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# Reactions of 13-Vertex Carboranes with Strong Bases: Synthesis and Structural Characterization of Carborane Monoanions with *exo*- $\pi$ Bonding

Fangrui Zheng, Jian Zhang, Xiaodu Fu, and Zuwei Xie\*<sup>[a]</sup>

**Abstract:** Several monoanions of 13-vertex carboranes were prepared in high yields from the reactions of C,C'-linked 13-vertex carboranes with *t*BuOK or NaH in dry THF at room temperature. These monoanions were characterized by various spectroscopic methods, elemental analysis, and single-crystal X-ray diffraction. The results showed substantial double-bond

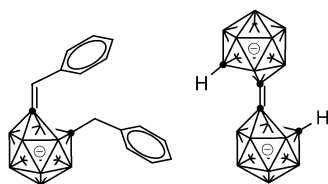
character between the cage-carbon atom and the *exo* vicinal carbon atom, thus leading to charge delocalization into the cage. As a result, the atom–atom distances within the cage were

elongated, with one broken C–B bond. However, the cage geometry of the monoanions remained very similar to that of their corresponding neutral 13-vertex *closo*-carboranes. These monoanions represent the first examples of 13-vertex carboranes with *exo*- $\pi$  bonding to hypercarbon atoms.

**Keywords:** boron • cage compounds • carboranes • deprotonation • pi interactions

## Introduction

The presence of *exo* C–X  $\pi$ -bonding interactions, where X is a  $\pi$ -donating moiety, has been observed in substituted *o*-carboranes (1,2-X<sub>2</sub>-*o*-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>).<sup>[1–4]</sup> The strength of such  $\pi$ -bonding interactions increases with the  $\pi$ -donating ability of X, thus leading to an elongation of the cage C–C bond. When X is a carbanion, an *exo* C=C double bond is formed, which results in the breaking of a cage C–C bond and the formation of *nido*-carboranes, such as [(*o*-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>)<sub>2</sub>]<sup>2–</sup><sup>[3]</sup> and [1-(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)-2-(C<sub>6</sub>H<sub>5</sub>CH)-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>]<sup>–</sup><sup>[4]</sup> (Scheme 1).



Scheme 1. *exo* C=C  $\pi$ -bonding interactions in [(*o*-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>)<sub>2</sub>]<sup>2–</sup> and [1-(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)-2-(C<sub>6</sub>H<sub>5</sub>CH)-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>]<sup>–</sup>.

Previously, we wondered whether an *exo* C=C double bond would be formed or if a *nido*-carborane would be generated if the two cage-carbon atoms were linked by a short carbon chain.<sup>[5]</sup> Unfortunately, the methylene hydrogen atom in 1,2-

(CH<sub>2</sub>)<sub>3</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> could not be deprotonated by strong bases, such as *n*BuLi, *t*BuOK, and KH.

On the other hand, significant recent progress has been made in the chemistry of supercarboranes (carboranes with more than 12 vertices).<sup>[6]</sup> A number of 13- and 14-vertex carboranes have been synthesized and structurally characterized.<sup>[7–12]</sup> These compounds can be reduced by Group 1 metals to afford their corresponding *nido*-supercarborane dianions.<sup>[8–12]</sup> The 13-vertex carborane 1,2-(CH<sub>2</sub>)<sub>3</sub>-1,2-C<sub>2</sub>B<sub>11</sub>H<sub>11</sub> can even undergo single-electron reduction to give a stable carborane radical anion with [2*n*+3] framework electrons.<sup>[13]</sup> This 13-vertex carborane can also react with various nucleophiles to give cage-boron- or cage-carbon-extrusion products *nido*-CB<sub>10</sub>, *closo*-CB<sub>10</sub>, *closo*-CB<sub>11</sub>, or *closo*-C<sub>2</sub>B<sub>10</sub>, depending on the nature of the nucleophile.<sup>[14–16]</sup> When NaH was used as a nucleophile in the reaction with 1,2-(CH<sub>2</sub>)<sub>3</sub>-1,2-C<sub>2</sub>B<sub>11</sub>H<sub>11</sub>, an unexpected  $\alpha$ -deprotonation species, [1,2-CH(CH<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>11</sub>H<sub>11</sub>]<sup>–</sup>, was obtained, which prompted us to study the deprotonation reaction of 13-vertex carboranes with strong bases. Herein, we report the synthesis and structural characterization of 13-vertex carborane monoanions with *exo* C=C  $\pi$  bonding.

