# Synthesis, Structural Characterization, and Reactivity of 'Carbons-Adjacent' nido- and arachno-Carborane Anions of the C<sub>2</sub>B<sub>10</sub> Systems and Their Metal Complexes

Guofu Zi, Hung-Wing Li, and Zuowei Xie\*

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, People's Republic of China

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Three cage carbons-linked *o*-carboranes  $\mu$ -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>10</sub> (1),  $\mu$ -1,2-[1,8- $C_{10}H_6(CH_2)_2]$ -1,2- $C_2B_{10}H_{10}$  (2), and  $\mu$ -1,2-[1,1'-( $C_6H_4$ )<sub>2</sub>-2,2'-( $CH_2$ )<sub>2</sub>]-1,2- $C_2B_{10}H_{10}$  (3) were prepared from the reactions of  $Li_2C_2B_{10}H_{10}$  with  $\rho$ -C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>Br)<sub>2</sub>, 1,8-C<sub>10</sub>H<sub>6</sub>(CH<sub>2</sub>Cl)<sub>2</sub>, and 1,1'-( $C_6H_4$ )<sub>2</sub>-2,2'-( $CH_2Br$ )<sub>2</sub>, respectively. The cage carbon atom adjacency of 1 and 2 was maintained during the reactions with excess Na or K metal in THF, leading to high yields of 'carbons-adjacent' *nido*-carborane group 1 complexes  $[{\mu-1,2-[o-C_6H_4(CH_2)_2]-1,2-C_2B_{10}H_{10}}]_2$  $Na_4(THF)_{6]n}$  (4),  $[\{\mu-1,2-[o-C_6H_4(CH_2)_2]-1,2-C_2B_{10}H_{10}\}_2K_3(18-crown-6)_2][K(18-crown-6)(CH_3-C_2)_3(18-crown-6)_2][K(18-crown-6)(CH_3-C_2)_3(18-crown-6)_2][K(18-crown-6)(CH_3-C_2)_3(18-crown-6)_2][K(18-crown-6)(CH_3-C_2)_3(18-crown-6)_2][K(18-crown-6)(CH_3-C_2)_3(18-crown-6)_2][K(18-crown-6)(CH_3-C_2)_3(18-crown-6)_2][K(18-crown-6)(CH_3-C_2)_3(18-crown-6)_2][K(18-crown-6)(CH_3-C_2)_3(18-crown-6)_2][K(18-crown-6)(CH_3-C_2)_3(18-crown-6)_2][K(18-crown-6)(CH_3-C_2)_3(18-crown-6)_2][K(18-crown-6)(CH_3-C_2)_3(18-crown-6)_2][K(18-crown-6)(CH_3-C_2)_3(18-crown-6)_2][K(18-crown-6)(CH_3-C_2)_3(18-crown-6)_2][K(18-crown-6)(CH_3-C_2)_3(18-crown-6)_2][K(18-crown-6)(CH_3-C_2)_3(18-crown-6)_2][K(18-crown-6)(CH_3-C_2)_3(18-crown-6)_2][K(18-crown-6)(CH_3-C_2)_3(18-crown-6)_2(18-crown-6)$  $(CN)_2$  (5), and  $[\{\mu-1,2-[1,8-C_{10}H_6(CH_2)_2]-1,2-C_2B_{10}H_{10}\}_2Na_4(THF)_6]_n$  (8), respectively. In sharp contrast, reaction of **3** with excess Li or Na metal resulted in the complete cleavage of the cage carbon-carbon bond, giving  $[\{\mu-1,4-[1,1'-(C_6H_4)_2-2,2'-(CH_2)_2]-1,4-C_2B_{10}H_{10}\}M_2(THF)_3]_n$ (M = Li (10), Na (11)), in which the two cage carbon atoms are in *para* positions. Surprisingly, Li metal was able to reduce directly **1** and **2** to the 'carbons-adjacent' *arachno*-carborane species, forming  $[\{\mu-1,2-[o-C_6H_4(CH_2)_2]-1,2-C_2B_{10}H_{10}\}Li_4(THF)_6]_2$  (13) and  $[\{\mu-1,2-[1,8-C_{10}H_6-1],2-(1,8-C_{10}H_6-1)\}Li_4(THF)_6]_2$  $(CH_2)_2$ ]-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>}Li<sub>4</sub>(THF)<sub>6</sub>]<sub>2</sub> (17), respectively. These results showed that the bridge length controls the formation of 'carbons-adjacent' or 'carbons-apart' carborane anions, and the 'carbons-adjacent' carboranes are more reactive than the 'carbons-apart' isomers. All these carborane anions are very air- and moisture-sensitive. Oxygen oxidizes them back to the neutral o-carboranes. Hydrolysis converts both nido-carborane dianions and arachnocarborane tetraanions into the corresponding carborane monoanions by one- or three-proton uptake from water molecules. All complexes were fully characterized by various spectroscopic data and elemental analyses. Some were subjected to single-crystal X-ray analyses.

## Introduction

Recognition of the isolobal analogy between the cyclopentadienyl ( $C_5H_5^-$ ) and discribulide ion ( $C_2B_9H_{11}^{2-}$ ) initiates the field of metallacarborane chemistry.<sup>1</sup> Subsequently, a large number of s-, p-, d-, and f-block elements have been prepared and structurally characterized.<sup>2</sup> They are finding many applications in catalysis,<sup>3</sup> boron neutron capture therapy (BNCT),<sup>4</sup> siloxane-

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linked polymers,<sup>5</sup> solvent extraction of radionuclides,<sup>6</sup> and ceramics.7

The versatility of carborane ligands has aided the development of metallacarborane chemistry.<sup>2</sup> For example, o-carborane (o-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>) can be converted into  $nido-C_2B_9H_{11}^{2-,2}$   $nido-C_2B_{10}H_{12}^{2-,2}$   $arachno-C_2B_{10}-H_{12}^{2-,2}$   $H_{12}^{4-,2,8-10}$  and C-alkylated derivatives  $o-R_2C_2B_{10}H_{10}^{10-12}$ shown in Scheme 1. These anions can be bound to transition metal ions in  $\eta^{5}$ -,  $\eta^{6}$ -, and  $\eta^{7}$ -fashion or via B–H–M  $\sigma$ -bonding interactions, leading to a very rich chemistry.<sup>2</sup>

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Chart 1. *nido*-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub><sup>2</sup>- Isomers



Chart 2. *o*-Carboranes with Different Sizes of Inner Rings



It is well-established that the reduction of o-R<sub>2</sub>C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> always results in the complete cleavage of the cage carbon–carbon bond, leading to the formation of 7,9*nido*-R<sub>2</sub>C<sub>2</sub>B<sub>10</sub>H<sub>10</sub><sup>2–</sup> (**m** in Chart 1); neither 7,8-*nido*-R<sub>2</sub>C<sub>2</sub>B<sub>10</sub>H<sub>10</sub><sup>2–</sup> nor 7,10-*nido*-R<sub>2</sub>C<sub>2</sub>B<sub>10</sub>H<sub>10</sub><sup>2–</sup> is reported during the reductive process (**o** and **p** in Chart 1).<sup>2,13</sup> Theoretical calculations indicate that 7,9-*nido*-R<sub>2</sub>C<sub>2</sub>-B<sub>10</sub>H<sub>10</sub><sup>2–</sup> is the most stable species in solution.<sup>14</sup> The chemical and physical properties of carborane isomers are highly related to the arrangement of the cage carbon atoms, and the 'carbons-adjacent' isomer is generally more reactive and less stable than its 'carbons-apart' one.<sup>14</sup> Thus 'carbons-adjacent' carborane anions may lead to metallacarborane complexes with higher reactivities and thus are amenable to further chemistry.

To force the two cage carbon atoms of an *o*-carborane to remain adjacent in *ortho* positions during the reduction process, the most effective way is probably to introduce a short linkage between these two cage carbon atoms. With this in mind, the reduction of  $\mu$ -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>10</sub> (**1** in Chart 2) is examined, which leads to the isolation of the 'carbons-adjacent' carborane anions.<sup>15</sup> To understand better the relationships between the bridge length and the cage carbon–carbon bond cleavage and to explore the reactivity patterns of the resulting anions, we have extended our research to include compounds **2** and **3**, shown in Chart 2. We report

herein a detailed study on the synthesis, structural characterization, and reactivity of compounds 1-3 and their group 1 metal complexes. The similarities and differences among 1-3 are also discussed in this paper.

### **Experimental Section**

General Procedures. All experiments were performed under an atmosphere of dry dinitrogen with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. All organic solvents (except CH<sub>3</sub>-CN) were freshly distilled from sodium benzophenone ketyl immediately prior to use. CH<sub>3</sub>CN was freshly distilled from CaH<sub>2</sub> immediately prior to use. 1,8-C<sub>10</sub>H<sub>6</sub>(CH<sub>2</sub>Cl)<sub>2</sub> was prepared according to the literature method.<sup>16</sup> 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 reference to the residual protons of the deuterated solvents for proton and carbon chemical shifts and to external BF3. 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  $\mu$ -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>10</sub> (1). This compound was prepared using a modified literature method.<sup>17</sup> To a solution of *o*-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> (7.20 g, 50.0 mmol) in a dry toluene/Et<sub>2</sub>O (2:1, 50 mL) was added a 1.60 M solution of n-BuLi in n-hexane (62.5 mL, 100.0 mmol) dropwise 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 o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>Br)<sub>2</sub> (13.2 g, 50.0 mmol) in toluene/Et<sub>2</sub>O (2:1, 30 mL) was slowly added with stirring. The reaction mixture was refluxed 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 (50 mL  $\times$  3). 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 (15 mL  $\times$  3) and dried under vacuum to afford 1 as a white powder (11.7 g, 95%). Recrystallization from acetone yielded colorless crystals. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.28 (m, 2H, aryl *H*), 7.12 (m, 2H, aryl *H*), 3.75 (s, 4H, C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 129.1, 128.7, 127.6 (C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>), 71.2 (cage C), 37.6 (C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>). <sup>11</sup>B NMR (CDCl<sub>3</sub>):  $\delta$  -5.40 (2B), -9.61 (8B). IR (KBr, cm<sup>-1</sup>):  $\nu$  2959 (m), 2911 (w), 2591 (vs), 1489 (m), 1430 (s), 1384 (m), 1260 (s), 1093 (vs), 1025 (vs), 801 (s).

