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  2909 (s), 2828 (s), 2484 (vs), 2434 (vs), 2355 (s), 1460 (m), 1208 (m), 1039 (s), 798 (m). Anal. Calcd for  $\text{C}_{24}\text{H}_{60}\text{B}_{20}\text{Er}_2\text{Na}_4\text{Na}_2\text{O}_4$ : C, 27.05; H, 5.68; N, 5.26. Found: C, 27.01; H, 5.56; N, 5.05.

**Preparation of  $[\{\eta^7\text{-}[(\text{CH}_3\text{OCH}_2\text{CH}_2)_2\text{C}_2\text{B}_{10}\text{H}_{10}]\text{Y}\}\{\text{Li}(\text{THF})\}_3]_2$  (**10**).** This complex was prepared from **2** (260 mg, 1.0 mmol), finely cut Li metal (69 mg, 10.0 mmol), and  $\text{YCl}_3$  (195 mg, 1.0 mmol) in THF using the identical procedure reported for **9**. Recrystallization from THF/toluene (1:1, 20 mL) gave **10** as yellow crystals (258 mg, 45%).  $^1\text{H}$  NMR (pyridine- $d_5$ ):  $\delta$  3.84 (br s, 4H,  $\text{CH}_2\text{CH}_2\text{OCH}_3$ ), 3.59 (m, 24H, THF), 3.20 (s, 6H,  $\text{CH}_2\text{CH}_2\text{OCH}_3$ ), 2.96 (br s, 4H,  $\text{CH}_2\text{CH}_2\text{OCH}_3$ ), 1.58 (m, 24H, THF).  $^{13}\text{C}$  NMR (pyridine- $d_5$ ):  $\delta$  74.8 ( $\text{CH}_2\text{CH}_2\text{OCH}_3$ ), 66.7 (THF), 57.1 ( $\text{CH}_2\text{CH}_2\text{OCH}_3$ ), 42.9 ( $\text{CH}_2\text{CH}_2\text{OCH}_3$ ), 24.6 (THF); the cage carbon atoms were not observed.  $^{11}\text{B}$  NMR (pyridine- $d_5$ ):  $\delta$  0.26 (3B), -6.6 (4B), -14.1 (1B), -22.3 (2B). IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  2957 (s), 2881 (s), 2490 (vs), 2460 (s), 2400 (s), 1668 (s), 1452 (s), 1260 (s), 1042 (vs), 802 (s). Anal. Calcd for  $\text{C}_{20}\text{H}_{56}\text{B}_{20}\text{Li}_2\text{O}_5\text{Y}_2$  (**9**-5THF): C, 30.62; H, 7.19. Found: C, 30.88; H, 7.39.

**Preparation of  $[\{\{\eta^7\text{-}[(\text{CH}_3\text{OCH}_2\text{CH}_2)_2\text{C}_2\text{B}_{10}\text{H}_{11}]\text{Er}(\text{THF})\}\{\text{Na}(\text{CH}_3\text{CN})(\text{THF})\}_2]_n$  (**11**).** This complex was prepared from **3** (202 mg, 1.0 mmol), finely cut Na metal (230 mg, 10.0 mmol), and  $\text{ErCl}_3$  (274 mg, 1.0 mmol) in THF using the identical procedure reported for **9**. Recrystallization from  $\text{CH}_3\text{-CN/THF}$  (1:1, 20 mL) gave **11** as orange crystals (225 mg, 39%).  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{11}\text{B}$  NMR (pyridine- $d_5$ ): many broad, unresolved resonances. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  2919 (s), 2519 (vs), 2171 (s), 1597

(s), 1420 (m), 1256 (w), 1023 (m), 800 (m), 531 (m). Anal. Calcd for  $\text{C}_{30}\text{H}_{74}\text{B}_{20}\text{Er}_2\text{N}_2\text{Na}_2\text{O}_6$ : C, 31.18; H, 6.45; N, 2.42. Found: C, 31.24; H, 6.33; N, 2.27.

**Preparation of  $[\{\{\eta^7\text{-}[(\text{CH}_3\text{OCH}_2\text{CH}_2)_2\text{C}_2\text{B}_{10}\text{H}_{11}]\text{Y}(\text{THF})\}\{\text{Na}(\text{THF})\}_3]_2$  (**12**).** This complex was prepared from **3** (202 mg, 1.0 mol), finely cut Na metal (230 mg, 10.0 mmol), and  $\text{YCl}_3$  (195 mg, 1.0 mmol) in THF using the identical procedure reported for **9**. Recrystallization from THF/toluene (1:1, 20 mL) gave **12** as yellow crystals (225 mg, 37%).  $^1\text{H}$  NMR (pyridine- $d_5$ ):  $\delta$  3.63 (m, 16H, THF), 3.30 (br s, 2H,  $\text{CH}_2\text{CH}_2\text{OCH}_3$ ), 3.16 (br s, 3H,  $\text{CH}_2\text{CH}_2\text{OCH}_3$ ), 2.20 (br s, 2H,  $\text{CH}_2\text{CH}_2\text{OCH}_3$ ), 1.64 (m, 16H, THF).  $^{13}\text{C}$  NMR (pyridine- $d_5$ ):  $\delta$  75.3 ( $\text{CH}_2\text{CH}_2\text{OCH}_3$ ), 67.1 (THF), 57.1 ( $\text{CH}_2\text{CH}_2\text{OCH}_3$ ), 43.0 ( $\text{CH}_2\text{CH}_2\text{OCH}_3$ ), 25.0 (THF); the cage carbon atoms were not observed.  $^{11}\text{B}$  NMR (pyridine- $d_5$ ):  $\delta$  -8.1 (3B), -12.6 (3B), -19.4 (2B), -20.8 (2B). IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  2957 (s), 2879 (s), 2436 (vs), 1611 (s), 1452 (s), 1257 (s), 1042 (vs), 801 (s). Anal. Calcd for  $\text{C}_{30}\text{H}_{74}\text{B}_{20}\text{Na}_2\text{O}_7\text{Y}_2$  (**12**-3THF): C, 36.51; H, 7.56. Found: C, 36.26; H, 7.69.

**X-ray Structure Determination.** All single crystals were immersed in Paraton-N oil and sealed under  $\text{N}_2$  in thin-walled glass capillaries. Data were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using  $\text{Mo K}\alpha$  radiation. An empirical absorption correction was applied using the SADABS program.<sup>7</sup> All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations on  $F^2$  using the SHELXTL program package.<sup>8</sup> For noncentrosymmetric structures **1** and **8**, the values of the Flack's parameter  $x$  are 1.0(2) and 0.0(7), respectively.<sup>9</sup> Most of the carborane hydrogen atoms were located from difference Fourier syntheses. All other hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and structure refinements are given in Tables 1 and 2. Selected bond distances are compiled in Table 3. Further details are included in the Supporting Information.