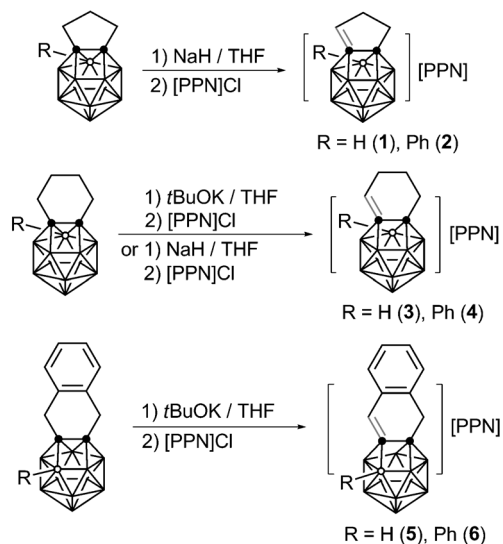
## Results and Discussion

### Synthesis

13-Vertex carboranes were prepared according to literature procedures.<sup>[7,9]</sup> The reaction of 1,2-(CH<sub>2</sub>)<sub>3</sub>-1,2-C<sub>2</sub>B<sub>11</sub>H<sub>11</sub> with an excess amount of NaH in THF at room temperature until no gas was evolved, followed by cation exchange with [PPN]Cl (PPN = bis(triphenylphosphine)iminium cation), gave monoanionic salt [1,2-CH(CH<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>11</sub>H<sub>11</sub>][PPN] (**1**) in 75% yield as brown crystals. The treatment of 1,2-(CH<sub>2</sub>)<sub>4</sub>-1,2-C<sub>2</sub>B<sub>11</sub>H<sub>11</sub> with one equivalent of *t*BuOK in THF

[a] F. Zheng, Dr. J. Zhang, X. Fu, Prof. Dr. Z. Xie  
Department of Chemistry and State Key Laboratory of Synthetic Chemistry  
The Chinese University of Hong Kong  
Shatin, NT, Hong Kong (China)  
Fax: (+852) 2603-5057  
E-mail: zxie@cuhk.edu.hk

at room temperature, followed by cation exchange with [PPN]Cl, afforded [1,2-CH(CH<sub>2</sub>)<sub>3</sub>-1,2-C<sub>2</sub>B<sub>11</sub>H<sub>11</sub>][PPN] (**3**) in 94% yield. The latter reaction was completed within 1 min. These reactions were monitored by <sup>11</sup>B NMR spectroscopy because the product showed a distinct spectrum to that of the starting material. In a similar manner, compounds **2** and **4–6** were isolated in 78–92% yield, as outlined in Scheme 2.



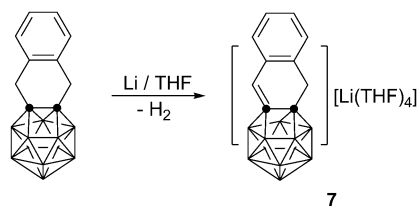
Scheme 2. Preparation of compounds **1–6**.

Notably, [1,2-*o*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)(CH)]-1,2-C<sub>2</sub>B<sub>11</sub>H<sub>11</sub>][Li(THF)<sub>4</sub>] (**7**) was also isolated as yellow crystals from an equimolar reaction of 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>11</sub>H<sub>11</sub> with finely cut lithium metal in THF at room temperature in 90% yield (Scheme 3).

Compounds **1–7** did not react further with *t*BuOK or NaH, but were readily protonated by 3 M HCl to produce their corresponding neutral 13-vertex carboranes. These compounds were stable at reflux in THF and soluble in acetone and CH<sub>2</sub>Cl<sub>2</sub>; however, they were insoluble in aromatic solvents and *n*-hexane.

#### Abstract in Chinese:

本文报道了一系列具笼外双键的十三顶点碳硼烷单阴离子化合物的合成和结构。它们由碳碳相连的十三顶点碳硼烷和叔丁醇钾或氢化钠以四氢呋喃为溶剂在室温下反应以较高的产率得到。实验结果表明其中一个笼碳原子与其相连的外部碳原子之间存在明显的双键特征，这导致了负电荷离域到碳硼烷笼子中，使碳硼烷笼子变大并有一碳硼键断裂。但是，这些笼子的几何构型和原料中性十三顶点碳硼烷非常接近。所有新化合物均通过多种波谱和元素分析表征，部分化合物的结构得到X射线单晶衍射确证。



Scheme 3. Preparation of compound **7**.

All of these compounds were fully characterized by various spectroscopic methods and by elemental analysis. Their <sup>1</sup>H NMR spectra displayed unique *exo* α-C(H)= signals within the range δ = 5.27–6.15 ppm, with *J* = 3.1 Hz (**1**), 3.0 Hz (**2**), 4.8 Hz (**3**), and 4.5 Hz (**4**). The corresponding <sup>13</sup>C NMR chemical shifts of the *exo* α-C(H)= atom ranged from δ = 140.1–150.1 ppm. These NMR data were in good agreement with typical values for olefinic proton and carbon atoms. Their <sup>11</sup>B NMR spectra exhibited similar patterns to those of their parent molecules, but with significantly different chemical shifts. Some signals were remarkably shifted to higher field, thus indicating that the electron density of the cage had significantly increased.