**Preparation of** *μ***-1,2-[1,8-C**<sub>10</sub>**H**<sub>6</sub>(**CH**<sub>2</sub>)<sub>2</sub>]**-**1,2-**C**<sub>2</sub>**B**<sub>10</sub>**H**<sub>10</sub> (2). This compound was prepared as a white solid from the reaction of *o*-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> (7.20 g, 50.0 mmol) with a 1.60 M solution of *n*-BuLi in *n*-hexane (62.5 mL, 100.0 mmol), followed by addition of 1,8-C<sub>10</sub>H<sub>6</sub>(CH<sub>2</sub>Cl)<sub>2</sub> (11.3 g, 50.0 mmol) in toluene/ Et<sub>2</sub>O (2:1, 60 mL) using procedures similar to those used in the synthesis of 1: yield 11.1 g (75%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): *δ* 7.80 (m, 2H, aryl *H*), 7.36 (m, 2H, aryl *H*), 7.22 (m, 2H, aryl *H*), 4.12 (s, 4H, ArC*H*<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): *δ* 135.7, 133.2, 132.9, 130.6, 129.6, 126.2 (aryl *C*), 75.4 (cage *C*), 44.5 (Ar *C*H<sub>2</sub>). <sup>11</sup>B NMR (CDCl<sub>3</sub>): *δ* -7.71 (3B), -13.81 (5B), -16.48 (2B). IR

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(KBr, cm<sup>-1</sup>):  $\nu$  3056 (w), 2955 (m), 2576 (vs), 1630 (s), 1447 (s), 1259 (m), 1087 (s), 1026 (s), 771 (s). Anal. Calcd for C<sub>14</sub>H<sub>20</sub>B<sub>10</sub>: C, 56.73; H, 6.80. Found: C, 56.68; H, 6.87.

Preparation of  $\mu$ -1,2-[1,1'-(C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>-2,2'-(CH<sub>2</sub>)<sub>2</sub>]-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (3). This compound was prepared as a white solid from the reaction of  $\textit{o-}C_2B_{10}H_{12}$  (7.20 g, 50.0 mmol) with a 1.60 M solution of n-BuLi in n-hexane (62.5 mL, 100.0 mmol), followed by addition of 1,1'-(C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>-2,2'-(CH<sub>2</sub>Br)<sub>2</sub> (17.0 g, 50.0 mmol) in toluene/Et<sub>2</sub>O (2:1, 60 mL) using procedures similar to those used in the synthesis of 1: yield 14.5 g (90%). Colorless crystals suitable for X-ray structural analysis were grown from an acetone solution at room temperature. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ 7.38–7.17 (m, 8H, aryl H), 3.41 (d, J = 15.0 Hz, 2H, ArCH<sub>2</sub>), 3.16 (d, J = 15.0 Hz, 2H, ArCH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  141.4, 134.0, 131.0, 128.8, 128.4 (aryl C), 75.2 (cage C), 40.9 (Ar CH<sub>2</sub>). <sup>11</sup>B NMR (CDCl<sub>3</sub>):  $\delta$  -6.95 (3B), -12.25 (5B), -14.63 (2B). IR (KBr, cm<sup>-1</sup>): v 2922 (m), 2565 (vs), 1636 (s), 1479 (m), 1437 (s), 1260 (m), 1097 (vs), 1024 (vs), 755 (vs). Anal. Calcd for C<sub>16</sub>H<sub>22</sub>B<sub>10</sub>: C, 59.60; H, 6.88. Found: C, 59.47; H, 6.60.

Preparation of  $[{\mu-1,2-[o-C_6H_4(CH_2)_2]-1,2-C_2B_{10}H_{10}}_2Na_4 (\text{THF})_6]_n$  (4). To a THF (25 mL) solution of  $\mu$ -1,2-[o-C<sub>6</sub>H<sub>4</sub>- $(CH_2)_2$ ]-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (1; 246 mg, 1.00 mmol) was added finely cut Na metal (210 mg, 9.13 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 (~10 mL) was added. 4 was isolated as colorless crystals after this solution stood at room temperature for 2 days (351 mg, 69%). <sup>1</sup>H NMR (pyridine- $d_5$ ):  $\delta$  7.11 (m, 2H, aryl H), 7.05 (m, 2H, aryl H), 4.06 (d, J = 15.6 Hz, 2H,  $C_6H_4(CH_2)_2$ , 3.93 (d, J = 15.6 Hz, 2H,  $C_6H_4(CH_2)_2$ ), 3.65 (m, 12H, THF), 1.61 (m, 12H, THF).  $^{13}$ C NMR (pyridine- $d_5$ ):  $\delta$ 140.1, 126.0, 125.7 (C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>), 48.3 (C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>), 67.5, 25.5 (THF); the cage carbon atoms were not observed. <sup>11</sup>B NMR (pyridine- $d_5$ ):  $\delta$  3.47 (2B), -2.89 (2B), -5.53 (1B), -11.25 (2B), -18.15 (1B), -21.87 (1B), -23.89 (1B). IR (KBr, cm<sup>-1</sup>): v 2955 (vs), 2869 (vs), 2513 (vs), 2430 (vs), 2365 (vs), 1584 (w), 1459 (s), 1364 (s), 1291 (s), 1046 (vs), 898 (s), 762 (s). Anal. Calcd for C44H84B20Na4O6: C, 51.95; H, 8.32. Found: C, 51.66; H, 8.11.

Preparation of  $[{\mu-1,2-[o-C_6H_4(CH_2)_2]-1,2-C_2B_{10}H_{10}}_2K_3-$ (18-crown-6)<sub>2</sub>][K(18-crown-6)(CH<sub>3</sub>CN)<sub>2</sub>] (5). To a THF (25 mL) solution of µ-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>10</sub> (1; 246 mg, 1.00 mmol) was added finely cut K metal (250 mg, 6.41 mmol), and the mixture was stirred at room temperature for a week. After removal of excess K, the clear orange solution was concentrated to about 10 mL, to which was added a CH<sub>3</sub>CN solution (10 mL) of 18-crown-6 ether (528 mg, 2.00 mmol). 5 was isolated as yellow crystals after this solution stood at room temperature for a week (564 mg, 74%). <sup>1</sup>H NMR (pyridine $d_5$ ):  $\delta$  7.22 (m, 2H, aryl H), 7.10 (m, 2H, aryl H), 4.29 (d, J = 15.0 Hz, 2H,  $C_6H_4(CH_2)_2$ ), 4.15 (d, J = 15.0 Hz, 2H,  $C_6H_4$ -(CH2)2), 3.47 (s, 36H, C12H24O6), 1.87 (s, 3H, CH3CN). 13C NMR (pyridine-d<sub>5</sub>): δ 141.3, 126.0, 124.7 (C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>), 117.6 (CH<sub>3</sub>CN), 69.5 ( $C_{12}H_{24}O_6$ ), 48.5 ( $C_6H_4(CH_2)_2$ ), 0.4 ( $CH_3CN$ ); the cage carbon atoms were not observed.  $^{11}\mathrm{B}$  NMR (pyridine-  $d_{5}\!):~\delta$  3.23 (2B), -3.25 (2B), -5.83 (1B), -11.59 (2B), -18.06 (1B), -22.28 (1B), -24.16 (1B). IR (KBr, cm<sup>-1</sup>): v 2950 (vs), 2901 (vs), 2456 (vs), 2398 (vs), 2351 (vs), 2165 (w), 1630 (w), 1459 (s), 1384 (s), 1256 (s), 1103 (vs), 1031 (vs), 961 (s), 803 (s). Anal. Calcd for C<sub>60</sub>H<sub>114</sub>B<sub>20</sub>K<sub>4</sub>N<sub>2</sub>O<sub>18</sub>: C, 47.28; H, 7.54; N, 1.84. Found: C, 46.92; H, 7.53; N, 1.94.

**Preparation of** [{ $\mu$ -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>) (6). To a THF (25 mL) solution of [({ $\mu$ -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>10</sub>}<sub>2</sub>K)(K(18-crown-6))<sub>2</sub>][K(18crown-6)(CH<sub>3</sub>CN)<sub>2</sub>] (5; 381 mg, 0.25 mmol) was added degassed H<sub>2</sub>O (2 mL), and the mixture was stirred at room temperature for 0.5 h. After removal of the solvent, the residue was extracted with acetone (10 mL × 2). The clear, colorless acetone solutions were combined and concentrated to about 5 mL. **6** was isolated as colorless crystals after this solution stood at room temperature for 2 days (230 mg, 82%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.06 (m, 4H, aryl *H*), 3.96 (d, J = 15.6 Hz, 2H, C<sub>6</sub>H<sub>4</sub>-(C*H*<sub>2</sub>)<sub>2</sub>), 3.88 (d, J = 15.6 Hz, 2H, C<sub>6</sub>H<sub>4</sub>(C*H*<sub>2</sub>)<sub>2</sub>), 3.59 (C<sub>12</sub>*H*<sub>24</sub>O<sub>6</sub>), 2.17 (s, 1H, *H*<sub>2</sub>O), 1.64 (s, 1H,  $\mu$ -*H*). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  137.8, 125.9, 125.5 (*C*<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>), 48.7 (C<sub>6</sub>H<sub>4</sub>(*C*H<sub>2</sub>)<sub>2</sub>), 70.1 (*C*<sub>12</sub>H<sub>24</sub>O<sub>6</sub>); the cage carbon atoms were not observed. <sup>11</sup>B NMR (CDCl<sub>3</sub>):  $\delta$  1.83 (2B), -4.51 (2B), -12.87 (2B), -19.45 (2B), -23.74 (1B), -25.36 (1B). IR (KBr, cm<sup>-1</sup>):  $\nu$  3541, (m), 3021 (w), 2900 (vs), 2516 (vs), 2453 (s), 2320 (m), 1628 (w), 1591 (w), 1465 (s), 1352 (s), 1247 (s), 1106 (vs), 1039 (s), 957 (s), 834 (s), 758 (s). Anal. Calcd for C<sub>44</sub>H<sub>88</sub>B<sub>20</sub>K<sub>2</sub>O<sub>13</sub>: C, 47.20; H, 7.92. Found: C, 47.44; H, 7.98.

Preparation of  $[{\mu-1,2-[o-C_6H_4(CH_2)_2]-1,2-C_2B_{10}H_{11}}-$ K(18-crown-6)], (7). To a THF (25 mL) solution of 5 (381 mg, 0.25 mmol) was added degassed H<sub>2</sub>O (2 mL), and the mixture was stirred at room temperature for 0.5 h. After removal of the solvent, the residue was extracted with hot acetone (10  $mL \times 2$ ). The clear colorless acetone solutions were combined and concentrated to about 4 mL. 7 was isolated as colorless crystals after this solution stood at room temperature for a week (237 mg, 86%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.10-6.96 (m, 4H, aryl H), 3.92 (d, J = 9.0 Hz, 1H, C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>), 3.68 (d, J = 9.0Hz, 1H,  $C_6H_4(CH_2)_2$ ), 3.60 (s, 24H,  $C_{12}H_{24}O_6$ ), 3.24 (d, J = 15.0Hz, 1H,  $C_6H_4(CH_2)_2$ ), 2.95 (d, J = 15.0 Hz, 1H,  $C_6H_4(CH_2)_2$ ), 1.70 (s, 1H,  $\mu$ -H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  138.6, 127.0, 125.6  $(C_6H_4(CH_2)_2)$ , 48.7, 39.2  $(C_6H_4(CH_2)_2)$ , 70.1  $(C_{12}H_{24}O_6)$ ; the cage carbon atoms were not observed. <sup>11</sup>B NMR (CDCl<sub>3</sub>):  $\delta$  -8.78 (1B), -13.06 (4B), -22.39 (3B), -37.01 (1B), -39.73 (1B). IR (KBr, cm<sup>-1</sup>): v 2898 (vs), 2824 (vs), 2525 (vs), 2460 (vs), 2379 (vs), 1470 (s), 1350 (s), 1246 (s), 1108 (vs), 1036 (s), 962 (s), 838 (s), 759 (s). Anal. Calcd for C44H86B20K2O12: C, 47.97; H, 7.87. Found: C, 47.82; H, 8.05.