## Results and Discussion

### Hydroxyethyl-*o*-carborane and Its Derivatives.

The synthesis of ether-*o*-carboranes 1- $\text{R}^1$ -2- $\text{R}^2$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$  ( $\text{R}^1 = (\text{CH}_2)_n\text{OCH}_3$ ,  $\text{R}^2 = \text{H}$ ,  $n = 1-3$ ;  $\text{R}^1 = \text{R}^2 = \text{CH}_2\text{OCH}_3$ ) was achieved by the addition of the appropriate substituted alkynes to activated borane  $\text{B}_{10}\text{H}_{12}(\text{SMe}_2)_2$ .<sup>5</sup> This method is not practical for those with more than one methylene unit separating the cage carbon and oxygen atoms since the isolation yields were  $<5\%$  for  $n = 2$  or 3.<sup>5</sup> A new methodology is desired. We then thought about the reactions of  $(\text{LiOCH}_2\text{CH}_2)_2\text{-C}_2\text{B}_{10}\text{H}_{10}$  with RX or  $\text{Li}_2\text{C}_2\text{B}_{10}\text{H}_{10}$  with  $\text{MeOCH}_2\text{CH}_2\text{Cl}$ , which would directly give ether-*o*-carboranes.

It has been reported that primary *o*-carboranyl alcohols can be prepared by transesterification,<sup>10</sup> hydrolysis of *o*-carboranyl ester,<sup>11</sup> and reaction of lithio-*o*-carborane with epoxides.<sup>11,12</sup> Among these, the reaction of  $\text{Li}_2\text{C}_2\text{B}_{10}\text{-H}_{10}$  with ethylene oxide drew our attention, although

(7) Sheldrick, G. M. *SADABS*, Program for Empirical Absorption Correction of Area Detector Data; University of Göttingen: Germany, 1996.

(8) Sheldrick, G. M. *SHELXTL*, 5.10 for Windows NT: Structure Determination Software Programs; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1997.

(9) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.

(10) Fein, M. M.; Grafstein, D.; Paustian, J. E.; Bobinski, J.; Lichstein, B. M.; Mayes, N.; Schwartz, N. N.; Cohen, M. S. *Inorg. Chem.* **1963**, *2*, 1115.

(11) (a) Heying, T. L.; Ager, J. W.; Clark, S. L.; Alexander, R. P.; Papetti, S.; Reid, J. A.; Trotz, S. I. *Inorg. Chem.* **1963**, *2*, 1097. (b) Grafstein, D.; Bobinski, J.; Dvorak, J.; Smith, H.; Schwartz, N.; Cohen, M. S. Fein, M. M. *Inorg. Chem.* **1963**, *2*, 1120.

**Table 1. Crystal Data and Summary of Data Collection and Refinement Details for 1 and 5–8**

	1	5	6	7	8
formula	C <sub>6</sub> H <sub>20</sub> B <sub>10</sub> O <sub>2</sub>	C <sub>18</sub> H <sub>43</sub> B <sub>10</sub> KO <sub>8</sub>	C <sub>18</sub> H <sub>44</sub> B <sub>9</sub> KO <sub>8</sub>	C <sub>11</sub> H <sub>34</sub> B <sub>9</sub> NO <sub>2</sub>	C <sub>12</sub> H <sub>32</sub> B <sub>10</sub> Na <sub>2</sub> O <sub>3</sub>
cryst size (mm)	0.28 × 0.25 × 0.20	0.38 × 0.34 × 0.15	0.60 × 0.55 × 0.45	0.60 × 0.50 × 0.38	0.55 × 0.36 × 0.35
fw	232.3	534.7	524.9	309.7	378.5
cryst syst	orthorhombic	triclinic	triclinic	triclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 1	<i>P</i> 1	<i>P</i> 1	<i>P</i> 2 <sub>1</sub>
<i>a</i> , Å	6.912(1)	8.961(1)	11.458(1)	8.204(1)	9.529(2)
<i>b</i> , Å	13.768(1)	9.252(1)	12.083(1)	11.400(2)	10.063(2)
<i>c</i> , Å	14.182(1)	18.935(2)	12.281(1)	11.586(2)	11.451(2)
α, deg	90.00	98.24(1)	73.12(1)	95.30(1)	90.00
β, deg	90.00	99.49(1)	65.37(1)	109.76(1)	98.01(1)
γ, deg	90.00	106.29(1)	77.75(1)	98.60(1)	90.00
<i>V</i> , Å <sup>3</sup>	1349.6(2)	1456.1(2)	1470.8(2)	996.3(2)	1087.3(3)
<i>Z</i>	4	2	2	2	2
<i>D</i> <sub>calcd</sub> , Mg/m <sup>3</sup>	1.143	1.220	1.185	1.032	1.156
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	4.12 to 50.00	2.22 to 50.00	3.54 to 50.00	3.66 to 50.00	3.60 to 50.00
μ, mm <sup>-1</sup>	0.063	0.221	0.218	0.059	0.102
<i>F</i> (000)	488	568	560	336	400
no. of obsd reflns	2382	3797	5147	3511	2579
no. of params refnd	163	389	340	222	277
goodness of fit	1.011	1.153	1.037	1.041	1.022
R1	0.055	0.075	0.056	0.060	0.079
wR2	0.141	0.188	0.160	0.182	0.196

**Table 2. Crystal Data and Summary of Data Collection and Refinement Details for 9–12**

	9	10	11	12
formula	C <sub>24</sub> H <sub>60</sub> B <sub>20</sub> Er <sub>2</sub> N <sub>4</sub> Na <sub>2</sub> O <sub>4</sub>	C <sub>40</sub> H <sub>96</sub> B <sub>20</sub> Li <sub>2</sub> O <sub>10</sub> Y <sub>2</sub>	C <sub>30</sub> H <sub>74</sub> B <sub>20</sub> Er <sub>2</sub> N <sub>2</sub> Na <sub>2</sub> O <sub>6</sub>	C <sub>42</sub> H <sub>100</sub> B <sub>20</sub> Na <sub>2</sub> O <sub>10</sub> Y <sub>2</sub>
cryst size (mm)	0.44 × 0.30 × 0.22	0.80 × 0.65 × 0.29	0.38 × 0.22 × 0.12	0.48 × 0.47 × 0.21
fw	1065.5	1145.1	1155.6	1205.2
cryst syst	triclinic	triclinic	monoclinic	triclinic
space group	<i>P</i> 1	<i>P</i> 1	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 1
<i>a</i> , Å	9.546(1)	9.974(1)	12.162(1)	10.503(1)
<i>b</i> , Å	9.707(1)	13.581(2)	9.608(1)	12.002(1)
<i>c</i> , Å	14.008(1)	14.813(2)	22.639(1)	14.249(1)
α, deg	96.98(1)	114.74(1)	90.00	104.54(1)
β, deg	107.18(1)	95.64(1)	103.18(1)	94.20(1)
γ, deg	111.57(1)	99.05(1)	90.00	111.65(1)
<i>V</i> , Å <sup>3</sup>	1113.8(1)	1769.4(4)	2575.5(2)	1588.3(2)
<i>Z</i>	1	1	2	1
<i>D</i> <sub>calcd</sub> , Mg/m <sup>3</sup>	1.588	1.075	1.490	1.260
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	3.16 to 56.04	4.74 to 50.00	3.58 to 56.08	3.00 to 56.02
μ, mm <sup>-1</sup>	3.797	1.672	3.292	1.878
<i>F</i> (000)	522	600	1148	632
no. of obsd reflns	5272	4271	6226	7543
no. of params refnd	317	337	299	358
goodness of fit	0.951	1.046	1.086	0.918
R1	0.029	0.084	0.048	0.060
wR2	0.070	0.205	0.118	0.145