#### Structure

The solid-state structures of compounds **1**, **3**, **4**, and **7** were further confirmed by single-crystal X-ray diffraction and are shown in Figure 1, Figure 2, Figure 3, and Figure 4, respec-

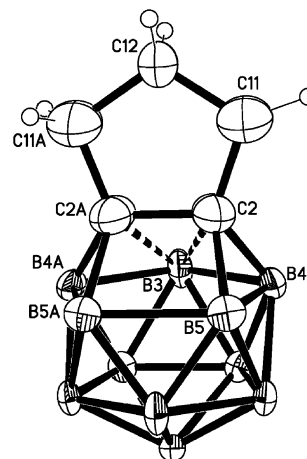


Figure 1. Molecular structure of monoanion [1,2-CH(CH<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>11</sub>H<sub>11</sub>]<sup>-</sup> in compound **1**; only the carbon-chain hydrogen atoms are shown for clarity.

tively. These structures consist of well-separated, alternating layers of discrete carborane monoanions and cations. The anions contain two trapezoidal faces, with the remaining being triangulated, thus giving one five-coordinate cage-carbon atom and one four-coordinate cage-carbon atom. Their geometries are similar to those that were observed in

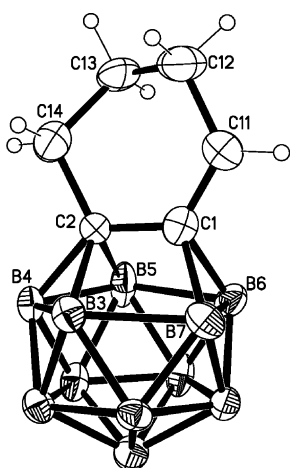


Figure 2. Molecular structure of monoanion  $[1,2\text{-CH}(\text{CH}_2)_3\text{-}1,2\text{-C}_2\text{B}_{11}\text{H}_{11}]^-$  in compound **3**; only the carbon-chain hydrogen atoms are shown for clarity.

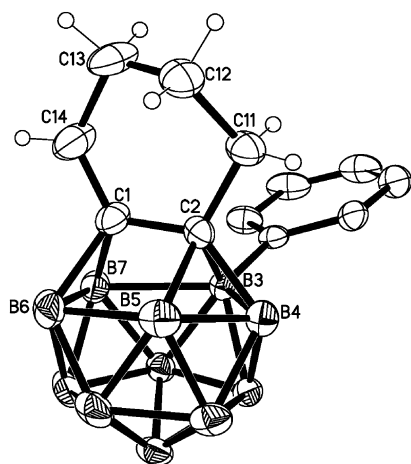
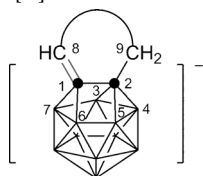


Figure 3. Molecular structure of monoanion  $[1,2\text{-CH}(\text{CH}_2)_3\text{-}3\text{-Ph-}1,2\text{-C}_2\text{B}_{11}\text{H}_{10}]^-$  in compound **4**; only the carbon-chain hydrogen atoms are shown for clarity.

Table 1. Selected bond lengths [ $\text{\AA}$ ] for the anions in compounds **1**, **3**, **4**, and **7-9**.



Bond	<b>1</b>	<b>3</b>	<b>4</b>	<b>7</b>	<b>8</b>	<b>9</b>
C1–C8	1.439(15)	1.364(5)	1.352(4)	1.446(7)	1.51(1)	1.537(3)
C1–C2	1.485(9)	1.448(4)	1.453(3)	1.454(5)	1.45(1)	1.421(3)
C1...B3	2.192(11)	2.264(5)	2.304(4)	2.016(9)	2.17(1)	1.852(3)
C1–B6	1.732(13)	1.779(5)	1.759(4)	1.784(9)	1.67(1)	1.807(4)
C1–B7	1.521(11)	1.649(5)	1.681(4)	1.598(8)	1.49(1)	1.597(3)
C2–C9	1.439(15)	1.547(4)	1.522(3)	1.460(7)	1.56(1)	1.537(3)
C2–B3	2.192(11)	1.848(5)	1.814(4)	1.937(9)	1.98(1)	1.881(4)
C2–B4	1.521(11)	1.661(5)	1.638(4)	1.621(8)	1.49(1)	1.594(3)
C2–B5	1.732(13)	1.789(5)	1.783(4)	1.800(8)	1.91(1)	1.807(3)

their corresponding 13-vertex carboranes, but with elongated cage-atom–cage-atom bond lengths. As shown in Table 1, the structural parameters of compound **1** are closer to those in radical anion  $[1,2\text{-(CH}_2)_3\text{-}1,2\text{-C}_2\text{B}_{11}\text{H}_{11}]^-$  (**8**)<sup>[13]</sup> than in neutral species  $1,2\text{-(CH}_2)_3\text{-}1,2\text{-C}_2\text{B}_{11}\text{H}_{11}$  (**9**).<sup>[17]</sup> The C1–C8 (*exo*- $\pi$  bonding) bond lengths range from 1.352(4) to 1.446(7)  $\text{\AA}$ ; this reveals the existence of substantial C=C double-bond character. Compared to the cage-C–cage-C distances in neutral 13-vertex carboranes (1.39–1.43  $\text{\AA}$ ),<sup>[9,17,18]</sup> the corresponding cage-C1–cage-C2 distances (1.45–1.49  $\text{\AA}$ ) in the monoanions are slightly longer. As a result of the formation of the *exo* C1=C8 bond, the negative charge is delocalized into the cage, thus leading to cleavage of the C1–B3 bond with a distance of  $>2$   $\text{\AA}$ .