**Isomerization of 6.** An NMR tube was charged with **6** (30 mg) and CDCl<sub>3</sub> (0.5 mL). The sample was maintained at 70 °C and monitored periodically by <sup>11</sup>B NMR. After 4 h the conversion to the thermodynamic isomer **7** was 65% complete. After 12 h the conversion to the thermodynamic isomer **7** was complete; no **6** was detected.

Preparation of  $[{\mu-1,2-[1,8-C_{10}H_6(CH_2)_2]-1,2-C_2B_{10}H_{10}}_2 Na_4(THF)_6]_n$  (8). To a THF (25 mL) solution of  $\mu$ -1,2-[1,8-C<sub>10</sub>H<sub>6</sub>(CH<sub>2</sub>)<sub>2</sub>]-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (**2**; 296 mg, 1.00 mmol) was added finely cut Na metal (180 mg, 7.83 mmol), and the mixture was stirred at room temperature for a week. After removal of excess Na, the clear brown solution was concentrated to about 10 mL, and toluene (~10 mL) was added. 8 was isolated as colorless microcrystals after this solution stood at room temperature for 2 days (291 mg, 52%). <sup>1</sup>H NMR (pyridine- $d_5$ ):  $\delta$  7.50 (d, J = 9.1 Hz, 2H, aryl H), 7.26 (m, 2H, aryl H), 6.94 (t, J = 7.5 Hz, 2H, aryl H), 4.86 (d, J = 13.5 Hz, 2H,  $C_{10}H_6(CH_2)_2$ ), 4.37 (d, J = 13.5 Hz, 2H,  $C_{10}H_6(CH_2)_2$ ), 3.65 (m, 12H, THF), 1.61 (m, 12H, THF). <sup>13</sup>C NMR (pyridine- $d_5$ ):  $\delta$  129.8, 129.0, 127.3, 126.7, 126.4, 126.1 ( $C_{10}H_6(CH_2)_2$ ), 54.1 ( $C_{10}H_6(CH_2)_2$ ), 68.2, 26.2 (THF); the cage carbon atoms were not observed. <sup>11</sup>B NMR (pyridine- $d_5$ ):  $\delta$  7.64 (3B), -2.19 (3B), -14.71 (2B), -20.01 (2B). IR (KBr, cm<sup>-1</sup>): v 2955 (vs), 2876 (vs), 2447 (vs), 2351 (m), 2316 (m), 1600 (w), 1452 (s), 1252 (s), 1013 (vs), 910 (m), 779 (s). Anal. Calcd for C<sub>52</sub>H<sub>88</sub>B<sub>20</sub>Na<sub>4</sub>O<sub>6</sub>: C, 55.89; H, 7.94. Found: C, 55.82; H, 8.13.

**Preparation of** { $\mu$ -1,2-[1,8-C<sub>10</sub>H<sub>6</sub>(CH<sub>2</sub>)<sub>2</sub>]-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>}-{**K(THF)(18-crown-6)**} (9). To a THF (25 mL) solution of [{ $\mu$ -1,2-[1,8-C<sub>10</sub>H<sub>6</sub>(CH<sub>2</sub>)<sub>2</sub>]-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>}<sub>2</sub>Na<sub>4</sub>(THF)<sub>6</sub>]<sub>*n*</sub> (8; 280 mg, 0.25 mmol) was added a THF (10 mL) solution of 18-crown-6 (132 mg, 0.50 mmol) and a degassed aqueous solution (2 mL) of KBr (600 mg, 5.0 mmol), and the mixture was stirred at room temperature for 0.5 h. After removal of the solvent, the residue was extracted with acetone (10 mL × 2). The clear, colorless acetone solutions were combined and concentrated to about 3 mL. **9** was isolated as colorless crystals after this solution stood at room temperature for 1 day (229 mg, 68%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.63 (d, J = 9.1 Hz, 2H, aryl *H*), 7.28 (m, 2H, aryl *H*), 7.12 (d, J = 6.6 Hz, 2H, aryl *H*), 4.07 (d, J = 16.8 Hz, 2H, C<sub>10</sub>H<sub>6</sub>(CH<sub>2</sub>)<sub>2</sub>), 3.80 (d, J = 16.8 Hz, 2H, C<sub>10</sub>H<sub>6</sub>(CH<sub>2</sub>)<sub>2</sub>),

3.74 (m, 4H, THF), 3.58 (s, 24H,  $C_{12}H_{24}O_6$ ), 1.85 (m, 4H, THF). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  127.3, 126.4, 126.0, 125.1 ( $C_{10}H_6(CH_2)_2$ ), 70.0 ( $C_{12}H_{24}O_6$ ), 43.9 ( $C_{10}H_6(CH_2)_2$ ), 67.9, 25.6 (THF); the cage carbon atoms were not observed. <sup>11</sup>B NMR (CDCl<sub>3</sub>):  $\delta$  6.26 (2B), -0.75 (2B), -2.46 (2B), -9.08 (2B), -19.06 (1B), -21.83 (1B). IR (KBr, cm<sup>-1</sup>):  $\nu$  2900 (vs), 2519 (vs), 2456 (s), 2320 (m), 1636 (s), 1596 (s), 1455 (w), 1421 (w), 1106 (vs), 959 (s). Anal. Calcd for  $C_{30}H_{53}B_{10}KO_7$ : C, 53.55; H, 7.94. Found: C, 53.63; H, 7.80.

**Isomerization of 9.** An NMR tube was charged with **9** (30 mg) and CDCl<sub>3</sub> (0.5 mL). The sample was maintained at 40 °C and monitored periodically by <sup>11</sup>B NMR. After 14 h the conversion to the thermodynamic isomer was 35% complete. After 48 h the conversion to the thermodynamic isomer was complete; no **9** was detected. <sup>11</sup>B NMR (CDCl<sub>3</sub>): 20.16 (1B), 12.13 (1B), -3.56 (1B), -6.86 (1B), -10.69 (1B), -24.72 (1B), -25.51 (2B), -30.87 (1B), -33.40 (1B).

Preparation of  $[{\mu-1,4-[1,1'-(C_6H_4)_2-2,2'-(CH_2)_2]-1,4-C_2-}$ B10H10}Li2(THF)3]n (10). To a THF (20 mL) solution of 3 (322 mg, 1.00 mmol) was added finely cut Li metal (100 mg, 14.3 mmol), and the mixture was stirred at room temperature for a week. After removal of excess Li, the clear colorless solution was concentrated to about 10 mL, and toluene (~10 mL) was added. 10 was isolated as colorless crystals after this solution stood at room temperature for 2 days (420 mg, 76%). <sup>1</sup>H NMR (pyridine- $d_5$ ):  $\delta$  7.56 (m, 4H, aryl H), 7.24 (m, 4H, aryl H), 4.75 (d, J = 11.4 Hz, 2H, ArCH<sub>2</sub>), 3.71 (d, J = 11.4 Hz, 2H, ArCH<sub>2</sub>), 3.66 (m, 12H, THF), 1.61 (m, 12H, THF). <sup>13</sup>C NMR (pyridine- $d_5$ ):  $\delta$  147.7, 144.8, 131.0, 130.3, 129.8, 129.0 (aryl C), 103.8 (cage C), 46.2 (ArCH<sub>2</sub>), 68.2, 26.2 (THF). <sup>11</sup>B NMR (pyridine- $d_5$ ):  $\delta - 9.92$  (3B), -17.25 (2B), -22.20 (2B), -27.16(3B). IR (KBr, cm<sup>-1</sup>): v 2926 (vs), 2885 (vs), 2829 (s), 2467 (vs), 2355 (vs), 2322 (s), 1632 (w), 1454 (m), 1217 (m), 1053 (vs), 796 (m). Anal. Calcd for C<sub>28</sub>H<sub>46</sub>B<sub>10</sub>Li<sub>2</sub>O<sub>3</sub>: C, 60.85; H, 8.39. Found: C, 60.81; H, 7.90.

Preparation of [{µ-1,4-[1,1'-(C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>-2,2'-(CH<sub>2</sub>)<sub>2</sub>]-1,4-C<sub>2</sub>.  $B_{10}H_{10}$   $Na_2(THF)_3 \cdot THF]_n$  (11 · THF). This compound was prepared as colorless crystals from the reaction of  $\mu$ -1,2-[1,1'- $(C_6H_4)_2$ -2,2'- $(CH_2)_2$ ]-1,2- $C_2B_{10}H_{10}$  (3; 322 mg, 1.00 mmol) and Na metal (210 mg, 9.13 mmol) in THF (25 mL) using procedures similar to those used in the synthesis of 10: yield 427 mg (65%). <sup>1</sup>H NMR (pyridine- $d_5$ ):  $\delta$  7.55 (m, 4H, aryl H), 7.22 (m, 4H, aryl H), 4.74 (d, J = 11.4 Hz, 2H, ArCH<sub>2</sub>), 3.70 (d, J = 11.4 Hz, 2H, ArCH<sub>2</sub>), 3.65 (m, 16H, THF), 1.61 (m, 16H, THF). <sup>13</sup>C NMR (pyridine- $d_5$ ):  $\delta$  147.6, 144.8, 130.9, 130.2, 129.8, 129.0 (aryl C), 103.7 (cage C), 46.2 (Ar CH<sub>2</sub>), 68.2, 26.2 (THF). <sup>11</sup>B NMR (pyridine- $d_5$ ):  $\delta$  -11.57 (3B), -18.97 (2B), -23.59 (2B), -28.81 (3B). IR (KBr, cm<sup>-1</sup>): v 2934 (s), 2583 (vs), 2428 (m), 2322 (m), 1655 (m), 1447 (s), 1252 (m), 1029 (vs), 778 (vs). Anal. Calcd for C<sub>32</sub>H<sub>54</sub>B<sub>10</sub>Na<sub>2</sub>O<sub>4</sub>: C, 58.51; H, 8.29. Found: C, 59.01; H, 8.14.