**Table 3. Selected Bond Lengths for Rare Earth Complexes<sup>a</sup>**

	9 (Er)	10 (Y)	11 (Er)	12 (Y)
Ln–C(2)	2.351(4)	2.344(8)	2.364(5)	2.392(4)
Ln–C(5)	2.352(4)	2.382(8)	2.352(6)	2.378(4)
Ln–B(3)	2.675(4)	2.674(9)	2.635(7)	2.640(5)
Ln–B(4)	2.667(4)	2.714(9)	2.649(7)	2.668(5)
Ln–B(6)	2.710(4)	2.726(10)	2.699(6)	2.742(5)
Ln–B(7)	2.745(5)	2.764(9)	2.784(6)	2.803(5)
Ln–B(8)	2.705(4)	2.738(10)	2.719(6)	2.761(5)
Ln···B	2.700(4)	2.746(9)	2.748(6)	2.755(4)
	2.924(4)	2.983(10)	2.851(6)	2.918(5)
Ln–H	2.20(4)	2.04(9)	2.32(6)	2.23(4)
	2.63(4)	2.76(9)	2.42(6)	2.52(4)
Ln–O(1)	2.562(3)	2.415(5)	2.494(5)	2.498(3)
Ln–O(2)	2.424(3)	2.486(6)	2.436(5) <sup>b</sup>	2.440(3) <sup>b</sup>

<sup>a</sup> All in Å. <sup>b</sup> Ln–O(THF) distances.

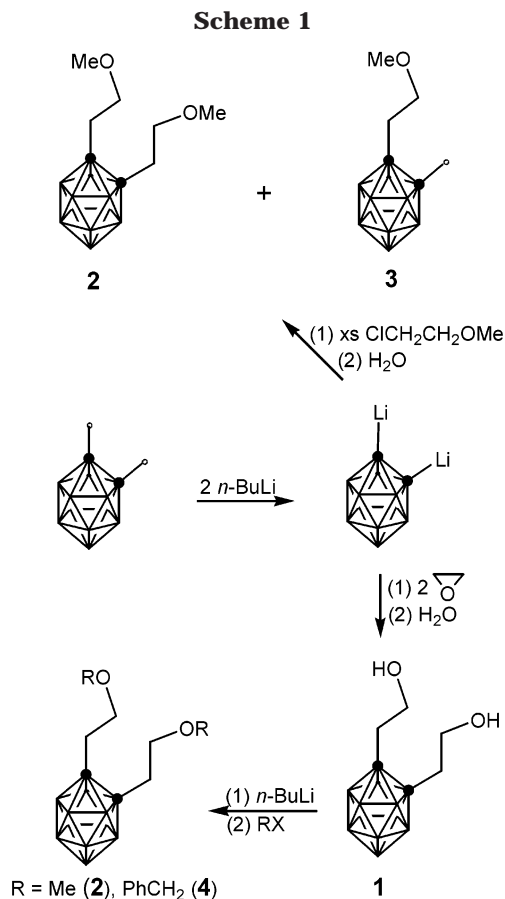
no characterization data were reported.<sup>11b</sup> We decided to examine this reaction. Reaction of Li<sub>2</sub>C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> with excess ethylene oxide in toluene/Et<sub>2</sub>O at 0 °C afforded 1,2-(HOCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (**1**) in 92% yield (Scheme 1). This reaction was very fast and clean. The <sup>1</sup>H NMR spectrum clearly exhibits two sets of methylene protons and a triplet at δ = 4.05 ppm attributable to the

hydroxyl protons. The <sup>13</sup>C NMR spectrum is consistent with the results derived from the <sup>1</sup>H NMR data. The <sup>11</sup>B NMR spectrum exhibits a 2:8 splitting pattern, which is commonly observed in disubstituted *o*-carboranes. The IR spectrum displays characteristic O–H and B–H absorptions at ca. 3236 and 2585 cm<sup>-1</sup>, respectively. The solid-state structure of **1** is confirmed by single-crystal X-ray analyses (Figure 1). The bond distances and angles are normal and comparable to other *o*-carborane derivatives.<sup>13,14</sup> Like other hydroxy-*o*-carboranes,<sup>14</sup> the hydroxyl groups in **1** are involved in hydrogen bonds to form linear polymeric chains (Figure 2). The O···O(H) distances are 2.681(4) and

(12) (a) Grafstein, D.; Bobinski, J.; Dvorak, J.; Paustian, J. E.; Smith, H. F.; Karlan, S.; Vogel, C.; Fein, M. M. *Inorg. Chem.* **1963**, *2*, 1125. (b) Zakharkin, L. I. *Tetrahedron Lett.* **1964**, *33*, 2255. (c) Gomez, F. A.; Hawthorne, M. F. *J. Org. Chem.* **1992**, *57*, 1384.

(13) Zi, G.; Li, H.-W.; Xie, Z. *Organometallics* **2002**, *21*, 5415.

(14) (a) Herzog, A.; Knobler, C. B.; Hawthorne, M. F. *Angew. Chem., Int. Ed.* **1998**, *37*, 1552. (b) Peymann, T.; Knobler, C. B.; Khan, S. I.; Hawthorne, M. F. *J. Am. Chem. Soc.* **2001**, *123*, 2182. (c) Maderna, A.; Herzog, A.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **2001**, *123*, 10423. (d) Herzog, A.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **2001**, *123*, 12791. (e) Maderna, A.; Huertas, R.; Hawthorne, M. F.; Luguaya, R.; Vicente, M. G. H. *Chem. Commun.* **2002**, 1784.



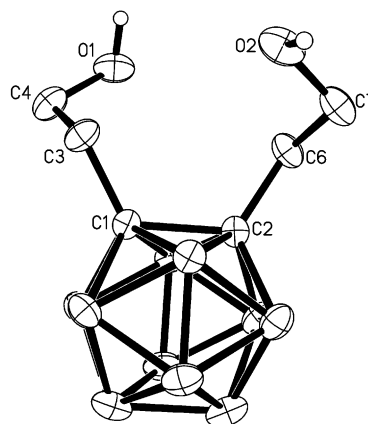
2.706(4) Å, respectively, which are at the long end of 2.4–2.7 Å normally observed in hydrated proton ions.<sup>15</sup>

Since hydroxyl can be converted into many other functional groups,<sup>16</sup> it is expected that **1** would be a very useful synthon. Reaction of **1** with 2 equiv of *n*-BuLi followed by treatment with excess iodomethane or benzyl bromide afforded 1,2-(CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (**2**) or 1,2-(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (**4**) in 83 or 43% yield, respectively (Scheme 1). The <sup>1</sup>H NMR spectra of **2** and **4** exhibit two triplets in the range 2.5–3.9 ppm attributable to –CH<sub>2</sub>–CH<sub>2</sub>– protons. The OCH<sub>3</sub> and OCH<sub>2</sub>Ph resonances are also observed. The <sup>13</sup>C NMR spectra are in line with their <sup>1</sup>H NMR data. Their <sup>11</sup>B NMR spectra exhibit a typical 2:8 splitting pattern for disubstituted *o*-carboranes. The IR spectra display a characteristic B–H absorption at about 2580 cm<sup>-1</sup>.