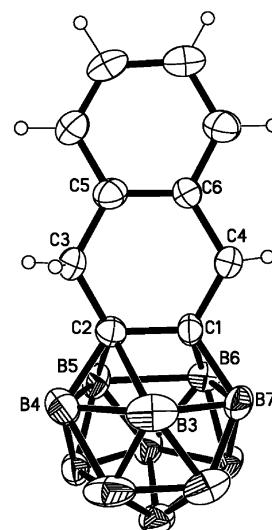


Figure 4. Molecular structure of monoanion  $[1,2\text{-}(o\text{-C}_6\text{H}_4\text{)(CH}_2\text{)(CH)-}1,2\text{-C}_2\text{B}_{11}\text{H}_{11}]^-$  in compound **7**; only the carbon-chain/aromatic-ring hydrogen atoms are shown for clarity.

## Conclusions

Several monoanions of 13-vertex carboranes were prepared by the deprotonation of C,C'-linked 13-vertex carboranes with strong bases or lithium metal. Their structures were confirmed by spectroscopic methods and single-crystal X-ray diffraction, thus revealing the existence of  $\text{C}_{\text{cage}}=\text{C}$  *exo*- $\pi$ -bonding interactions. The cages contain two trapezoidal faces, with the others being triangulated, thus giving one five-coordinate cage-carbon atom and one four-coordinate cage-carbon atom. These monoanions represent the first examples of 13-vertex carboranes that contain *exo*- $\pi$ -bonding interactions to hypercarbon atoms.

Our results suggest that 13-vertex carboranes are more electron deficient than the corresponding 12-vertex species because the  $\alpha$ -methylene hydrogen atom in  $1,2\text{-(CH}_2)_3\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$  cannot be deprotonated by strong bases. This work also shows that a short carbon chain between two cage-carbon atoms can prevent the cleavage of the cage-C–C–B bond, but rather lead to the breaking of a cage-C–B bond after the delocalization of the negative charge from the *exo* carbon atom into the cage. The presence of such a short chain might force the monoanions to adopt a *closo*-like geometry, even though they should be  $[2n+4]$  systems. It is anticipated that a similar phenomenon might be observed in other C,C'-linked carboranes.

## Experimental Section

## General Procedures

All experiments were performed under an atmosphere of dry argon with the rigid exclusion of air and moisture by using standard Schlenk or canula techniques or in a glovebox. All organic solvents were heated at reflux over sodium benzophenone ketyl for several days and freshly distilled prior to use. All chemicals were either purchased from Aldrich or Acros Chemical Co. and used as received, unless otherwise noted. 1,2-(CH<sub>2</sub>)<sub>3</sub>-1,2-C<sub>2</sub>B<sub>11</sub>H<sub>11</sub>,<sup>[9]</sup> 1,2-(CH<sub>2</sub>)<sub>3</sub>-3-Ph-1,2-C<sub>2</sub>B<sub>11</sub>H<sub>10</sub>,<sup>[9]</sup> 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>11</sub>H<sub>11</sub>,<sup>[9]</sup> and 1,2-[*o*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>]-3-Ph-1,2-C<sub>2</sub>B<sub>11</sub>H<sub>10</sub><sup>[7]</sup> were prepared according to literature procedures. IR spectra were obtained on a Perkin–Elmer 1600 Fourier transform spectrometer for KBr pellets that were prepared in a glovebox. <sup>1</sup>H NMR spectra were recorded on Bruker DPX 300 or Bruker DPX 400 spectrometers at 300 MHz and 400 MHz, respectively. <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on Bruker DPX 300 or Bruker DPX 400 spectrometers at 75 MHz and 100 MHz, respectively. <sup>11</sup>B NMR spectra were recorded on Bruker DPX 300 or Bruker DPX 400 spectrometers at 96 MHz and 128 MHz, respectively. All of the chemical shifts ( $\delta$ ) are reported relative to the residual solvent resonances of the deuterated solvents for (<sup>1</sup>H and <sup>13</sup>C) or to external BF<sub>3</sub>·OEt<sub>2</sub> (<sup>11</sup>B,  $\delta$  = 0.00 ppm). Elemental analysis was performed by the Shanghai Institute of Organic Chemistry, CAS, China.

Preparation of 1,2-(CH<sub>2</sub>)<sub>4</sub>-1,2-C<sub>2</sub>B<sub>11</sub>H<sub>11</sub>

Finely cut Na metal (0.50 g, 21.7 mmol) and a catalytic amount of naphthalene (0.10 g, 0.78 mmol) were added to a solution of 1,2-(CH<sub>2</sub>)<sub>3</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (1.98 g, 10.0 mmol) in THF (30 mL) and the mixture was stirred at RT for 1 day. The removal of THF and excess Na metal afforded a brown solid, presumably [*nido*-(CH<sub>2</sub>)<sub>4</sub>-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>][Na<sub>2</sub>(THF)<sub>x</sub>]. Then, toluene (30 mL) was added, thus giving a yellow suspension, to which was slowly added HBBBr<sub>2</sub>·SMe<sub>2</sub> (20.0 mL, 1.0 M in CH<sub>2</sub>Cl<sub>2</sub>, 20.0 mmol) at –78 °C. The reaction mixture was stirred at –78 °C for 1 h and then at RT for 6 h. Removal of solvent gave a yellow solid. Purification by column chromatography on silica gel (300–400 mesh, *n*-hexane) afforded 1,2-(CH<sub>2</sub>)<sub>4</sub>-1,2-C<sub>2</sub>B<sub>11</sub>H<sub>11</sub> (0.78 g, 37% yield) as a white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 3.05 (t, *J* = 6.6 Hz, 4H; CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.78 ppm (m, 4H; CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 44.58 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 20.89 ppm (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), cage carbon atoms were not observed; <sup>11</sup>B NMR (CDCl<sub>3</sub>):  $\delta$  = 4.6 (1B), 0.9 (5B), –0.5 ppm (5B); IR (KBr):  $\tilde{\nu}$  = 2568 cm<sup>–1</sup> (vs); HRMS: *m/z* calcd for C<sub>6</sub>H<sub>13</sub>B<sub>11</sub><sup>+</sup>: 209.2499; found: 209.2499.

