

## NEW MULTIGRAM-SCALE PREPARATION OF 1,10-DICARBA-*closo*-DECABORANE

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*Dedicated to Professor Jaromír Plešek on the occasion of his 75th birthday in recognition of his outstanding contributions to the areas of borane chemistry.*

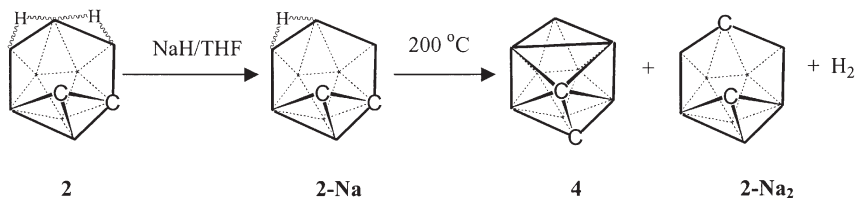
Ten vertex *p*-carborane, 1,10-C<sub>2</sub>B<sub>8</sub>H<sub>10</sub> (**1**), has been prepared in high yield from *nido*-carborane 5,6-C<sub>2</sub>B<sub>8</sub>H<sub>12</sub> (**2**) in one pot reaction by thermal dehydrogenation followed by skeletal rearrangement.

**Keywords:** Boranes; Carboranes; Ten-vertex; *nido*-Carborane; *p*-Carborane; *closo*-Carborane; Plešek oxidation; Rearrangements.

Carbaborane and borane *closo* clusters are considered to be three-dimensional aromatic compounds and are often regarded as inorganic analogues of benzene<sup>1</sup>. Twelve- and ten-vertex *closo*-dicarbaboranes with the carbon atoms in *para* positions are valuable synthetic tools for the preparation of liquid-crystalline materials<sup>2</sup>, molecular rods<sup>3</sup>, tinkertoys<sup>4</sup> or potential  $\pi$ -linkers for electronics materials<sup>5</sup> and non-linear optics<sup>6</sup>. The use of *p*-carboranes in the construction of molecular wires, an application that comes under the umbrella term "molelectronics", is currently under much study<sup>7</sup>. Such nanotechnology is a new field carrying a very large potential for the use of *p*-carboranes in modular construction. A long-term plan<sup>8,9</sup> is to develop these molecular modules into the construction of firmly connected regular two-dimensional grid shaped polymers with trigonal, square and hexagonal lattices.

The synthesis and electrochemistry of a new star-type trigonal connector that uses the twelve-vertex *p*-carborane as the basic molecular unit has already been published<sup>10</sup>. The electrochemical behavior of a similar compound with ten-vertex *p*-carborane **1** has also been studied<sup>11</sup> and it is our intention to publish its synthesis soon<sup>12</sup>.

However, the use of ten-vertex *p*-carborane<sup>13</sup>, 1,10-C<sub>2</sub>B<sub>8</sub>H<sub>10</sub> (**1**) is constrained by its limited availability. So far, the best methods for its preparation have started from *nido*-carborane<sup>14</sup>, 5,6-C<sub>2</sub>B<sub>8</sub>H<sub>12</sub> (**2**). The first method is based on the dehydroisomerization of **2** via the *m*-carborane<sup>13</sup>, 1,6-C<sub>2</sub>B<sub>8</sub>H<sub>10</sub> (**3**), achieved by the passing of carborane **2** through an evacuated quartz tube at 550 °C. A mixture of the resulting carboranes **1** and **3** is repeatedly sublimed in a quartz tube at 350 °C until compound **1** is obtained exclusively. The amount of carborane **1** that can be prepared by this method is limited by the size of the quartz apparatus. In the other method, carborane **2** can be converted to its sodium salt **2-Na**, which disproportionates to form the carborane *closo*-1,2-C<sub>2</sub>B<sub>8</sub>H<sub>10</sub> (**4**) and the disodium salt *nido*-6,9-C<sub>2</sub>B<sub>8</sub>H<sub>10</sub><sup>2-</sup> (**2-Na<sub>2</sub>**), upon vacuum sublimation at 200 °C (Scheme 1, ref.<sup>15</sup>).



SCHEME 1

The yield of *ortho*-carborane<sup>14</sup>, 1,2-C<sub>2</sub>B<sub>8</sub>H<sub>10</sub> (**4**) is only 50% and **4** subsequently undergoes almost quantitative rearrangement to *para*-carborane **1** at 380 °C. The overall yield of **1** can be raised by additional oxidation of the dianion **2-Na<sub>2</sub>** with CuCl<sub>2</sub>, leading to the formation of a mixture of all three isomeric carboranes<sup>10</sup> **1**, **3** and **4**. This mixture can be then converted to isomer **1**. Unfortunately, this reaction also produces side products consisting of a complex and so far inseparable mixture of chloro derivatives, *closo*-C<sub>2</sub>B<sub>8</sub>H<sub>9</sub>Cl and oligomeric compounds of the *closo*-(C<sub>2</sub>B<sub>8</sub>H)<sub>2</sub>(C<sub>2</sub>B<sub>8</sub>H<sub>8</sub>)<sub>*n*</sub> type<sup>16</sup>.