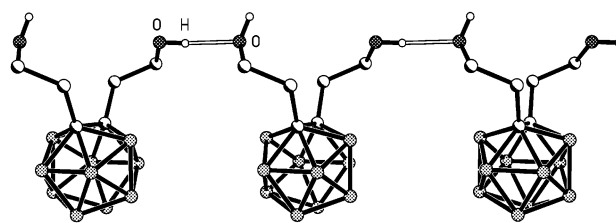
Reaction of Li<sub>2</sub>C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> with excess MeOCH<sub>2</sub>CH<sub>2</sub>Cl in toluene/Et<sub>2</sub>O at reflux temperature gave, after column chromatographic separation, **2** and monosubstituted *o*-carborane 1-(CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>)-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> (**3**) in a molar ratio of 7:3 (Scheme 1). This reaction was closely monitored by <sup>11</sup>B NMR spectroscopy, which indicated that the molar ratio of **2**:**3**:*o*-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> was about 6:3:1 in the reaction mixture. This ratio stayed almost unchanged even when a large excess of MeOCH<sub>2</sub>CH<sub>2</sub>Cl was used. The <sup>11</sup>B NMR also showed that this is a stepwise substitution reaction. The oxygen atom of the sidearm in the monosubstituted species may coordinate

(15) Joesten, M. D.; Schaad, L. J. *Hydrogen Bonding*; Marcel Dekker: New York, 1974.

(16) Morrison, R. T.; Boyd, R. N. *Organic Chemistry*, 6th ed.; Prentice Hall: NJ, 1992; p 692.



**Figure 1.** Molecular structure of 1,2-(HOCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (**1**). Selected bond distances (Å): C(1)–C(2) = 1.684(3), C(1)–C(3) = 1.521(3), C(3)–C(4) = 1.518(4), C(4)–O(1) = 1.422(4), C(2)–C(6) = 1.525(4), C(6)–C(7) = 1.502(4), C(7)–O(2) = 1.417(4).



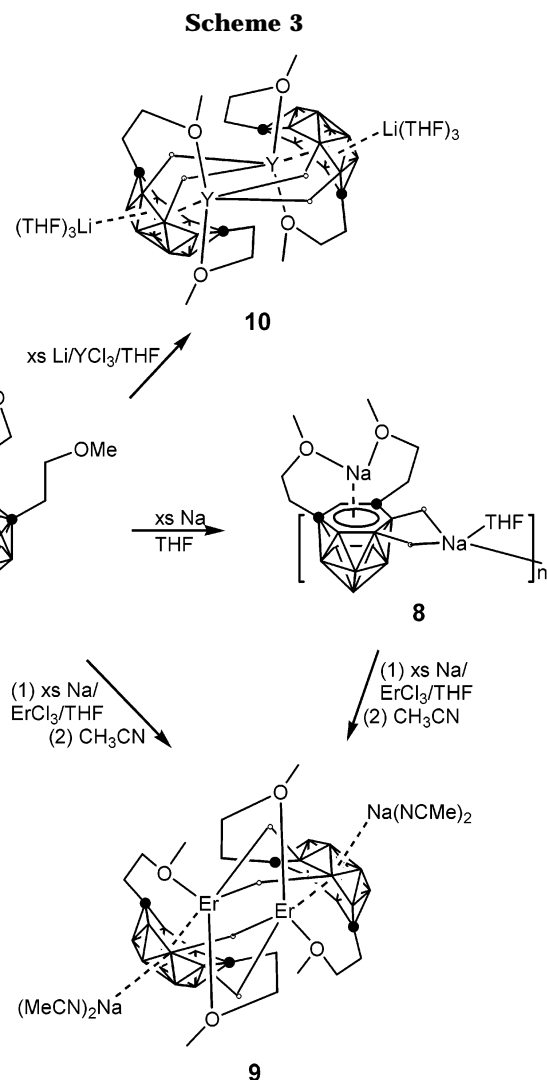
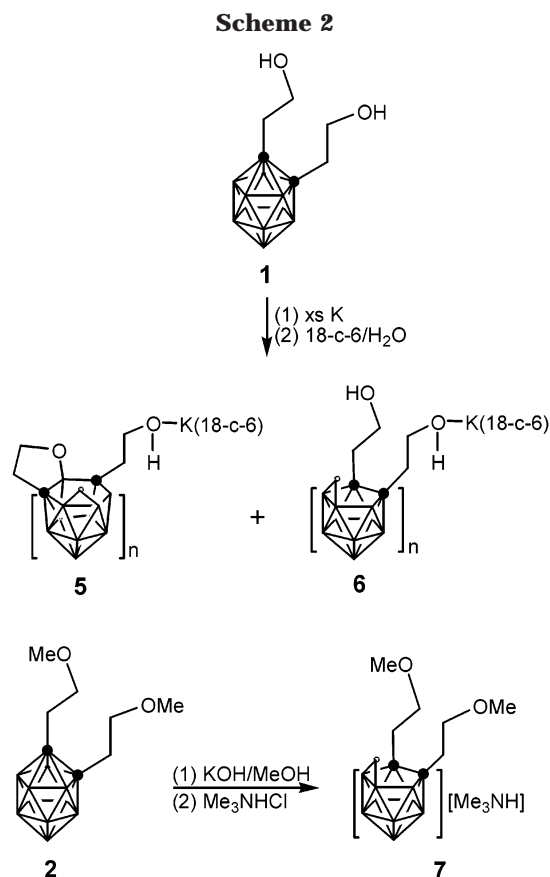
**Figure 2.** Intermolecular O···H–O interactions in **1**.

to the lithium atom, which probably blocks the second step of the reaction to some extent, leading to the formation of both mono- and disubstituted carboranes. A similar result was achieved if MeOCH<sub>2</sub>CH<sub>2</sub>Cl was replaced by MeOCH<sub>2</sub>CH<sub>2</sub>OTs. The <sup>1</sup>H NMR spectrum of **3** shows two triplets and one singlet corresponding to the CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub> unit and a broad singlet at 3.92 ppm assignable to the cage CH proton.<sup>5</sup> Its <sup>11</sup>B NMR spectrum exhibits a 1:1:2:2:2:2 splitting pattern, which is significantly different from that of **2**.

**Alkali Metal Complexes.** Treatment of **1** with excess K metal in THF gave, after recrystallization from an acetone solution of 18-crown-6, a mixture of products on the basis of <sup>11</sup>B NMR analyses. The products were separated by fractional crystallization after hydrolysis, affording [{*nido*-(HOCH<sub>2</sub>CH<sub>2</sub>)(OCH<sub>2</sub>CH<sub>2</sub>)C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>}{K(18-crown-6)}]<sub>n</sub> (**5**) and [{*nido*-(HOCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>}{K(18-crown-6)}]<sub>n</sub> (**6**) in a molar ratio of 1:2. It is assumed that **1** reacts with K metal to produce the intermediate K<sub>4</sub>[(OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>], in which one of the ethoxide groups attacks the more electron-deficient boron bonded to two cage carbon atoms in the C<sub>2</sub>B<sub>4</sub> bonding face to give the deprotonated form of **5** in an intramolecular manner. On the other hand, the potassium ethoxide can serve as a deboronating reagent<sup>17</sup> to attack the boron atom of the icosahedral cage in an intermolecular way to generate the deprotonated form of **6**. A derivative of **6**, [Me<sub>3</sub>NH][*nido*-(CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] (**7**), was prepared from the reaction of **2** with KOMe in MeOH, followed by treatment with Me<sub>3</sub>NHCl. These transformations are summarized in Scheme 2.