Preparation of 1,2-(CH<sub>2</sub>)<sub>4</sub>-3-Ph-1,2-C<sub>2</sub>B<sub>11</sub>H<sub>10</sub>

Following the procedures described for 1,2-(CH<sub>2</sub>)<sub>4</sub>-1,2-C<sub>2</sub>B<sub>11</sub>H<sub>11</sub>, PhBCl<sub>2</sub> (2.60 mL, 20.0 mmol) was treated with a suspension of [*nido*-(CH<sub>2</sub>)<sub>4</sub>-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>][Na<sub>2</sub>(THF)<sub>x</sub>] (10.0 mmol) in toluene (30 mL) to afford 1,2-(CH<sub>2</sub>)<sub>4</sub>-3-Ph-1,2-C<sub>2</sub>B<sub>11</sub>H<sub>10</sub> as a white solid (0.88 g, 31% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 7.38 (m, 5H; C<sub>6</sub>H<sub>5</sub>), 3.04 (t, *J* = 6.6 Hz, 4H; CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.49 ppm (m, 4H; CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 148.3, 135.2, 130.8, 129.2 (C<sub>6</sub>H<sub>5</sub>), 44.09 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 20.82 ppm (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), cage-carbon atoms were not observed; <sup>11</sup>B NMR (CDCl<sub>3</sub>):  $\delta$  = 7.1 (1B), 6.0 (1B), 4.4 (2B), 1.9 (2B), 0.5 (2B), –1.1 (2B), –4.4 ppm (1B); IR (KBr):  $\tilde{\nu}$  = 2566 cm<sup>–1</sup> (vs); HRMS: *m/z* calcd for C<sub>12</sub>H<sub>23</sub>B<sub>11</sub><sup>+</sup>: 284.2734; found: 284.2734.

Preparation of [1,2-CH(CH<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>11</sub>H<sub>11</sub>][PPN] (1)

NaH (48 mg, 2.0 mmol) was added to a solution of 1,2-(CH<sub>2</sub>)<sub>3</sub>-1,2-C<sub>2</sub>B<sub>11</sub>H<sub>11</sub> (98 mg, 0.50 mmol) in THF (20 mL) at RT and the mixture was stirred for 8 h until no gas was evolved. After filtration, [PPN]Cl (287 mg, 0.50 mmol) was added to the brown filtrate and the mixture was stirred at RT overnight. Removal of the precipitate afforded a clear solution that was concentrated to about 5 mL. Layering with *n*-hexane gave compound **1** as brown crystals (275 mg, 75% yield). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 7.68 (m, 6H; PPN), 7.49 (m, 24H; PPN), 5.45 (t, *J* = 3.1 Hz, 1H; CH), 2.65 (m, 2H; CHCH<sub>2</sub>), 2.39 ppm (t, *J* = 10.5 Hz, 2H; CCH<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 140.8 (CH), 133.1, 131.0, 128.9, 125.6 (PPN), 87.1 (cage CCH), 60.2 (cage CCH<sub>2</sub>), 40.9 (CCH<sub>2</sub>), 33.0 ppm (CHCH<sub>2</sub>);

<sup>11</sup>B NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 7.1 (1B), 0.4 (5B), –20.4 ppm (5B); IR (KBr):  $\tilde{\nu}$  = 2519 cm<sup>–1</sup> (vs); elemental analysis calcd (%) for C<sub>41</sub>H<sub>46</sub>B<sub>11</sub>NP<sub>2</sub> (**1**): C 67.12, H 6.32, N 1.91; found: C 67.47; H 6.45, N 1.59.