## EXPERIMENTAL

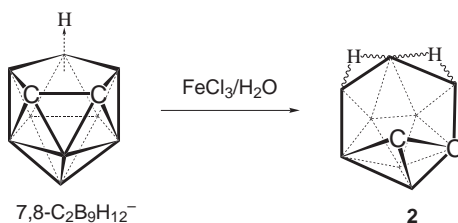
All reactions were carried out in a stainless pressure autoclave. The purity of the products was checked by analytical TLC on Silufol (Kavalier, silica gel on aluminium foil; detection by iodine vapor, followed by spraying with 2% aqueous AgNO<sub>3</sub>) and by NMR spectroscopy on a Varian XL-500 spectrometer. <sup>1</sup>H, <sup>13</sup>C and <sup>11</sup>B NMR spectra were obtained in CDCl<sub>3</sub> and referenced to the solvent (<sup>1</sup>H and <sup>13</sup>C) or to B(OMe)<sub>3</sub> (18.1 ppm). Low-resolution mass spectra were obtained using a Magnum GC/MS ion trap (Finnigan MAT, U.S.A.). Individual components of the reaction mixture were separated on an on-line Varian 3400 gas chromatograph equipped with a Varian 1075 injector. A DB-ms capillary column (JW Scientific, U.S.A., 30 m × 0.25 mm, 0.25 μm film thickness and He (99.96%) carrier gas 36 cm/s and 60 °C were used. Carborane **2** was synthesized by the Plešek oxidation<sup>14</sup> of anion 7,8-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>.

Dicarbadeccaborane *closo*-1,10-C<sub>2</sub>B<sub>8</sub>H<sub>10</sub> (**1**)

In a typical experiment, freshly sublimed *nido*-carborane **2** (12.3 g, 0.1 mol) was placed under an argon atmosphere into a stainless autoclave and heated at 380 °C overnight. After cooling down, the autoclave was connected to dry-ice finger sublimator and compound **1** was sublimed out at 30 °C. The yield of **1** was 10.3 g (86%). M.p. 158–159 °C, literature<sup>13</sup> gives 161–162 °C. <sup>11</sup>B NMR: δ -13.73 ppm (d),  $J_{\text{BH}} = 165$  Hz (in agreement with ref.<sup>17</sup>; -12.7 ppm resp. 161 Hz in ref.<sup>18</sup>). <sup>1</sup>H NMR: δ 2.02 ppm (8 H, B-H) (7.0 ppm (2 H, C-H) in ref.<sup>18</sup>). <sup>13</sup>C NMR: δ 102 ppm (d,  $J_{\text{CH}} = 188$  Hz) (102.9 ppm in ref.<sup>19</sup>).

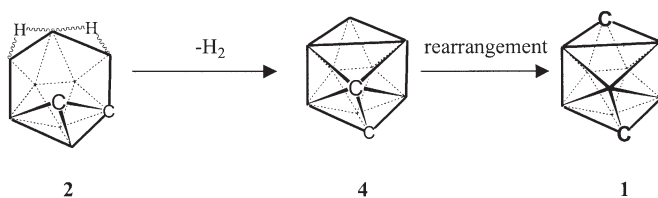
## RESULTS AND DISCUSSION

In respect of the fact that carborane **2** is easily accessible from the 7,8-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub><sup>-</sup> anion by the well known Plešek oxidation route<sup>14</sup> (Scheme 2), we have tried to avoid the low-yield yielding disproportionation<sup>9</sup> of **2** *via* salt **2**-Na (Scheme 1) and the two step dehydroisomerization of carborane **2** at 550 °C (ref.<sup>13</sup>) which is at best rather dangerous.



SCHEME 2

Therefore, we heated carborane **2** in a stainless autoclave at 380 °C overnight. The amount of carborane **2** utilizable in the reaction is almost unlimited and the yield of carborane **1** is very high (more than 85%). A simple proposed mechanism is shown in Scheme 3 (simplified structures: the C vertices stand for /CH/ units and the unmarked vertices denote /BH/ groups). In the first step dehydrogenation to carborane **4**, followed by a *dsd*-type rearrangement<sup>20</sup> is assumed to give isomer **1** with the most stable arrangement of the {CH} vertices.



SCHEME 3

When using a pressure stainless tube sealed with a copper gasket for the reaction, the yield of carborane **1** dramatically decreased whereas that of liquid oligomers of the  $(C_2B_8H_9)_2(C_2B_8H_8)_n$  type increased. The presence of these oligomers seems to indicate involvement of a Cu-assisted radical-chain mechanism.

A new multigram-scale preparation of *p*-carborane **1** avoids the need to use expensive quartz apparatus and high temperatures in its synthesis. Presented here is a safe new method that engenders carborane **1** in high yield thus permitting its use in further applications.

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