Complexes **5**–**7** were characterized by various spectroscopic data and X-ray diffraction studies. The <sup>11</sup>B

(17) Wiesboeck, R. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1964**, *86*, 1642.



NMR spectra exhibit a 1:1:2:1:1:1:1:1 splitting pattern for **5** and a 2:1:2:2:1:1 splitting pattern for both **6** and **7**, respectively. In addition, the proton-coupled <sup>11</sup>B NMR spectrum of **5** shows that the peak at 32.0 ppm does not split, indicating boron bonding to the oxygen atom.

Treatment of **2** with excess finely cut Na metal in THF gave, after recrystallization from THF/toluene, [ $\eta^6$ -[(CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>][Na]{Na(THF)}<sub>n</sub> (**8**) in 52% yield (Scheme 3). It is highly air- and moisture-sensitive, but remains stable for months at room temperature under an inert atmosphere. The <sup>1</sup>H NMR spectrum supports the ratio of one THF molecule per carboranyl ligand. The <sup>13</sup>C NMR spectrum is consistent with the result derived from the <sup>1</sup>H NMR data. Its <sup>11</sup>B NMR spectrum exhibits a 3:3:2:2 splitting pattern. The solid-state IR spectrum displays a very strong B–H absorption at 2577 cm<sup>-1</sup> and a strong peak at 2426 cm<sup>-1</sup>, implying B–H–M interactions.<sup>18,19</sup>

Single-crystal X-ray analyses reveal that **5** is a kinetic isomer generated from the hydrolysis of the potassium salt of the corresponding carborane dianion.<sup>13,20</sup> Six- and five-membered rings share one common edge of the

B(2)–C(3) bond. The K atom is disordered over two sets of positions with 0.5:0.5 occupancies (named as K(1) and K(2), respectively), and both sit at the inversion centers. As shown in Figure 3, K(2) is located at the center of 18-crown-6 and coordinates to two additional oxygen atoms from the two sidearms, while K(1) bonds to two additional B–H bonds from two cages, resulting in the formation of polymeric chains. The B(2)–O(7) distance of 1.398(8) Å is comparable to the value of 1.413(2) Å found in Co[(C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>OR)(C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)]<sup>-</sup>.<sup>21</sup> The K(2)–O(8) distance of 2.831(5) Å compares to the K–O(THF) distance of 2.840(5) Å in [(THF)<sub>2</sub>K(18-crown-6)][*nido*-(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>]<sup>22</sup> and the K–O(H<sub>2</sub>O) distance of 2.769(1) Å in [{ $\mu$ -1,2-[*o*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>]-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>]}K(18-crown-6)]<sub>2</sub>( $\mu$ -OH<sub>2</sub>).<sup>13</sup> The K(1)⋯H(10)–B(10) distance of 3.01(2) Å is very close to the K⋯H–C distance of 3.00(2) Å observed in {K(18-crown-6)}{[(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>]}K(18-crown-6).<sup>22</sup> The average K–O(18-crown-6) distances of 2.819(3) and 2.800(3) Å are comparable to those normally observed in the complexes containing the [K(18-crown-6)] moiety.<sup>13,22</sup>

Like **5**, the K atom in **6** is also disordered over two sets of positions with 0.5:0.5 occupancies, and both of them sit at the inversion centers. Each K atom in the

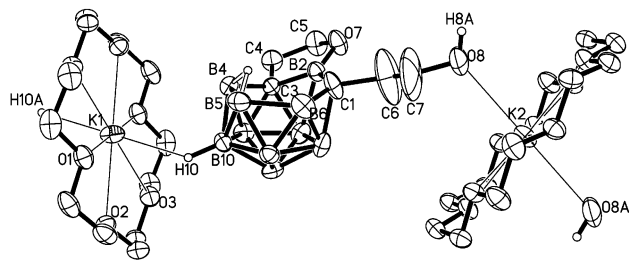
(18) (a) Xie, Z.; Wang, S.; Zhou, Z.-Y.; Xue, F.; Mak, T. C. W. *Organometallics* **1998**, *17*, 489. (b) Xie, Z.; Wang, S.; Zhou, Z.-Y.; Mak, T. C. W. *Organometallics* **1998**, *17*, 1907. (c) Xie, Z.; Wang, S.; Zhou, Z.-Y.; Mak, T. C. W. *Organometallics* **1999**, *18*, 1641. (d) Xie, Z.; Wang, S.; Yang, Q.; Mak, T. C. W. *Organometallics* **1999**, *18*, 2420. (e) Wang, S.; Yang, Q.; Mak, T. C. W.; Xie, Z. *Organometallics* **1999**, *18*, 4478. (f) Wang, S.; Yang, Q.; Mak, T. C. W.; Xie, Z. *Organometallics* **1999**, *18*, 1578.

(19) (a) Khattar, R.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1990**, *29*, 2191. (b) Khattar, R.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1990**, *112*, 4962.

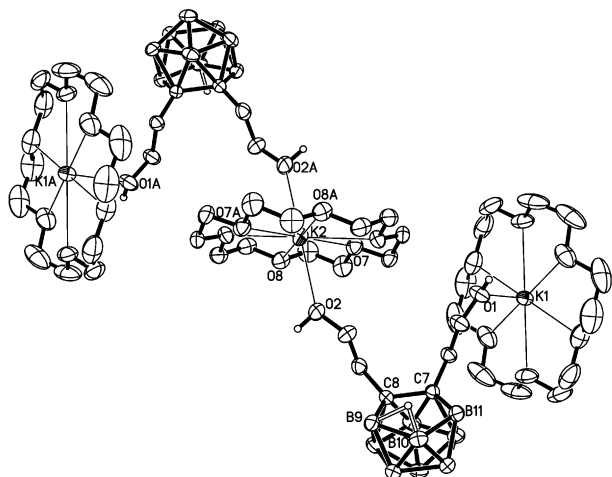
(20) (a) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1973**, *12*, 2674. (b) Dunks, G. B.; Wiersema, R. J.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1973**, *95*, 3174. (c) Getman, T. G.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1990**, *29*, 158.

(21) Sivaev, I. B.; Starikova, Z. A.; Sjöberg, S.; Bregadze, V. I. *J. Organomet. Chem.* **2002**, *649*, 1.

(22) Chui, K.; Li, H.-W.; Xie, Z. *Organometallics* **2000**, *19*, 5447.



**Figure 3.** Molecular structure of  $[\{nido-(HOCH_2CH_2)-(OCH_2CH_2)_2C_2B_{10}H_{10}\}\{K(18\text{-crown-}6)\}]_n$  (**5**), showing a portion of the infinite polymeric chain. Selected bond distances (Å): C(1)–B(2) = 1.551(7), C(3)–B(2) = 1.581(6), C(1)–C(6) = 1.494(8), O(8)–K(2) = 2.831(8), C(3)–C(4) = 1.510(7), C(4)–C(5) = 1.493(7), C(5)–O(7) = 1.456(7), O(7)–B(2) = 1.398(8), C(1)–B(6) = 1.557(7), B(6)–B(5) = 1.838(13), B(5)–B(4) = 1.869(12), C(3)–B(4) = 1.620(7).