Preparation of  $\{\mu - 1, 4 - [1, 1' - (C_6H_4)_2 - 2, 2' - (CH_2)_2] - 1, 4 - C_2 - C_3 - C_4 -$ **B**<sub>10</sub>**H**<sub>11</sub>}{**Na(THF)**<sub>3</sub>} (12). To a THF (25 mL) solution of 11 (289 mg, 0.50 mmol) was added degassed  $H_2O$  (~0.5 mL), and the mixture was stirred at room temperature for 0.5 h. The clear, colorless solution was then concentrated to about 4 mL. 12 was isolated as microcrystals after this solution stood at room temperature for a week (236 mg, 84%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.49–7.21 (m, 8H, aryl *H*), 3.74 (m, 12H, THF), 3.45 (d, J = 15.0 Hz, 2H, ArC $H_2$ ), 3.20 (d, J = 15.0 Hz, 2H, ArCH<sub>2</sub>), 1.86 (m, 12H, THF). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 141.2, 133.7, 130.8, 128.8, 128.5, 128.2 (aryl C), 74.9 (cage C), 40.7 (ArCH<sub>2</sub>), 67.7, 25.4 (THF). <sup>11</sup>B NMR (CDCl<sub>3</sub>): δ -6.81 (2B), -12.28 (5B), -14.55 (3B). IR (KBr, cm<sup>-1</sup>): v 2965 (vs), 2873 (vs), 2566 (vs), 2441 (s), 1439 (vs), 1053 (vs), 905 (s), 745 (vs). Anal. Calcd for C<sub>16</sub>H<sub>23</sub>B<sub>10</sub>Na (**12** – 3THF): C, 55.47; H, 6.69. Found: C, 55.14; H, 6.98.

**Isomerization of 12.** An NMR tube was charged with **11** (35 mg) and CDCl<sub>3</sub> (0.5 mL), to which was added one drop of degassed H<sub>2</sub>O at room temperature. The sample was periodically monitored by <sup>11</sup>B NMR. <sup>11</sup>B NMR (CDCl<sub>3</sub>, 20 °C):  $\delta$  –6.81

(2B), -12.28 (5B), -14.55 (3B). This spectrum did not show any changes even after refluxing for 3 days.

Preparation of [{µ-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>10</sub>}Li<sub>4</sub>-(THF)<sub>6</sub>]<sub>2</sub> (13). To a THF (25 mL) solution of  $\mu$ -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>10</sub> (1; 246 mg, 1.00 mmol) was added finely cut Li metal (110 mg, 15.8 mmol), and the mixture was stirred at room temperature for a week. Excess Li metal was removed by hot filtration. The resulting solution was cooled to room temperature, giving 13 as orange crystals (537 mg, 76%). <sup>1</sup>H NMR (pyridine- $d_5$ ):  $\delta$  7.17 (m, 2H, aryl H), 7.11 (m, 2H, aryl H), 4.13 (d, J = 15.3 Hz, 2H, C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>), 3.94 (d, J = 15.3Hz, 2H, C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>), 3.65 (m, 24H, THF), 1.62 (m, 24H, THF). <sup>13</sup>C NMR (pyridine- $d_5$ ):  $\delta$  140.0, 126.2, 125.4 ( $C_6H_4(CH_2)_2$ ), 48.8  $(C_6H_4(CH_2)_2)$ , 67.6, 25.5 (THF); the cage carbon atoms were not observed. <sup>11</sup>B NMR (pyridine- $d_5$ ):  $\delta$  7.87 (2B), 5.99 (2B), -3.08 (2B), -13.44 (1B), -18.99 (3B). IR (KBr, cm<sup>-1</sup>): v 2958 (s), 2908 (s), 2507 (s), 2395 (s), 2310 (s), 1456 (s), 1094 (vs), 1033 (vs), 797 (s). Anal. Calcd for C34H64B20Li8O3.5 (13 -8.5THF): C, 51.01; H, 8.06. Found: C, 50.70; H, 8.23.

**Preparation of**  $[\{\mu$ -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>10</sub> $\}$ Li<sub>4</sub>-(THF)<sub>4</sub>(DME)]<sub>2</sub> (14). Recrystallization of 13 from a THF/DME solution gave 14 as orange crystals. <sup>1</sup>H NMR (pyridine- $d_5$ ):  $\delta$  7.17 (m, 2H, aryl *H*), 7.11 (m, 2H, aryl *H*), 4.15 (d, J = 15.3 Hz, 2H, C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>), 3.95 (d, J = 15.3 Hz, 2H, C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>), 3.65 (m, 16H, THF), 3.51 (s, 4H, DME), 3.28 (s, 6H, DME), 1.62 (m, 16H, THF). <sup>13</sup>C NMR (pyridine- $d_5$ ):  $\delta$  140.6, 126.8, 126.1 ( $C_6$ H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>), 49.4 (C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>), 72.4, 59.0 (DME), 68.2, 26.2 (THF); the cage carbon atoms were not observed. <sup>11</sup>B NMR (pyridine- $d_5$ ):  $\delta$  7.42 (2B), 5.64 (2B), -3.39 (2B), -13.78 (1B), -19.12 (3B). IR (KBr, cm<sup>-1</sup>):  $\nu$  2959 (s), 2916 (s), 2512 (m), 2402 (s), 2312 (s), 1618 (m), 1454 (s), 1384 (s), 1259 (s), 1089 (vs), 1033 (vs), 802 (s). Anal. Calcd for C<sub>52</sub>H<sub>104</sub>B<sub>20</sub>Li<sub>8</sub>O<sub>10</sub> (14 – 2THF): C, 53.79; H, 9.03. Found: C, 53.53; H, 9.32.

**Preparation of [{CH<sub>3</sub>C(NH)CHCN}Li(THF)]**<sub>*n*</sub> (15). Recrystallization of 13 from CH<sub>3</sub>CN at room temperature resulted in the isolation of a small amount of colorless crystals identified as 15. <sup>1</sup>H NMR (pyridine-*d*<sub>5</sub>): δ 6.16 (br, 1H, N*H*), 3.65 (m, 4H, THF), 3.46 (s, 1H, *CH*), 1.99 (s, 3H, *CH*<sub>3</sub>), 1.62 (m, 4H, THF). <sup>13</sup>C NMR (pyridine-*d*<sub>5</sub>): δ 177.4 (*C*(NH)CHCN), 135.1, 133.1 (C(NH)*C*H*C*N), 47.0 (*C*H<sub>3</sub>), 69.3, 27.3 (THF). IR (KBr, cm<sup>-1</sup>): ν 3046 (w), 2950 (s), 2918 (s), 2877 (s), 2185 (s), 1638 (s), 1594 (s), 1521 (s), 1423 (s), 1309 (w), 1045 (s), 911 (m), 803 (m). Anal. Calcd for C<sub>7</sub>H<sub>11</sub>LiN<sub>2</sub>O<sub>0.75</sub> (15 – 0.25THF): C, 59.15; H, 7.80; N, 19.72. Found: C, 58.90; H, 7.99; N, 19.91.

Preparation of {µ-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>13</sub>}{K(18crown-6)(THF)}·THF (16·THF). To a THF (25 mL) solution of 13 (706 mg, 0.50 mmol) was added a degassed H<sub>2</sub>O (2 mL) solution of KBr (600 mg, 5.00 mmol) and a THF (10 mL) solution of 18-crown-6 ether (528 mg, 2.00 mmol). The mixture was refluxed overnight. After removal of the solvent, the residue was washed with degassed  $H_2O$  (10 mL  $\times$  3) and dried under vacuum to give a white solid. This solid was then extracted with THF (10 mL  $\times$  2). The colorless THF solutions were combined and concentrated to about 3 mL. 16. THF was isolated as colorless crystals after this solution stood at room temperature for two weeks (523 mg, 75%). <sup>1</sup>H NMR (pyridine $d_5$ ):  $\delta$  7.02–6.94 (m, 4H, aryl *H*), 3.73 (s, 4H, C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>), 3.65 (m, 8H, THF), 3.55 (s, 24H, C<sub>12</sub>H<sub>24</sub>O<sub>6</sub>), 1.78 (m, 8H, THF). <sup>13</sup>C NMR (pyridine-d<sub>5</sub>):  $\delta$  139.7, 128.0, 126.7 (C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>), 40.7  $(C_6H_4(CH_2)_2)$ , 70.7  $(C_{12}H_{24}O_6)$ , 68.2, 26.2 (THF); the cage carbon atoms were not observed. <sup>11</sup>B{<sup>1</sup>H} NMR (pyridine- $d_5$ ):  $\delta$ -10.30 (3B), -11.64 (1B), -19.82 (2B), -20.74 (2B), -34.72 (1B), -37.15 (1B). <sup>11</sup>B NMR (pyridine- $d_5$ ):  $\delta$  -10.29 (d, B7,9,-12,  $J_{\rm BH} =$  136 Hz), -11.53 (d, B8,  $J_{\rm BH} =$  182 Hz), -19.77 (d, B4,10,  $J_{BH} = 125$  Hz), -20.79 (d, B3,11,  $J_{BH} = 136$  Hz), -34.71(dd, B5,  $J_{BH} = 125$  Hz,  $J_{(BH)H} = 43$  Hz), -37.14 (d, B6,  $J_{BH} =$ 137 Hz). <sup>11</sup>B-<sup>11</sup>B 2D-COSY NMR (pyridine-d<sub>5</sub>) cross-peaks: B3,11-B4,10; B3,11-B6; B3,11-B7,9,12; B4,10-B5; B4,10-B7,9,-12; B5-B7,9,12; B6-B8; B6-B7,9,12; B7,9,12-B8. IR (KBr, cm<sup>-1</sup>): v 2900 (vs), 2514 (vs), 2456 (s), 2317 (m), 1459 (s), 1352

Table 1. Crystal Data and Summary of Data Collection and Refinement for 1 and 3-5

	1	3	4	5
formula	$C_{10}H_{18}B_{10}$	$C_{16}H_{22}B_{10}$	$C_{22}H_{42}B_{10}Na_2O_3$	$C_{60}H_{114}B_{20}K_4N_2O_{18}$
cryst size (mm)	0.56 imes 0.32 imes 0.30	0.70 imes 0.53 imes 0.32	0.68  imes 0.54  imes 0.47	0.98  imes 0.64  imes 0.20
fw	246.3	322.4	508.6	1524.1
cryst syst	monoclinic	orthorhombic	triclinic	triclinic
space group	$P2_1/c$	Pccn	$P\overline{1}$	$P\overline{1}$
a, Å	7.235(1)	6.680(1)	11.767(2)	11.645(1)
b, Å	20.900(3)	12.698(3)	11.782(2)	12.209(1)
<i>c</i> , Å	9.337(1)	21.689(4)	12.420(2)	16.194(1)
α, deg	90	90	103.81(1)	97.77(1)
$\beta$ , deg	90.89(1)	90	90.04(1)	103.46(1)
γ, deg	90	90	116.46(1)	104.23(1)
$V, Å^3$	1411.7(3)	1839.7(6)	1485.6(4)	2124.7(2)
Ζ	4	4	2	1
$D_{\text{calcd}}$ , Mg/m <sup>3</sup>	1.159	1.164	1.137	1.197
radiation ( $\lambda$ ), Å	Μο Κα (0.71073)	Μο Κα (0.71073)	Μο Κα (0.71073)	Μο Κα (0.71073)
$2\theta$ range, deg	3.9 to 52.0	4.9 to 50.0	3.4 to 50.0	3.9 to 50.0
$\mu$ , mm <sup>-1</sup>	0.054	0.057	0.091	0.269
F(000)	512	672	540	808
no. of obsd reflns	2773	1613	5207	7439
no. of params refnd	221	119	407	509
goodness of fit	1.052	1.022	0.949	0.858
$R_1$	0.057	0.066	0.068	0.060
$wR_2$	0.140	0.194	0.168	0.158

(s), 1253 (s), 1106 (vs), 960 (s), 800 (s). Anal. Calcd for  $C_{30}H_{61}B_{10}KO_8$ : C, 51.69; H, 8.82. Found: C, 51.24; H, 8.55.