Preparation of [1,2-CH(CH<sub>2</sub>)<sub>2</sub>-3-Ph-1,2-C<sub>2</sub>B<sub>11</sub>H<sub>10</sub>][PPN] (2)

The title compound was prepared as brown crystals from 1,2-(CH<sub>2</sub>)<sub>3</sub>-3-Ph-1,2-C<sub>2</sub>B<sub>11</sub>H<sub>10</sub> (136 mg, 0.50 mmol) and NaH (48 mg, 2.0 mmol) in THF (20 mL) at RT by using the same procedure as for compound **1**. Yield: 316 mg (78%); <sup>1</sup>H NMR ([D<sub>6</sub>]acetone):  $\delta$  = 7.70 (m, 18H; PPN), 7.56 (m, 12H; PPN), 7.13 (m, 5H; BC<sub>6</sub>H<sub>5</sub>), 5.27 (t, *J* = 3.0 Hz, 1H; CH), 2.25 (m, 2H; CH<sub>2</sub>), 2.15 ppm (m, 2H; CH<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR ([D<sub>6</sub>]acetone):  $\delta$  = 140.1 (CH), 135.0, 134.6, 133.2, 133.1, 130.5, 130.3, 128.8, 127.3, 127.1, 126.6 (PPN and BC<sub>6</sub>H<sub>5</sub>), 40.9, 34.5 ppm (CH<sub>2</sub>), cage-carbon atoms were not observed; <sup>11</sup>B NMR ([D<sub>6</sub>]acetone):  $\delta$  = 13.3 (1B), 7.7 (1B), 1.3 (2B), –1.6 (2B), –18.6 (3B), –21.2 ppm (2B); IR (KBr):  $\tilde{\nu}$  = 2515 cm<sup>–1</sup> (vs); elemental analysis calcd (%) for C<sub>47</sub>H<sub>50</sub>B<sub>11</sub>NP<sub>2</sub> (**2**): C 69.71, H 6.22, N 1.73; found: C 70.22; H 6.55, N 1.89.

Preparation of [1,2-CH(CH<sub>2</sub>)<sub>3</sub>-1,2-C<sub>2</sub>B<sub>11</sub>H<sub>11</sub>][PPN] (3)

The title compound was prepared as brown crystals from 1,2-(CH<sub>2</sub>)<sub>4</sub>-1,2-C<sub>2</sub>B<sub>11</sub>H<sub>11</sub> (105 mg, 0.50 mmol) and NaH (48 mg, 2.0 mmol) in THF (20 mL) at RT by using the same procedure as for compound **1**. Yield: 350 mg (94%); <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 7.69 (m, 6H; PPN), 7.54 (m, 24H; PPN), 5.76 (t, *J* = 4.8 Hz, 1H; CH), 2.14 (m, 2H; CHCH<sub>2</sub>), 2.11 (t, *J* = 6.1 Hz, 2H; CCH<sub>2</sub>), 1.56 ppm (m, *J* = 6.0 Hz, 2H; CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 150.3 (CH), 134.2, 132.6, 129.6, 127.4 (PPN), 80.4 (cage CCH), 53.5 (cage CCH<sub>2</sub>), 42.3 (CCH<sub>2</sub>), 29.0 (CHCH<sub>2</sub>), 19.4 ppm (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); <sup>11</sup>B NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 6.6 (1B), –1.4 (5B), –21.4 ppm (5B); IR (KBr):  $\tilde{\nu}$  = 2526 cm<sup>–1</sup> (vs); elemental analysis calcd (%) for C<sub>42</sub>H<sub>48</sub>B<sub>11</sub>NP<sub>2</sub> (**3**): C 67.47, H 6.47, N 1.87; found: C 67.13; H 6.40, N 1.96.

Preparation of [1,2-CH(CH<sub>2</sub>)<sub>3</sub>-3-Ph-1,2-C<sub>2</sub>B<sub>11</sub>H<sub>10</sub>][PPN] (4)

*t*BuOK (56 mg 0.50 mmol) was added to a solution of 1,2-(CH<sub>2</sub>)<sub>4</sub>-3-Ph-1,2-C<sub>2</sub>B<sub>11</sub>H<sub>10</sub> (143 mg, 0.50 mmol) in THF (20 mL) under stirring at RT. The reaction was finished within 1 min. A saturated solution of [PPN]Cl in MeOH was added until the precipitation was complete. After washing with MeOH (3 × 2 mL), compound **4** was collected as a bright-orange solid (375 mg, 91% yield). X-ray-quality crystals were grown from a saturated solution in acetone at RT. <sup>1</sup>H NMR ([D<sub>6</sub>]acetone):  $\delta$  = 7.72 (m, 18H; PPN), 7.58 (m, 12H; PPN), 7.12 (m, 5H; BC<sub>6</sub>H<sub>5</sub>), 5.69 (t, *J* = 4.5 Hz, 1H; CH), 1.91 (m, 2H; CH<sub>2</sub>), 1.80 (m, 2H; CH<sub>2</sub>), 1.25 ppm (m, 2H; CH<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR ([D<sub>6</sub>]acetone):  $\delta$  = 148.0 (CH), 135.4, 134.6, 133.3, 133.2, 133.1, 130.5, 130.4, 130.3, 128.9, 127.5, 127.4, 126.6 (PPN and BC<sub>6</sub>H<sub>5</sub>), 40.3, 28.8, 18.9 ppm (CH<sub>2</sub>), cage-carbon atoms were not observed; <sup>11</sup>B NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 9.6 (1B), 7.7 (1B), –0.9 (4B), –17.3 (1B), –18.7 (2B), –22.6 ppm (2B); IR (KBr):  $\tilde{\nu}$  = 2523 cm<sup>–1</sup> (vs); elemental analysis calcd (%) for C<sub>48</sub>H<sub>52</sub>B<sub>11</sub>NP<sub>2</sub> (**4**): C 69.98, H 6.36, N 1.70; found: C 70.43; H 6.35, N 1.60.