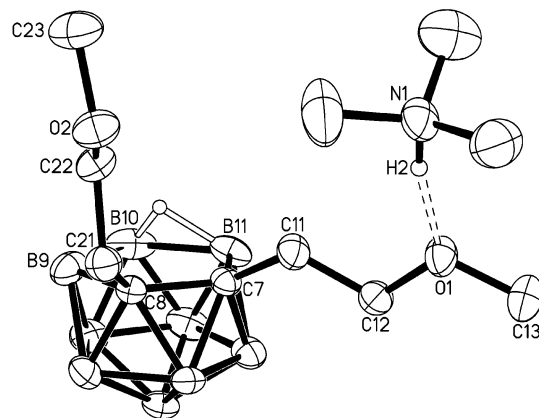


**Figure 4.** Molecular structure of  $[\{nido-(HOCH_2CH_2)_2-C_2B_9H_{10}\}\{K(18\text{-crown-}6)\}]_n$  (**6**), showing a portion of the infinite polymeric chain. Selected bond distances (Å): C(7)–C(8) = 1.585(3), O(1)–K(1) = 2.785(2), O(2)–K(2) = 2.791(2), C(7)–B(11) = 1.624(3), B(10)–B(11) = 1.824(4), B(9)–B(10) = 1.841(4), C(8)–B(9) = 1.620(4).

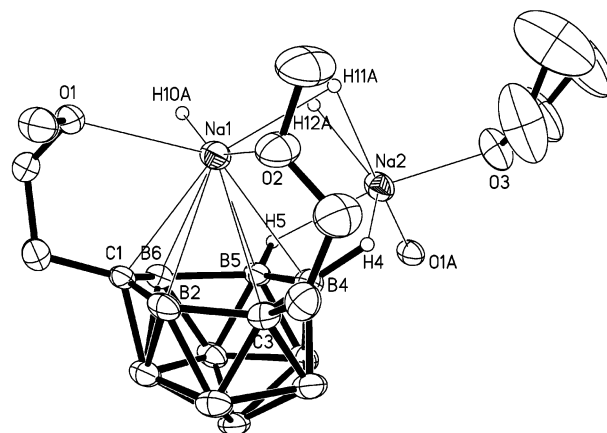
complex cation  $K(18\text{-crown-}6)^+$  coordinates, in addition to the six oxygen atoms of the crown ether, to two oxygen atoms of the hydroxyethyl groups from different cages, leading to the formation of infinite polymeric chains, shown in Figure 4. The average K–O(crown) distances of 2.780(2) and 2.810(2) Å and the K–O(OH) distances of 2.785(2) and 2.791(2) Å are all shorter than the corresponding values found in **5**.

The solid-state structure of **7** is shown in Figure 5. It consists of a *nido*- $C_2B_9$  cage and an associated cation  $HNMe_3^+$  via a N(1)–H···O(1) hydrogen bond with a distance of 2.762(3) Å.<sup>15</sup> The geometry of the  $C_2B_9$  cage is similar to that in **6** and other  $C_2B_9$  derivatives.<sup>23</sup>

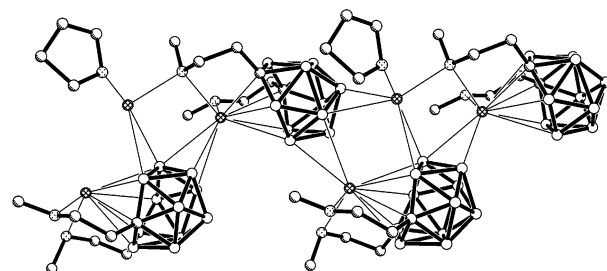
Single-crystal X-ray analyses confirm that **8** contains only one THF molecule (Figure 6), which compares to the highly solvated analogue  $[\eta^6-(C_6H_5CH_2)_2C_2B_{10}H_{10}][Na(THF)]\{Na(THF)_3\}$ .<sup>22</sup> One of the Na atoms is  $\eta^6$ -bound to the hexagonal  $C_2B_4$  face and  $\eta^3$ -bound to the  $B_3$  face of the neighboring *nido*-carborane cage and is coordinated to two oxygen atoms of the side-



**Figure 5.** Molecular structure of  $[Me_3NH][nido-(CH_3OCH_2CH_2)_2C_2B_9H_{10}]$  (**7**). Selected bond distances (Å): C(7)–C(8) = 1.574(3), C(7)–C(11) = 1.534(3), C(11)–C(12) = 1.477(3), C(12)–O(1) = 1.433(3), O(1)–C(13) = 1.420(3), C(8)–C(21) = 1.527(3), C(21)–C(22) = 1.508(3), C(22)–O(2) = 1.407(3), O(2)–C(23) = 1.420(3), C(7)–B(11) = 1.616(3), B(11)–B(10) = 1.839(5), B(10)–B(9) = 1.815(5), B(9)–C(8) = 1.611(3).



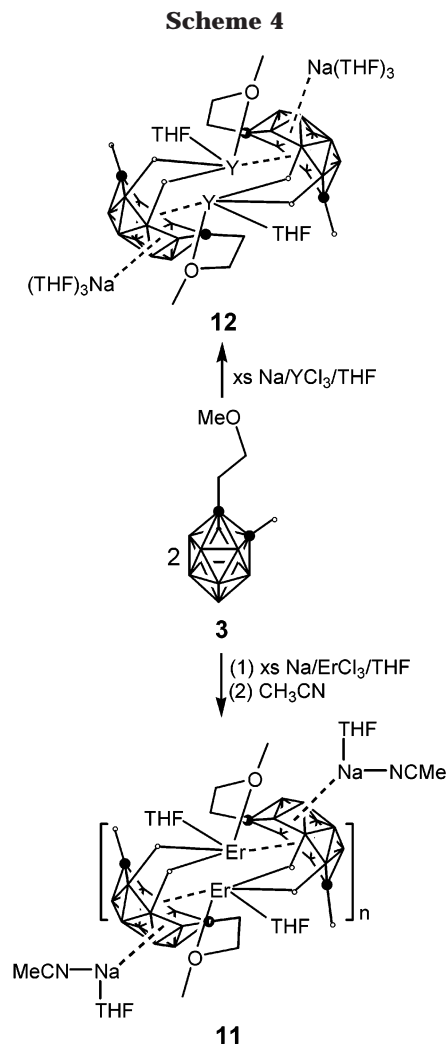
**Figure 6.** Molecular structure of  $[\{\eta^6-[(CH_3OCH_2CH_2)_2-C_2B_{10}H_{10}][Na]\{Na(THF)\}\}]_n$  (**8**), showing one asymmetric unit of the infinite polymeric chain. Selected bond distances (Å): Na(1)–C(1) = 2.661(5), Na(1)–B(2) = 2.802(6), Na(1)–C(3) = 2.944(5), Na(1)–B(4) = 2.763(6), Na(1)–B(5) = 2.964(6), Na(1)–B(6) = 2.955(7), Na(1)–O(1) = 2.546(4), Na(1)–O(2) = 2.379(5), Na(2)–O(3) = 2.282(5), Na(2)–B(4) = 2.880(7), Na(2)–B(5) = 2.797(6).