**Isomerization of 16.** An NMR tube was charged with **13** (35 mg) and pyridine- $d_5$  (0.5 mL), to which was added one drop of degassed H<sub>2</sub>O. The color of the solution immediately changed from orange to colorless. <sup>11</sup>B NMR (pyridine- $d_5$ ):  $\delta$  3.85 (2B), -2.31 (2B), -10.96 (2B), -18.03 (2B), -21.45 (1B), -23.38 (1B). The sample was maintained at 50 °C and monitored periodically by <sup>11</sup>B NMR. After 12 h the conversion to the thermodynamic isomer was 35% complete. After 36 h the conversion to the thermodynamic isomer was complete. <sup>11</sup>B NMR (pyridine- $d_5$ ):  $\delta$  -10.30 (3B), -11.64 (1B), -19.82 (2B), -20.74 (2B), -34.722 (1B), -37.15 (1B).

Preparation of [{µ-1,2-[1,8-C<sub>10</sub>H<sub>6</sub>(CH<sub>2</sub>)<sub>2</sub>]-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>}-Li<sub>4</sub>(THF)<sub>6</sub>]<sub>2</sub> (17). To a THF (25 mL) solution of µ-1,2-[1,8-C10H6(CH2)2]-1,2-C2B10H10 (2; 296 mg, 1.00 mmol) was added finely cut Li metal (100 mg, 14.3 mmol), and the mixture was stirred at room temperature for a week. After removal of excess Li, the clear, dark red solution was concentrated to about 10 mL, and toluene (~10 mL) was added. 17 was isolated as orange-red microcrystals after this solution stood at room temperature for 2 days (341 mg, 45%). <sup>1</sup>H NMR (pyridine- $d_5$ ):  $\delta$  7.46 (d, J = 9.1 Hz, 2H, aryl H), 7.19 (m, 2H, aryl H), 6.91 (t, J = 6.9 Hz, 2H, aryl *H*), 4.88 (d, J = 13.5 Hz, 2H, C<sub>10</sub>H<sub>6</sub>- $(CH_2)_2$ , 4.38 (d, J = 13.5 Hz, 2H,  $C_{10}H_6(CH_2)_2$ ), 3.65 (m, 24H, THF), 1.61 (m, 24H, THF). <sup>13</sup>C NMR (pyridine- $d_5$ ):  $\delta$  129.8, 129.0, 127.2, 126.7, 126.3, 126.1 (C10H6(CH2)2), 54.1 (C10H6- $(CH_2)_2$ ), 68.2, 26.2 (THF); the cage carbon atoms were not observed. <sup>11</sup>B NMR (pyridine- $d_5$ ):  $\delta$  -7.92 (2B), -13.60 (3B), -25.23 (2B), -28.17 (3B). IR (KBr, cm<sup>-1</sup>): v 2959 (vs), 2915 (s), 2512 (vs), 2399 (s), 2347 (s), 2314 (s), 1614 (w), 1454 (s), 1259 (s), 1091 (vs), 1028 (vs), 801 (vs). Anal. Calcd for C<sub>52</sub>H<sub>88</sub>B<sub>20</sub>Li<sub>8</sub>O<sub>6</sub> (17 - 6THF): C, 57.78; H, 8.21. Found: C, 57.94; H, 8.34.

**Protonation of 17.** An NMR tube was charged with **17** (38 mg) and CDCl<sub>3</sub> (0.5 mL), to which was added one drop of degassed H<sub>2</sub>O. The color of the solution immediately changed from orange to colorless. <sup>11</sup>B NMR (CDCl<sub>3</sub>):  $\delta$  6.55 (2B), 1.75 (1B), -0.38 (2B), -8.73 (2B), -15.86 (1B), -18.67 (1B), -21.49 (1B). The sample was maintained at 40 °C and monitored periodically by <sup>11</sup>B NMR. After 12 h the conversion to the thermodynamic isomer was 45% complete. After 48 h the conversion to the thermodynamic isomer was complete. <sup>11</sup>B NMR (CDCl<sub>3</sub>):  $\delta$  0.91 (2B), -10.37 (2B), -18.72 (2B), -26.18 (1B), -31.54 (1B), -34.96 (1B), -37.58 (1B).

X-ray Structure Determination. All single crystals were immersed in Paraton-N oil and sealed under  $N_2$  in thin-walled

glass capillaries. Data were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo Ka radiation. An empirical absorption correction was applied using the SADABS program.<sup>18</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>19</sup> Most of the carborane hydrogen atoms were located from difference Fourier syntheses. All other hydrogen atoms were geometrically fixed using the riding model. For the noncentrosymmetric structure, the appropriate enantiomorph was chosen by refining Flack's parameter x toward zero.<sup>20</sup> Crystal data and details of data collection and structure refinements are given in Tables 1-3. Key structural data are listed in Table 4. Further details are included in the Supporting Information.

## **Results and Discussion**

**Neutral** *o*-Carboranes.  $\mu$ -1,2-[*o*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>]-1,2- $C_2B_{10}H_{10}$  (1) was prepared using a slightly modified literature method<sup>17</sup> from  $Li_2C_2B_{10}H_{10}$  and  $1,2-C_6H_4(CH_2-$ Br)<sub>2</sub> in toluene/Et<sub>2</sub>O (2:1, v/v).  $\mu$ -1,2-[1,8-C<sub>10</sub>H<sub>6</sub>(CH<sub>2</sub>)<sub>2</sub>]- $1,2-C_2B_{10}H_{10}$  (2) and  $\mu$ -1,2-[1,1'-(C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>-2,2'-(CH<sub>2</sub>)<sub>2</sub>]-1,2- $C_2B_{10}H_{10}$  (3) were prepared in a similar manner, shown in Scheme 2. They are air-stable and guite soluble in polar organic solvents such as THF, DME, and ether and slightly soluble in n-hexane. Recrystallization from hot acetone often gave nice colorless crystals. 1-3 were characterized by various spectroscopic data and elemental analyses. The solid-state structures of 1 and 3 were further confirmed by single-crystal X-ray analyses. The <sup>1</sup>H NMR spectra show that the two methylene protons in both 1 and 2 are equivalent, while those of 3 are nonequivalent with the coupling constant J = 15.0 Hz. The <sup>13</sup>C NMR spectra are consistent with the results derived from their <sup>1</sup>H NMR spectra. The <sup>11</sup>B NMR spectrum of **1** exhibits a 2:8 splitting pattern, while

<sup>(18)</sup> Sheldrick, G. M. *SADABS*, Program for Empirical Absorption Correction of Area Detector Data; University of Göttingen: Germany, 1996.

<sup>(19)</sup> Sheldrick, G. M. *SHELXTL*, 5.10 for Windows NT: Structure Determination Software Programs; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1997.

<sup>(20)</sup> Flack, H. D. Acta Crystallogr. 1983, A39, 876.

Table 2. Crystal Data and Summary of Data Collection and Refinement for 6, 7, 9, and 11 THF

	6 7		9	11.THF
formula	$C_{44}H_{88}B_{20}K_2O_{13}$	$C_{22}H_{43}B_{10}KO_6$	C <sub>30</sub> H <sub>53</sub> B <sub>10</sub> KO <sub>7</sub>	$C_{32}H_{54}B_{10}Na_2O_4$
cryst size (mm)	0.55 imes 0.40 imes 0.22	$0.87\times0.65\times0.51$	$0.57 \times 0.47 \times 0.10$	0.72 imes 0.32 imes 0.28
fw	1119.5	550.8	672.9	656.8
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$	$P2_1/n$	$P2_{1}/c$	$Pca2_1$
a, Å	13.253(3)	8.953(1)	12.962(1)	25.203(2)
b, Å	11.361(2)	18.667(2)	19.384(1)	13.921(1)
<i>c</i> , Å	21.675(4)	18.642(2)	15.698(2)	11.469(1)
$\beta$ , deg	106.01(3)	101.12(1)	105.07	90
V, Å <sup>3</sup>	3136(1)	3056.9(6)	3808.7(4)	4023.8(4)
Ζ	2	4	4	4
$D_{\text{calcd}}$ , Mg/m <sup>3</sup>	1.185	1.197	1.174	1.084
radiation $(\lambda)$ , Å	Μο Κα (0.71073)	Μο Κα (0.71073)	Μο Κα (0.71073)	Μο Κα (0.71073)
$2\theta$ range, deg	4.1 to 50.0	3.1 to 50.0	3.3 to 50.0	3.2 to 50.0
$\mu$ , mm <sup>-1</sup>	0.205	0.208	0.181	0.082
F(000)	1188	1168	1432	1400
no. of obsd reflns	5503	4787	6708	5180
no. of params refnd	403	387	613	435
goodness of fit	1.007	1.039	0.961	0.930
$\tilde{R}_1$	0.079	0.063	0.059	0.070
$wR_2$	0.208	0.171	0.137	0.173

Table 3. Crystal Data and Summary of Data Collection and Refinement for 13-15 and 16 THF