Preparation of [1,2-[*o*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>](CH)-1,2-C<sub>2</sub>B<sub>11</sub>H<sub>11</sub>][PPN] (5)

The title compound was prepared as a bright-orange solid from 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>11</sub>H<sub>11</sub> (128 mg, 0.50 mmol) and *t*BuOK (56 mg 0.50 mmol) in THF (20 mL) at RT by using the same procedure as for compound **4**. Yield: 366 mg (92%); <sup>1</sup>H NMR ([D<sub>6</sub>]acetone):  $\delta$  = 7.73 (m, 18H; PPN), 7.57 (m, 12H; PPN), 6.94 (m, 2H; C<sub>6</sub>H<sub>4</sub>), 6.77 (d, *J* = 6.9 Hz, 1H; C<sub>6</sub>H<sub>4</sub>), 6.66 (d, *J* = 6.9 Hz, 1H; C<sub>6</sub>H<sub>4</sub>), 6.13 (s, 1H; CH), 3.48 ppm (s, 2H; CH<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR ([D<sub>6</sub>]acetone):  $\delta$  = 144.0 (CH), 134.6, 133.3, 133.2, 133.1, 130.5, 130.4, 130.3, 128.9, 128.0, 127.6, 127.5, 122.8 (PPN and C<sub>6</sub>H<sub>4</sub>), 46.1 ppm (CH<sub>2</sub>), cage-carbon atoms were not observed; <sup>11</sup>B NMR ([D<sub>6</sub>]acetone):  $\delta$  = 6.9 (1B), –0.2 (5B), –17.8 ppm (5B); IR (KBr):  $\tilde{\nu}$  = 2530 cm<sup>–1</sup> (vs); elemental analysis calcd (%) for C<sub>46</sub>H<sub>48</sub>B<sub>11</sub>NP<sub>2</sub> (**5**): C 69.43, H 6.08, N 1.76; found: C 69.54, H 6.31, N 1.61.

Preparation of [1,2-[*o*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>](CH)-3-Ph-1,2-C<sub>2</sub>B<sub>11</sub>H<sub>10</sub>][PPN] (6)

The title compound was prepared as a bright-orange solid from 1,2-[*o*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>]-3-Ph-1,2-C<sub>2</sub>B<sub>11</sub>H<sub>10</sub> (167 mg, 0.50 mmol) and *t*BuOK (56 mg 0.50 mmol) in THF (20 mL) at RT by using the same procedure as for

compound **4**. Yield: 392 mg (90 %); <sup>1</sup>H NMR ([D<sub>6</sub>]acetone): δ = 7.72 (m, 18H; PPN), 7.58 (m, 14H; PPN and BC<sub>6</sub>H<sub>5</sub>), 7.11 (m, 3H; BC<sub>6</sub>H<sub>5</sub>), 6.83 (m, 2H; C<sub>6</sub>H<sub>4</sub>), 6.58 (m, 2H; C<sub>6</sub>H<sub>4</sub>), 6.15 (s, 1H; CH), 3.25 ppm (s, 2H; CH<sub>2</sub>); <sup>13</sup>C[<sup>1</sup>H] NMR ([D<sub>6</sub>]acetone): δ = 143.9 (CH), 135.6, 134.6, 133.3, 133.2, 130.4, 130.3, 128.8, 127.9, 127.7, 127.5, 127.2, 122.7 (PPN; C<sub>6</sub>H<sub>4</sub> and BC<sub>6</sub>H<sub>5</sub>), 43.2 ppm (CH<sub>2</sub>), cage-carbon atoms were not observed; <sup>11</sup>B NMR ([D<sub>6</sub>]acetone): δ = 10.9 (1B), 7.1 (1B), 0.1 (2B), -2.0 (2B), -15.3 (1B), -17.4 (2B), -20.2 ppm (2B); IR (KBr): ν̄ = 2521 cm<sup>-1</sup> (vs); elemental analysis calcd (%) for C<sub>52</sub>H<sub>52</sub>B<sub>11</sub>NP<sub>2</sub> (**6**): C 71.64, H 6.01, N 1.61; found: C 71.71, H 5.97, N 1.53.

*Preparation of [1,2-[o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)]-1,2-C<sub>2</sub>B<sub>11</sub>H<sub>11</sub>][Li(THF)<sub>d</sub>] (**7**)*