**Figure 7.** Intermolecular Na···H–B interactions in **8**.

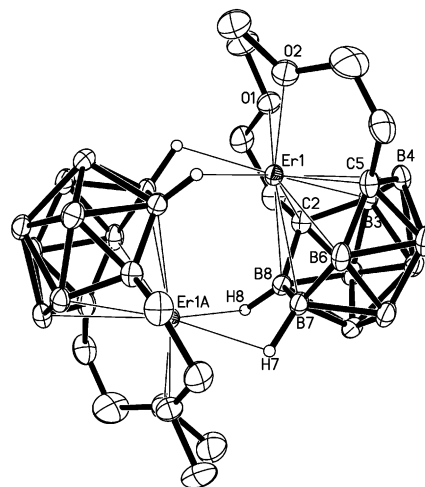
arms. The other Na atom is  $\eta^2$ -bound to each of two cages and is coordinated to two oxygen atoms from one THF molecule and one sidearm, respectively. Thus, a coordination polymeric structure of **8** is generated, as shown in Figure 7. The Na(1)–cage atom distances range from 2.661(5) to 2.964(6) Å with an average value of 2.848(6) Å, indicating a highly asymmetrical  $\eta^6$ -

(23) (a) Saxena, A. K.; Hosmane, N. S. *Chem. Rev.* **1993**, *93*, 1081. (b) Grimes, R. N. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: New York, 1995; Vol. 1, p 373. (c) Xie, Z. *Coord. Chem. Rev.* **2002**, *23*, 231.



bonding. This measured value is much larger than the 2.776(2) Å found in  $\{\eta^6\text{-}(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_{10}\text{H}_{10}\}\text{Na}(\text{THF})\}\{\text{Na}(\text{THF})_3\}$ ,<sup>22</sup> in which the Na atom is bonded to the open  $\text{C}_2\text{B}_4$  face in a symmetrical  $\eta^6$ -fashion. Such a slip distortion may result from the relatively stronger interactions between the Na(1) and two oxygen atoms of the sidearms (2.379(5) and 2.564(4) Å). This type of intramolecular interaction also reduces the level of solvation. Other structural parameters in **8** are similar to those reported in the literature.<sup>22</sup>

**Rare Earth Metal Complexes.** Treatment of **2** with excess finely cut Li or Na metal in THF, followed by reaction with 1 equiv of  $\text{LnCl}_3$  in the presence of excess alkali metal, gave, after recrystallization from  $\text{CH}_3\text{CN}$ /toluene,  $\{[\eta^7\text{-}[(\text{CH}_3\text{OCH}_2\text{CH}_2)_2\text{C}_2\text{B}_{10}\text{H}_{10}]\text{Er}]\{\text{Na}(\text{CH}_3\text{CN})_2\}\}_2$  (**9**) or  $\{[\eta^7\text{-}[(\text{CH}_3\text{OCH}_2\text{CH}_2)_2\text{C}_2\text{B}_{10}\text{H}_{10}]\text{Y}]\{\text{Li}(\text{THF})_3\}\}_2$  (**10**) if recrystallizing from THF/toluene. **9** was also prepared from the reaction of **8** with  $\text{ErCl}_3$  in the presence of excess Na, followed by recrystallization from  $\text{CH}_3\text{CN}$ /toluene (Scheme 3).  $[[\{\eta^7\text{-}(\text{CH}_3\text{OCH}_2\text{CH}_2)\text{-C}_2\text{B}_{10}\text{H}_{11}\}\text{Er}(\text{THF})]\{\text{Na}(\text{CH}_3\text{CN})(\text{THF})\}]_2$  (**11**) and  $[[\{\eta^7\text{-}(\text{CH}_3\text{OCH}_2\text{CH}_2)\text{-C}_2\text{B}_{10}\text{H}_{11}\}\text{Y}(\text{THF})]\{\text{Na}(\text{THF})_3\}]_2$  (**12**) were prepared from **3**, finely cut Na metal, and  $\text{LnCl}_3$  in THF using the same procedure reported for **9**, followed by recrystallization from  $\text{CH}_3\text{CN}$ /THF or THF/toluene, respectively (Scheme 4). It is noteworthy that only half-sandwich lanthanacarboranes were isolated even if 2 equiv of carborane (carborane: $\text{LnCl}_3 = 2:1$ ) was em-



**Figure 8.** Molecular structure of the  $\{\eta^7\text{-}[(\text{CH}_3\text{OCH}_2\text{-CH}_2)_2\text{C}_2\text{B}_{10}\text{H}_{10}]\text{Er}\}_2^{2-}$  ion in **9**.

ployed in the reactions. Reactions of **5–7** with excess NaH in THF, followed by treatment with 1 or 0.5 equiv of  $\text{LnCl}_3$ , were also attempted. No pure products, however, were isolated.

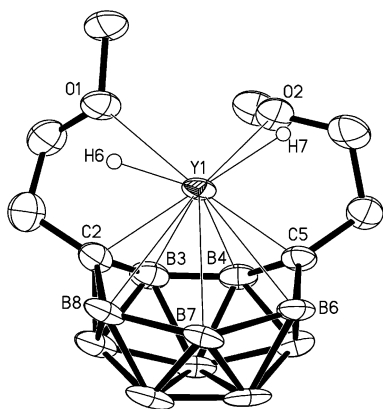
Complexes **9–12** are extremely air- and moisture-sensitive, but remain stable for months at room temperature under an inert atmosphere. They are quite soluble in polar organic solvents such as THF,  $\text{CH}_3\text{CN}$ , and pyridine, sparsely soluble in toluene, and insoluble in *n*-hexane.

The NMR spectra of **9** and **11** are not informative because of the strong paramagnetism of  $\text{Er}^{3+}$ . The diamagnetic yttrium complexes **10** and **12** are, however, found to provide the interpretable NMR data. The  $^1\text{H}$  NMR spectrum of **10** shows that two sidearms have the same chemical environment in solution and supports the ratio of three THF molecules per carborane cage. Its  $^{11}\text{B}$  NMR spectrum exhibits a 3:4:1:2 splitting pattern with the chemical shifts ranging from 0.3 to  $-22.3$  ppm. The  $^1\text{H}$  NMR spectrum of **12** indicates the presence of  $\text{MeOCH}_2\text{CH}_2$  and cage *CH* protons and supports the ratio of four THF molecules per carborane cage. A 3:3:2:2 splitting pattern is observed in the  $^{11}\text{B}$  NMR spectrum of **12** with the chemical shifts spanning from  $-8.1$  to  $-20.8$  ppm. The IR spectra of **9–12** display a very strong peak at about  $2490\text{ cm}^{-1}$  and a medium strong peak at about  $2355\text{ cm}^{-1}$ , implying B–H–Ln interactions.<sup>18,19</sup>

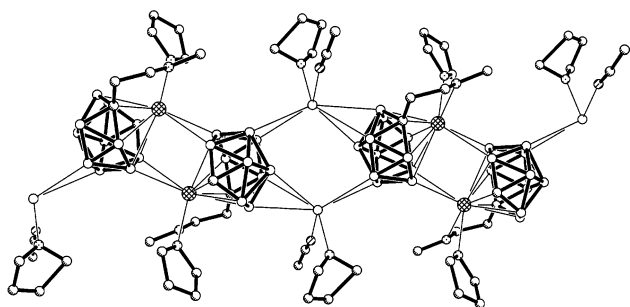
The molecular structures of **9** and **10** are confirmed by single-crystal X-ray diffraction studies. They are very similar except for the associated complex cations,  $\text{Na}(\text{CH}_3\text{CN})_2^+$  in **9** and  $\text{Li}(\text{THF})_3^+$  in **10**, respectively. Both **9** and **10** are centrosymmetrical dimers. Each rare earth metal is  $\eta^7$ -bound to the *arachno*-carborane ligand and  $\sigma$ -bound to two B–H bonds from the neighboring *arachno*-carborane and coordinated to two oxygen atoms of the pendant ether substituents in a four-lagged piano stool arrangement (Figures 8 and 9). The complex cations or the solvation environments of the  $\text{Na}^+$  or  $\text{Li}^+$  ions seem to have very little effect on the geometry of the metallacarboranes. In comparison with  $[[\eta^7\text{-}[(\text{C}_6\text{H}_5\text{-CH}_2)_2\text{C}_2\text{B}_{10}\text{H}_{10}]\text{Ln}(\text{THF})]\{\text{Na}(\text{THF})_3\}]_2$ ,<sup>24</sup> the intramo-

(24) Chui, K.; Yang, Q.; Mak, T. C. W.; Lam, W. H.; Lin, Z.; Xie, Z. *J. Am. Chem. Soc.* **2000**, *122*, 5758.