	13	14	15	<b>16</b> •THF
formula	$C_{34}H_{66}B_{10}Li_4O_6$	$C_{30}H_{60}B_{10}Li_4O_6$	C <sub>8</sub> H <sub>13</sub> LiN <sub>2</sub> O	$C_{30}H_{61}B_{10}KO_8$
cryst size (mm)	0.42 imes 0.34 imes 0.32	0.44 imes 0.42 imes 0.38	0.56 imes 0.50 imes 0.48	0.53 imes 0.45 imes 0.42
fw	706.7	652.6	160.1	697.0
cryst syst	triclinic	triclinic	monoclinic	orthorhombic
space group	$P\overline{1}$	$P\overline{1}$ $P\overline{1}$ $P2_1/c$		$Pna2_1$
a, Å	11.922(8)	14.429(3) 8.900(3)		26.977(2)
<i>b</i> , Å	12.742(8)	12.784(3)	9.559(3)	12.829(1)
c, Å	14.538(10)	14.486(4)	11.956(4)	11.663(1)
α, deg	88.42(2)	69.77(1)	90	90
$\beta$ , deg	89.10(2)	79.78(1)	104.45(1)	90
$\gamma$ , deg	86.10(2)	86.33(1)	90	90
V, Å <sup>3</sup>	2202(2)	1954.4(8)	985.0(5)	4036.5(5)
Ζ	2	2	4	4
$D_{\text{calcd}}, \text{Mg/m}^3$	1.066	1.109	1.080	1.147
radiation (λ), Å	Μο Κα (0.71073)	Μο Κα (0.71073)	Μο Κα (0.71073)	Μο Κα (0.71073)
$2\theta$ range, deg	3.2 to 50.0	3.0 to 50.0	4.7 to 50.0	3.0 to 50.0
$\mu$ , mm <sup>-1</sup>	0.064	0.067	0.071	0.174
F(000)	760	700	344	1496
no. of obsd reflns	5248	6105	1291	4857
no. of params refnd	527	491	117	442
goodness of fit	0.943	0.959	1.152	0.920
$\overline{R}_1$	0.086	0.077	0.079	0.075
$wR_2$	0.242	0.202	0.247	0.192

Table 4. Selected Structural Data for *o*-Carboranes and Their Metal Complexes

	$C_{cage} - C_{cage}$	av M-C <sub>cage</sub>	av M-B <sub>cage</sub>	av M-C <sub>2</sub> B <sub>4</sub>	av M····B <sub>3</sub>	av C <sub>cage</sub> -C-C <sub>aryl</sub>
1	1.646(3)					115.6(2)
3	1.667(5)					117.8(3)
<b>4</b> (M = Na)	1.444(4)	2.876(4)	2.844(4)	2.854(4)	3.026(4)	114.8(3)
<b>5</b> (M = K)	1.437(4)	2.969(3)	3.112(4)	3.064(4)	3.425(5)	113.8(3)
<b>6</b> (M = K)	1.445(3)				3.440(3)	113.4(2)
7 (M = K)	1.512(2)				3.822(2)	112.6(2)
<b>9</b> (M = K)	1.441(5)				3.618(5)	112.0(3)
<b>11</b> (M = Na)					3.031(3)	109.7(2)
<b>13</b> ( $M = Li$ )	1.562(6)	2.297(8)	2.325(9)	2.315(9)	2.654(10)	111.0(4)
14 (M = Li)	1.564(3)	2.280(5)	2.310(5)	2.300(5)	2.651(6)	112.4(2)
<b>16</b> $(M = K)$	1.432(4)				3.788(4)	114.6(3)

those of **2** and **3** show a similar 3:5:2 splitting pattern. The IR spectra all display a typical strong and broad characteristic B–H absorption at about 2570 cm<sup>-1</sup>.

eight-membered ring (C1AC3AC4AC9AC9C4C3C1) in **3** is highly twisted and the dihedral angle between the two aromatic rings is 66.1°.

The molecular structures of **1** and **3** are shown in Figures 1 and 2, respectively. As indicated in Table 4, the cage C–C distance and  $C_{cage}$ –C– $C_{aryl}$  angle in **3** are slightly larger than those observed in **1**. As expected, the inner six-membered ring (C1C2C10C9C4C3) in **1** is not planar with C3 and C10 being ca. 0.17 Å above the least-squares plane. In sharp contrast, the inner

Compounds 1-3 bear a six-, seven-, and eightmembered inner ring constructed by the cage and the aromatic moiety, respectively, which enables us to investigate the relationships between the bridge length and the cage C-C bond cleavage during reductive processes.

Dianionic Salts. Treatment of 1 with excess finely



**Figure 1.** Molecular structure of  $\mu$ -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>10</sub> (1).



**Figure 2.** Molecular structure of  $\mu$ -1,2-[1,1'-(C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>-2,2'-(CH<sub>2</sub>)<sub>2</sub>]-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (**3**).

Scheme 2



cut Na or K metal in THF at room temperature gave a half-sandwich complex  $[\{\mu-1,2-[o-C_6H_4(CH_2)_2]-1,2-C_2-B_{10}H_{10}\}_2Na_4(THF)_6]_n$  (4) in 68% isolated yield after recrystallization from a THF/toluene solution, or a full-sandwich complex  $[\{\mu-1,2-[o-C_6H_4(CH_2)_2]-1,2-C_2B_{10}H_{10}\}_2-K_3(18-crown-6)_2][K(18-crown-6)(CH_3CN)_2]$  (5) in 74% yield after recrystallization from a THF/CH\_3CN solution of 18-crown-6 ether, respectively (Scheme 3). Reaction of 18-crown-6 ether, respectively (Scheme 3). Reaction of 2 with excess finely cut Na metal in THF at room temperature afforded  $[\{\mu-1,2-[1,8-C_{10}H_6(CH_2)_2]-1,2-C_2B_{10}H_{10}\}_2Na_4(THF)_6]_n$  (8) in 52% yield (Scheme 4). Interaction of 3 with excess finely cut Li or Na metal in THF at room temperature generated  $[\{\mu-1,4-[1,1'-(C_6H_4)_2-2,2'-(CH_2)_2]-1,4-C_2B_{10}H_{10}\}_M_2(THF)_3]_n$  (M = Li (10), Na (11)) in good yields (Scheme 5).

These compounds are extremely air- and moisturesensitive, but remain stable for months at room tem-



perature under an inert atmosphere. They are quite soluble in polar organic solvents such as THF,  $CH_3CN$ , and pyridine, sparely soluble in toluene, and insoluble in *n*-hexane.

The <sup>1</sup>H NMR spectra indicate that the two methylene protons in all complexes are nonequivalent and support the ratio of three THF molecules per carboranyl ligand for **4**, **8**, **10**, and **11** and one CH<sub>3</sub>CN and 1.5 18-crown-6 ether molecules per carboranyl ligand for **5**, respectively. The <sup>13</sup>C NMR spectra are in line with the results derived from their <sup>1</sup>H NMR spectra. The <sup>11</sup>B NMR spectra exhibit a 2:2:1:2:1:1:1 splitting pattern for **4** and **5**, a 3:3:2:2 splitting pattern for **8**, and a 3:2:2:3 splitting pattern for **10** and **11**, respectively. Their solid-state IR spectra all display a characteristic doublet centered around 2450 cm<sup>-1</sup> and a shoulder at about 2360 cm<sup>-1</sup> attributable to a M–H–B stretching mode.<sup>9,10</sup>

The solid-state structures of **4**, **5**, and **11** were confirmed by single-crystal X-ray analyses. **4** adopts a polymeric structure in which the sodium and 'carbonsadjacent' *nido*-carborane serve as alternating bridging groups to give a zigzag metallacarborane-Na-metallacarborane-Na chain that is maintained in one dimension throughout the lattice. Each asymmetric unit consists of two [{ $\mu$ -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>10</sub>}Na<sub>2</sub>(THF)<sub>3</sub>] structural motifs that are related to each other by an inversion center (Figure 3). One sodium is  $\eta^6$ -bound to the open six-membered C<sub>2</sub>B<sub>4</sub> face and coordinated to one THF molecule and one neighboring 'carbons-adjacent' *nido*-carborane via two B–H–Na bonds. The other is bonded to a trigonal B<sub>3</sub> face through three B–H–Na **Scheme 4** 





bonds and to the neighboring 'carbons-adjacent' *nido*carborane via two B–H–Na bonds and coordinated to two THF molecules. The average Na(1)-cage atom and Na(2)…B(H) distances of 2.854(4) and 3.026(4) Å are comparable to the corresponding values found in [(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>]Na<sub>2</sub>(THF)<sub>4</sub><sup>13</sup> and [{(Me<sub>3</sub>Si)<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>}Na<sub>2</sub>-(THF)<sub>4</sub>]<sub>2</sub>,<sup>21</sup> respectively.

In contrast, **5** is a centrosymmetric molecule consisting of well-separated, alternating layers of discrete cations  $[K(18\text{-}crown\text{-}6)(CH_3CN)_2]^+$  and the complex anions  $[\{\mu\text{-}1,2\text{-}[o\text{-}C_6H_4(CH_2)_2]\text{-}1,2\text{-}C_2B_{10}H_{10}\}_2K_3(18\text{-}crown\text{-}6)(CH_3CN)_2]^+$ 



**Figure 3.** Molecular structure of  $[{\mu-1,2-[o-C_6H_4(CH_2)_2]-1,2-C_2B_{10}H_{10}}_2Na_4(THF)_6]_n$  (4), showing one asymmetric unit of the infinitive polymeric chain.



Figure 4. Molecular structure of the anion  $[\{\mu\text{-}1,2\text{-}[\textit{o}\text{-}C_{6}H_{4}\text{-}(CH_{2})_{2}]\text{-}1,2\text{-}C_{2}B_{10}H_{10}\}_{2}K_{3}(18\text{-}crown\text{-}6)_{2}]^{-}$  in 5.

 $6)_2$ ]<sup>-</sup>. In the anion, the K(2) atom sits at an inversion center to form a fully sandwiched metallacarborane, shown in Figure 4. Like in complex 4, the six atoms of the hexagonal C<sub>2</sub>B<sub>4</sub> bonding face are almost coplanar compared with the staggered arrangement of the two cage carbon atoms of the hexagonal face in the 'carbons-apart' dianionic species [*nido*-R<sub>2</sub>C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>]<sup>2-</sup>.<sup>13</sup> The average K(2)-cage atom distance of 3.064(4) Å is close to the corresponding value of 3.174(2) Å observed in [{(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<sub>2</sub>(THF)<sub>2</sub>(O<sub>2</sub>C<sub>4</sub>H<sub>8</sub>)<sub>0.5</sub>]<sub>n</sub>.<sup>13</sup> In comparison with 1, the 'carbons-adjacent' *nido*-carborane dianions in both 4 and 5 have the shorter cage C-C bond distances and more distorted inner six-membered rings.