A solution of 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>11</sub>H<sub>11</sub> (256 mg, 1.00 mmol) in THF (15 mL) and finely cut Li metal (7 mg, 1.00 mmol) were stirred at RT for 48 h to give a bright-yellow solution. Removal of the solvent afforded a yellow solid. Recrystallization from THF/*n*-hexane at RT gave compound **7** as yellow crystals (497 mg, 90 % yield). <sup>1</sup>H NMR ([D<sub>8</sub>]THF): δ = 6.87 (m, 2H; C<sub>6</sub>H<sub>4</sub>), 6.68 (d, *J* = 7.2 Hz, 1H; C<sub>6</sub>H<sub>4</sub>), 6.56 (d, *J* = 7.2 Hz, 1H; C<sub>6</sub>H<sub>4</sub>), 6.04 (s, 1H; CH), 3.47 ppm (s, 2H; CH<sub>2</sub>); <sup>13</sup>C[<sup>1</sup>H] NMR ([D<sub>8</sub>]THF): δ = 143.1 (CH), 127.8, 127.1, 126.9, 122.4 (C<sub>6</sub>H<sub>4</sub>), 46.4 ppm (CH<sub>2</sub>), cage-carbon atoms were not observed; <sup>11</sup>B NMR ([D<sub>8</sub>]THF): δ = 7.5 (1B), 0.3 (5B), -17.4 ppm (5B); IR (KBr): ν̄ = 2526 cm<sup>-1</sup> (vs); elemental analysis calcd (%) for C<sub>20</sub>H<sub>38</sub>B<sub>11</sub>LiO<sub>2.5</sub> (**7**-1.5 THF): C 54.06, H 8.62; found: C 54.18, H 8.95.

*X-ray Crystallography*

All of the single crystals were immersed in Paratone-N oil and sealed in thin-walled glass capillaries under an argon atmosphere. Data were collected at 293 K on a Bruker SMART 1000 CCD diffractometer by using MoK<sub>α</sub> radiation (0.71073 Å). An empirical absorption correction was applied by using the SADABS program.<sup>[19]</sup> All of the structures were solved by using direct methods and subsequent Fourier difference techniques and were refined anisotropically for all non-hydrogen atoms by using full-matrix least-squares techniques on *F*<sup>2</sup> with the SHELXTL program package.<sup>[20]</sup> For noncentrosymmetric structure **7**, the appropriate enantiomorph was chosen by refining Flack's parameter (*χ*) towards zero.<sup>[21]</sup> All

hydrogen atoms were geometrically fixed by using the riding model, so that a detailed discussion of the B-H distances was not warranted. Notably, the solid-state structure of compound **1** has crystallographically imposed mirror symmetry with the mirror plane passing through the C(12)B(3)B(10) and B(13) atoms, thus leading to indistinguishable cage-carbon atoms. Crystal data and details of the data collection and structure refinements are given in Table 2. CCDC 925566 (**1**), CCDC 925567 (**3**), CCDC 925568 (**4**), CCDC 925569 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

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Table 2. Crystal data and summary of data-collection and data-refinement parameters for compounds **1**, **3**, **4**, and **7**.

	<b>1</b>	<b>3</b>	<b>4</b>	<b>7</b>
formula	C <sub>41</sub> H <sub>46</sub> B <sub>11</sub> NP <sub>2</sub>	C <sub>42</sub> H <sub>48</sub> B <sub>11</sub> NP <sub>2</sub>	C <sub>48</sub> H <sub>52</sub> B <sub>11</sub> NP <sub>2</sub>	C <sub>52</sub> H <sub>100</sub> B <sub>22</sub> Li <sub>2</sub> O <sub>8</sub>
crystal size [mm]	0.50 × 0.40 × 0.30	0.40 × 0.30 × 0.30	0.40 × 0.30 × 0.20	0.20 × 0.10 × 0.10
<i>M<sub>w</sub></i>	733.6	747.7	823.8	1105.0
crystal system	orthorhombic	monoclinic	monoclinic	orthorhombic
space group	<i>Pbcm</i>	<i>P2<sub>1</sub>/c</i>	<i>C2/c</i>	<i>Pna2<sub>1</sub></i>
<i>a</i> [Å]	9.085(1)	12.794(1)	32.444(1)	19.642(2)
<i>b</i> [Å]	18.203(1)	17.317(1)	9.754(1)	15.127(2)
<i>c</i> [Å]	24.873(2)	18.353(1)	30.977(1)	11.638(1)
β [°]	90	97.12(1)	97.43(1)	90
<i>V</i> [Å <sup>3</sup> ]	4113.1(5)	4034.9(5)	9720.2(6)	3457.6(6)
<i>Z</i>	4	4	8	2
ρ <sub>calcd</sub> [mgm <sup>-3</sup> ]	1.185	1.231	1.126	1.061
λ(MoK <sub>α</sub> ) [Å]	0.71073	0.71073	0.71073	0.71073
2θ <sub>max</sub> [°]	50.0	50.0	50.5	50.0
μ [mm <sup>-1</sup> ]	0.137	0.141	0.123	0.062
<i>F</i> (000)	1536	1568	3456	1184
measured reflections	32794	39889	49722	18184
observed reflections [ <i>I</i> > 2σ( <i>I</i> )]	3718	7099	8808	6059
parameters	255	505	559	387
GOF on <i>F</i> <sup>2</sup>	1.071	1.017	1.047	1.029
final <i>R</i> indices	<i>R</i> <sub>1</sub> = 0.079	<i>R</i> <sub>1</sub> = 0.050	<i>R</i> <sub>1</sub> = 0.049	<i>R</i> <sub>1</sub> = 0.096
[ <i>I</i> > 2σ( <i>I</i> )]	<i>wR</i> <sub>2</sub> = 0.238	<i>wR</i> <sub>2</sub> = 0.119	<i>wR</i> <sub>2</sub> = 0.128	<i>wR</i> <sub>2</sub> = 0.261

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