**Figure 9.** Closer view of the coordination environment of Y in **10**.



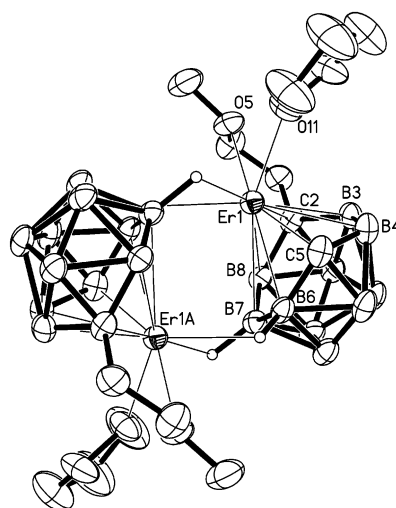
**Figure 10.** Intermolecular Na...H-B interactions in **11**.

molecular interactions between the central metal atoms and the oxygen atoms of the sidearms in **9** and **10** make the rare earth metal unsolvated and pull the metal atoms toward the B(3,4) side of the  $C_2B_5$  bonding face.

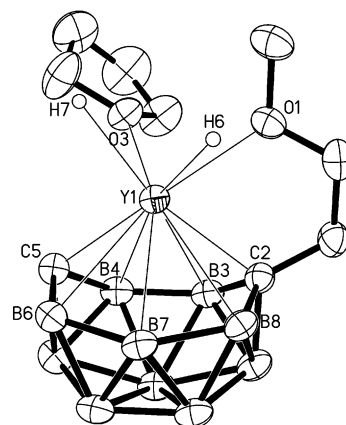
The average Ln-C(cage) distances of 2.352(4) Å in **9** and 2.363(8) Å in **10** are shorter than the corresponding values of 2.366(2) and 2.392(3) Å found in  $[\{\eta^7\text{-}[(C_6H_5CH_2)_2C_2B_{10}H_{10}]\text{Ln(THF)}\}\{\text{Na(THF)}_3\}]_2$  (Ln = Er, Y),<sup>24</sup> respectively (Table 3). The average Ln-B(cage) distances of 2.700(4) Å in **9** and 2.723(10) Å in **10** are longer than the corresponding values of 2.665(2) and 2.685(3) Å observed in  $[\{\eta^7\text{-}[(C_6H_5CH_2)_2C_2B_{10}H_{10}]\text{Ln(THF)}\}\{\text{Na(THF)}_3\}]_2$  (Ln = Er, Y),<sup>24</sup> respectively. The average Ln-O distances of 2.493(3) Å in **9** and 2.451(6) Å in **10** are significantly longer than the values of 2.341(1) and 2.352(2) Å found in  $[\{\eta^7\text{-}[(C_6H_5CH_2)_2C_2B_{10}H_{10}]\text{Ln(THF)}\}\{\text{Na(THF)}_3\}]_2$  (Ln = Er, Y),<sup>24</sup> respectively. These data indicate that the substituents on the cage carbon atoms have some effects on the structural parameters and coordination environments of the central metal atoms.

Single-crystal X-ray analyses reveal that **11** adopts a polymeric structure with less solvated Na atoms as linkers (Figure 10), whereas that for **12** is a centrosymmetrical dimer. However, the coordination environments of the central metal atoms in **11** and **12** are identical and similar to those observed in **9** and **10** except for one THF molecule replacing one methoxyethyl moiety, as shown in Figure 11. Figure 12 shows the closer view of the fragment  $\{\eta^7\text{-}[(CH_3OCH_2CH_2)\text{-}C_2B_{10}H_{11}]\text{Y(THF)}\}^-$  in **12**.

The average Er-C(cage) distance of 2.358(6) Å and Er-B(cage) distance of 2.697(7) Å in **11** are almost identical with the values of 2.352(4) and 2.700(4) in **9**. The average Y-C(cage) distance of 2.385(4) Å and Y-B(cage) distance of 2.723(8) Å in **12** compare to the



**Figure 11.** Molecular structure of the  $\{\eta^7\text{-}[(CH_3OCH_2CH_2)C_2B_{10}H_{11}]\text{Er}\}_2^{2-}$  ion in **11**.



**Figure 12.** Closer view of the coordination environment of Y in **12**.

corresponding values of 2.363(8) and 2.723(10) Å in **10**. The Ln-O(sidearm) distances are 2.494(5) Å in **11** and 2.498(3) Å in **12**, which compare to the values of 2.493(3) Å in **9** and 2.451(6) Å in **10**. These data indicate that the bond distances in yttrium complexes are much more sensitive than lanthanides to the coordination environments, suggesting there may be different bonding interactions between ligands and metal. The yttrium's d-orbitals can participate in  $\pi$  bonding, while only ionic interactions are present between lanthanides and ligands since f-orbitals do not involve in  $\pi$  bonding.

## Conclusion

Facile and practical syntheses of hydroxyethyl- and alkoxyethyl-*o*-carboranes were reported. These complexes are useful precursors to *nido*- $R_2C_2B_9H_9^{2-}$ , *nido*- $R_2C_2B_{10}H_{10}^{2-}$ , and *arachno*- $R_2C_2B_{10}H_{10}^{4-}$  types of ligands. They may find many applications in organometallic chemistry<sup>23</sup> and carborane-based materials.<sup>1</sup>

Several half-sandwich 13-vertex lanthanacarboranes incorporating *arachno*-carborane ligands were prepared and structurally characterized. They did not react with another equivalent of carboranyl ligand to form full-sandwich species. Structural studies show that the Lewis base-functionalized sidearms have some effects on the coordination environments of the central metal

atom through intramolecular interactions between the donor atoms of the sidearms and Lewis acidic metal ions, but do not change the gross structures of the 13-vertex lanthanacarboranes.

The structural parameters of yttrium complexes are more sensitive to the changes in coordination environments than those of f-block analogues probably because of the differences in the bonding nature between the metal atoms and *arachno*-carborane ligands: more covalent interactions in d-block complexes versus pure ionic interactions in f-block ones. For example, obvious differences in Y-cage atom distances are observed among **10**, **12**, and [ $\eta^7$ -[(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>]Y(THF)]- $\{Na(THF)_3\}_2$ ,<sup>24</sup> whereas those for Er complexes are almost identical.

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**Supporting Information Available:** Tables of crystallographic data collection details, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates for complexes **1** and **5–12**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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