An X-ray analysis reveals that compound **11** adopts a polymeric structure in which the sodium and *nido*-1,4-carborane serve as alternating bridging groups to give a zigzag metallacarborane-Na-metallacarborane-Na chain that is maintained in one dimension throughout the lattice (Figure 5). The novel  $[nido-\mu-1, 4 R_2C_2B_{10}H_{10}]^{2-}$  dianion represents a completely new type of carboranyl ligand and the third form of *nido*- $R_2C_2B_{10}H_{10}^{2-}$ . It has a basket structure with a highly distorted six-membered  $C_2B_4$  ring. The average  $C_{cage} C-C_{aryl}$  angle of 109.7(2)° is much smaller than that of 117.8(3)° in its parent molecule **3**, and the dihedral angle between the two aromatic rings is 68.9° versus 66.1° in **3**.

Although **8** has not been subjected to the X-ray analyses yet, the structural characterization of its

<sup>(21)</sup> Hosmane, N. S.; Jia, L.; Zhang, H.; Bausch, J. W.; Prakash, G. K. S.; Williams, R. E.; Onak, T. P. *Inorg. Chem.* **1991**, *30*, 3793.



**Figure 5.** Molecular structure of  $[\{\mu-1,4-[1,1'-(C_6H_4)_2-2,2'-(CH_2)_2]-1,4-C_2B_{10}H_{10}\}Na_2(THF)_3]_n$  (**11**), showing one asymmetric unit of the infinitive polymeric chain.

hydrolysis product **9** (vide infra) confirms the formation of a 'carbons-adjacent' *nido*-carborane dianion. **8** is suggested to have a structure that is similar to **5**.

The above results show that (1) if the number of bridging carbon atoms between two cage carbon atoms of an *o*-carborane is five or less, the cage carbon atom adjacency is maintained during the reductive process, (2) if this number is six or more, the cage carbon-carbon bond is completely broken, giving a 'carbons-apart' carborane anion in which the two cage carbon atoms are in para positions, and (3) in the absence of the linkage, 'carbons-apart' carborane anions in which the cage carbon atoms are in meta positions are often isolated during the reductive processes.<sup>2,13</sup> Thus, three isomers of nido-carborane dianion of the C2B10 system can be prepared in a controlled manner, as shown in Chart 1. The effects of the bridge length on the cage carbon-carbon bond cleavage are very obvious. Of course, the rigidity of the bridge may also affect the cage carbon-carbon bond cleavage.

Tetraanionic Salts. Excess group 1 metals can only reduce  $1,2-R_2C_2B_{10}H_{10}$  to the 'carbons-apart' nido- $R_2C_2B_{10}H_{10}^{2-}$  in the absence of transition metal ions; namely, the 'carbons-apart' nido-R<sub>2</sub>C<sub>2</sub>B<sub>10</sub>H<sub>10</sub><sup>2-</sup> cannot be reduced by group 1 metals to the arachno-R<sub>2</sub>C<sub>2</sub>- $B_{10}H_{10}^{4-}$  tetraanions.<sup>2,13</sup> Do the 'carbons-adjacent' *nido*carborane dianions follow the same reactivity pattern? Treatment of 1 with excess finely cut lithium metal in THF at room temperature gave a novel 'carbonsadjacent' arachno compound [{µ-1,2-[o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>]-1,2- $C_2B_{10}H_{10}$  Li<sub>4</sub>(THF)<sub>6</sub>]<sub>2</sub> (13) in 76% yield. Recrystallization of 13 from a mixed solvent of DME/THF afforded [ $\{\mu$ -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>10</sub>}Li<sub>4</sub>(THF)<sub>4</sub>(DME)]<sub>2</sub> (14). However, recrystallization of 13 from CH<sub>3</sub>CN at room temperature produced a lithium salt [{ $CH_3C(NH)$ -CHCNLi(THF)]<sub>n</sub> (15) and other unidentified species, suggesting that the *arachno*-carborane tetraanion could abstract the acidic proton from CH<sub>3</sub>CN (Scheme 6). Under the same reaction conditions, interaction between 2 and excess finely cut lithium metal also gave the 'carbons-adjacent' arachno-species [{µ-1,2-[1,8-C<sub>10</sub>H<sub>6</sub>- $(CH_2)_2$ ]-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>}Li<sub>4</sub>(THF)<sub>6</sub>]<sub>2</sub> (17) (Scheme 4). In sharp contrast, reaction of 3 with excess finely cut lithium metal in THF afforded only the 'carbons-apart' *nido*-carborane dianionic salt  $[{\mu-1,4-[1,1'-(C_6H_4)_2-2,2'-$ (CH<sub>2</sub>)<sub>2</sub>]-1,4-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>}Li<sub>2</sub>(THF)<sub>3</sub>]<sub>n</sub> (10); no arachno spe-

Scheme 6



cies was detected by <sup>11</sup>B NMR even at reflux temperature (Scheme 5), which is understood since the cage C-C bond is completely broken during the reaction.

The <sup>11</sup>B NMR data suggest that excess Li metal was also able to reduce complexes **4**, **5**, and **8** to the corresponding *arachno* species. These results indicate that (1) the 'carbons-adjacent' carboranes are more reactive than their 'carbons-apart' isomers, and (2) lithium metal is a stronger reducing agent than sodium and potassium at least with respect to these electron-transfer reactions.<sup>22</sup>

These complexes are extremely air- and moisturesensitive, but remain stable for months at room temperature under an inert atmosphere. They are soluble in pyridine and hot THF, slightly soluble in cooled THF, and insoluble in toluene and *n*-hexane. They were fully characterized by various spectroscopic data and elemental analyses. The solid-state structures of complexes **13–15** were further confirmed by single-crystal X-ray analyses.

The <sup>1</sup>H NMR spectra show that the two methylene protons of the ligands in **13**, **14**, and **17** are nonequivalent in solution and support our conclusion that there are six THF molecules per carboranyl ligand for **13** and **17** and four THF and one DME molecules per carboranyl ligand for **14**, respectively. The <sup>11</sup>B NMR spectra exhibit a similar 2:2:2:1:3 splitting pattern for both **13** and **14**, while that of **17** shows a 2:3:2:3 splitting pattern. The IR spectra of **13**, **14**, and **17** display a characteristic doublet centered around 2450 cm<sup>-1</sup> and a shoulder at about 2310 cm<sup>-1</sup> attributable to a M–H–B stretching mode.<sup>9,10</sup>

<sup>(22)</sup> Reducing power of lithium ( $E^{\circ} = 3.040$  V), sodium ( $E^{\circ} = 2.714$  V), and potassium ( $E^{\circ} = 2.936$  V), see: Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; Harper Collins College: New York, 1993; p A-35.



**Figure 6.** Molecular structure of  $[{\mu-1,2-[o-C_6H_4(CH_2)_2]} 1,2-C_2B_{10}H_{10}$  Li<sub>4</sub>(THF)<sub>4</sub>(DME)]<sub>2</sub> (14).

Single-crystal X-ray analyses reveal that both 13 and 14 are centrosymmetric dimers. Their solid-state structures are very similar to each other except for the coordinating solvents around Li(2), THF in 13 and DME in 14, shown in Figure 6. The arachno-carborane consists of one open six-membered C2B4 face and one open five-membered C<sub>2</sub>B<sub>3</sub> face that are bonded to two lithium atoms in  $\eta^6$ - and  $\eta^5$ -fashion, respectively, to form a novel 14-vertex *closo*-metallacarborane. These two open faces share one common edge of C(1)-C(2). Careful examination of molecular structures of 13 and 4 indicates that the open five-membered face is generated by breaking the B(7)-B(11) connectivity of the nidocarborane in 4 via two-electron uptake from lithium. This is a novel isomer of *arachno*-R<sub>2</sub>C<sub>2</sub>B<sub>10</sub>H<sub>10</sub><sup>4-</sup> tetraanion and represents the first example in which the cage C-C connectivity remains intact after the four-electron reduction of an o-carborane.

The average Li(1)-cage ( $C_2B_4$  face) atom and Li(2)cage (C<sub>2</sub>B<sub>3</sub> face) atom distances of 2.315(8) and 2.309(10) Å in 13 are very close to the corresponding values of 2.300(5) and 2.301(5) Å in 14. These measured values can be compared to the 2.332(9) Å in [(Me<sub>3</sub>-Si)<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>]Li<sub>2</sub>(TMEDA)<sub>2</sub><sup>23</sup> and 2.45(2) Å in [{(Me<sub>3</sub>Si)<sub>2</sub>- $C_2B_4H_5$ <sub>2</sub>Li]<sup>-.24</sup> It is noted that the Li(2)-B(12) distances of 2.572(10) Å in **13** and 2.580(5) Å in **14** are significantly longer than the other Li-cage atom distances due to the larger out-of-plane (C1C2B7B11) displacement of B(12), 0.60 Å in 13 and 0.61 Å in 14, respectively. The weak interactions between Li(2) and C(11) and C(16) (2.595(9)-2.660(6) A) lead to the smaller angles of C(1)-C(3)-C(16) and C(2)-C(4)-C(4)C(11) (110.4(4)-112.6(2)°) compared to the corresponding values  $(114.6(3)-114.9(3)^\circ)$  in 4, and the shorter Li(2)-C<sub>aryl</sub> distance is associated with the smaller C<sub>cage</sub>- $C-C_{aryl}$  angle.

Complex **15** is a coordination polymer with a twodimensional sheetlike structure in which the lithium ions serve as locks to link [NH-C(CH<sub>3</sub>)=CHCN]<sup>-</sup> units together, forming square-grid architectures, shown in Figure 7.





**Figure 7.** (top) Molecular structure of [{CH<sub>3</sub>C(NH)-CHCN Li(THF)]<sub>*n*</sub> (15), showing one asymmetric unit of the infinitive polymeric chain. (bottom) Projection view of one layer of 15.

# Chart 3. arachno-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub><sup>4</sup>- Isomers В Δ С

The electron-accepting ability of 'carbons-adjacent' and 'carbons-apart' nido-carborane dianions is different. The former can accept two electrons from Li metal to form the 'carbons-adjacent' arachno-carborane tetraanion, and the latter shows no reaction with excess Li metal, probably owing to the electronic effects of the cage carbon atoms.14 Together with the earlier reported arachno- $R_2C_2B_{10}H_{10}^{4-}$  tetraanions,<sup>8-10</sup> three isomers are now known, shown in Chart 3. They have different shapes and bonding faces. Among them, isomers **B** and C have been confirmed by X-ray analyses.

Monoanionic Salts. Protonation of 5 with degassed water in THF at room temperature generated, after recrystallization from an acetone solution at room temperature, a monoanionic salt  $[\{\mu-1,2-[o-C_6H_4(CH_2)_2]-$ 

<sup>(23)</sup> Hosmane, N. S.; Saxena, A. K.; Barreto, R. D.; Zhang, H.; Maguire, J. A.; Jia, L.; Wang, Y.; Oki, A. R.; Grover, K. V.; Whitten, S. J.; Dawson, K.; Tolle, M. A.; Siriwardane, U.; Demissie, T.; Fagner, J. S. Organometallics **1993**, *12*, 3001. (24) Hosmane, N. S.; Yang, J.; Zhang, H.; Maguire, J. A. J. Am.

Chem. Soc. 1996, 118, 5150.

 $1,2-C_2B_{10}H_{11}$  K(18-crown-6)]<sub>2</sub>( $\mu$ -OH<sub>2</sub>) (6) in 82% isolated yield. Recrystallization of **6** from hot acetone gave the thermodynamic isomer  $[\{\mu-1,2-[o-C_6H_4(CH_2)_2]-1,2-C_2B_{10} H_{11}$  K(18-crown-6)]<sub>*n*</sub> (7) in 86% yield. This isomerization was closely monitored by <sup>11</sup>B NMR spectroscopy, showing that the kinetic isomer 6 was completely converted into the more stable thermodynamic isomer 7 in ca. 12 h at 70 °C (Scheme 3). Protonation of 8 with degassed water afforded, after addition of an aqueous solution of KBr in 18-crown-6 ether, the kinetic isomer  $\{\mu$ -1,2-[1,8- $C_{10}H_6(CH_2)_2$ ]-1,2- $C_2B_{10}H_{11}$ }{K(THF)(18-crown-6)} (9) in 68% yield (Scheme 4). 9 was completely isomerized into the thermodynamic isomer within 48 h at 40 °C on the basis of <sup>11</sup>B NMR spectroscopic analyses. In contrast, only one protonation product was observed during the protonation of **11** with degassed water at temperature range 0-60 °C as indicated by <sup>11</sup>B NMR. This monoanionic salt was formulated as  $\{\mu$ -1,4-[1,1'-(C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>-2,2'- $(CH_2)_2$ ]-1,4-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>}{Na(THF)\_3} (12) on the basis of elemental analyses and various spectroscopic data.

Complex **13** contains the *arachno*-carborane tetraanion. Treatment of **13** with a degassed aqueous solution of KBr and a THF solution of 18-crown-6 ether at reflux temperature gave the monoanionic salt { $\mu$ -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>13</sub>}{K(18-crown-6)(THF)} (**16**) in 75% yield (Scheme 6). The <sup>11</sup>B NMR data suggest that **16** is apparently a thermodynamic isomer. The corresponding kinetic isomer was not isolated because of relatively rapid isomerization even at room temperature. It is interesting to note that the *arachno* species was able to take three protons from H<sub>2</sub>O molecules. Protonation of **17** with degassed water was also investigated by <sup>11</sup>B NMR spectroscopy. Two isomers were detected, and the kinetic isomer could be converted into the thermodynamic one even at room temperature.

The <sup>1</sup>H NMR spectra show two sets of methylene protons from the ligands in **6**, **7**, **9**, **12**, and **16** and support the ratio of one 18-crown-6 ether molecule per carboranyl ligand for both **6** and **7**, one 18-crown-6 ether molecule and one THF molecule per carboranyl ligand for both **9** and **16**, and three THF molecules per carboranyl ligand for **12**, respectively. These results are in line with their <sup>13</sup>C NMR spectroscopic data. The <sup>11</sup>B NMR spectra show 2:2:2:2:1:1, 1:4:3:1:1, 2:2:2:2:1:1, 2:5: 3, and 3:1:2:2:1:1 splitting patterns for **6**, **7**, **9**, **12**, and **16**, respectively. The IR spectra of **6**, **7**, **9**, **12**, and **16** all exhibit a characteristic doublet centered around 2450 cm<sup>-1</sup> and a shoulder at about 2310 cm<sup>-1</sup> attributable to a M–H–B stretching mode.<sup>9,10</sup>

An X-ray analysis reveals that **6** is a centrosymmetric dimer with the O(7) (H<sub>2</sub>O molecule) atom sitting at the inversion center, shown in Figure 8. The anion possesses an open  $C_2B_4$  face and a pentagonal  $B_5$  belt that is capped by a BH vertex, a structural motif that is very similar to its parent ion in **5**. The shape of this cage resembles that of the kinetic isomer isolated from the protonation of the 'carbons-apart' *nido*-R<sub>2</sub>C<sub>2</sub>B<sub>10</sub>H<sub>10</sub><sup>2-</sup> dianion.<sup>13,25</sup>

The thermodynamic isomer **7** adopts a polymeric structure in which the carboranyl and potassium ions



**Figure 8.** (top) Molecular structure of  $[{\mu-1,2-[o-C_6H_4-(CH_2)_2]-1,2-C_2B_{10}H_{11}}K(18-crown-6)]_2(\mu-OH_2)$  (6). (bottom) Closer view of the cage in 6.



**Figure 9.** (top) Molecular structure of  $[\{\mu-1,2-[o-C_6H_4-(CH_2)_2]-1,2-C_2B_{10}H_{11}\}K(18-crown-6)]_n$  (7), showing a portion of the infinitive polymeric chain. (bottom) Closer view of the cage in 7.

serve as alternating bridging groups to give a zigzag carborane-K-carborane-K chain that is maintained in one dimension throughout the lattice (Figure 9). The most significant part of this structure is the arrangement of the cage atoms: five-coordinate carbon and boron (C1, C2, and B11), six-coordinate boron (B3–B5, B7, B8, B10, and B12), and seven-coordinate boron (B9 and B12). There are two pentagonal belts: one (B6B7B8-B9B10) is capped by two boron atoms (B11 and B12) and the other (C1C2B3B4B5) is partially capped by one  $\mu_3$ -H atom, shown in Figure 9. This isomer of the [R<sub>2</sub>C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>]<sup>-</sup> monoanion has not been observed previ-

<sup>(25) (</sup>a) Getman, T. G.; Knobler, C. B.; Hawthorne, M. F. Inorg. Chem. **1990**, 29, 158. (b) Tolpin, E. I.; Lipscomb, W. N. Inorg. Chem. **1973**, 12, 2257. (c) Churchill M. R.; DeBoer, B. G. Inorg. Chem. **1973**, 12, 2674.



Figure 10. Molecular structure of  $\{\mu$ -1,2-[1,8-C<sub>10</sub>H<sub>6</sub>(CH<sub>2</sub>)<sub>2</sub>]-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>}{K(THF)(18-crown-6)} (9).



**Figure 11.** (top) Molecular structure of  $\{\mu$ -1,2-[o-C<sub>6</sub>H<sub>4</sub>- $(CH_2)_2]$ -1,2-C<sub>2</sub>B<sub>10</sub>H<sub>13</sub> $\{K(18$ -crown-6)(THF) $\}$  (**16**). (bottom) Closer view of the cage in **16**.

ously. It is very obvious that the presence of a short bridge plays a significant role in the generation of the novel carborane monoanion in **7**.

The solid-state structure of **9** is shown in Figure 10. It consists of the monoanion  $[\mu-1,2-[1,8-C_{10}H_6(CH_2)_2]-1,2-C_2B_{10}H_{11}]^-$  and the cation  $[K(THF)(C_{12}H_{24}O_6)]^+$  that are linked to each other via B-H-K interactions. The carborane cage of the anion is almost identical to that in **6**, confirming that **9** is a kinetic isomer.

An X-ray diffraction study shows that **16** is a monomer consisting of the anion  $[\mu-1,2-[o-C_6H_4(CH_2)_2]-1,2-C_2B_{10}H_{13}]^-$  and the cation  $[K(18-crown-6)(THF)]^+$  that are associated with each other through B-H-K interactions (Figure 11). The novel monoanion possesses two open  $C_2B_3$  five-membered faces, and they share two bonds, C(1)-C(2) and C(1)-B(5), shown in Figure 11, which is completely different from its parent tetraanion. Apparently, one proton is added to C(1), generating the tetrahedral carbon. Assignment of the other two  $\mu$ -H atom positions is completed with the help of  ${}^{11}B-{}^{11}B$ 2D-COSY NMR and proton-coupled  ${}^{11}B$  NMR spectroscopy.<sup>26</sup> Note that the degassed water must be used;



otherwise both the *arachno*- and *nido*-carborane anions can be oxidized by  $O_2$  back to the corresponding neutral starting materials.

It is demonstrated, for the first time, that hydrolysis of an *arachno*-carborane tetraanion leads to the formation of the carborane monoanion via three-proton uptake from water molecules. Protonation of *nido*-carborane dianions often gives two isomers,<sup>13,25</sup> the kinetic one and the thermodynamic product except for **12**, in which the cage atoms are probably locked in place by the rigid bridge, showing only one isomer. For comparison, Scheme 7 illustrates the similarities and differences between the hydrolysis products of 'carbons-adjacent' and 'carbons-apart' *nido*-carborane dianions. The differences in the thermodynamic products are very obvious, suggesting the effects of the bridge on the stability of the products.

#### Conclusion

This study shows that a short bridge between the two cage carbon atoms of an o-carborane can indeed force the two cage carbon atoms to remain adjacent in *ortho* positions during two- and four-electron reduction processes, leading to the isolation and structural characterization of a novel class of 'carbons-adjacent' nido- and arachno-carborane group 1 complexes. When the number of the bridging carbon atoms changes from 5 to 6, the cage carbon-carbon bond in 3 is completely broken during two-electron reduction to generate the nidocarborane dianion in which the two cage carbon atoms are in para positions. Thus, three isomers of the nido- $R_2C_2B_{10}H_{10}^{2-}$  dianion in which the two cage carbon atoms are in ortho, meta, and para positions, respectively, can be prepared in a controlled manner. Although the bridge length between the two cage carbon atoms of an o-carborane obviously controls the arrangement of the two cage carbon positions during the reductive processes, the effect of the rigidity of such a bridge on the cage carbon-carbon bond cleavage cannot be ruled out at this stage.

The 'carbons-adjacent' carboranes are more reactive than their 'carbons-apart' isomers. For example, **1** and **2** can be directly reduced by Li metal to the 'carbonsadjacent' *arachno*-carborane tetraanions, while **3** and other non-carbon-bridged *o*-carboranes can only be reduced to the corresponding 'carbons-apart' *nido*-carborane dianions. Thus, three isomers of *arachno*-carborane tetraanions can be prepared in a controlled

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manner (shown in Chart 3). Protonation of both *nido*carborane dianions and *arachno*-carborane tetraanion all leads to the formation of the corresponding carborane monoanions via one- or three-proton uptake from water molecules. However, their molecular structures are very different from each other.

These group 1 salts of 'carbons-adjacent' *nido-* and *arachno-*carborane anions are useful synthons for the production of other metallacarboranes.<sup>27</sup>

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**Supporting Information Available:** Tables of crystallographic data and data collection details, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates and figures giving atomnumbering schemes for complexes **1**, **3**–**7**, **9**, **11**, and **13**–**16**. This material is available free of charge via the Internet at http://pubs.acs.org.

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