

## Li<sup>+</sup>-Induced $\sigma$ -Bond Metathesis: Aryl for Methyl Exchange on Boron in a Methylated Monocarbadodecaborate Anion

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We report a formal  $\sigma$ -bond metathesis between the B–CH<sub>3</sub> bond in position 12 of the lithium monocarbadodecaborate derivative **1a** and the C–Si(CH<sub>3</sub>)<sub>3</sub> bond in *p*-bromophenyltrimethylsilane, which produces a salt of the arylated carborate anion **2** and Si(CH<sub>3</sub>)<sub>4</sub> (Scheme 1). This reaction requires the presence of active Li<sup>+</sup> cations: it occurs neither when 12-crown-4 is added to the lithium salt **1a** nor with the cesium salt **1b**.

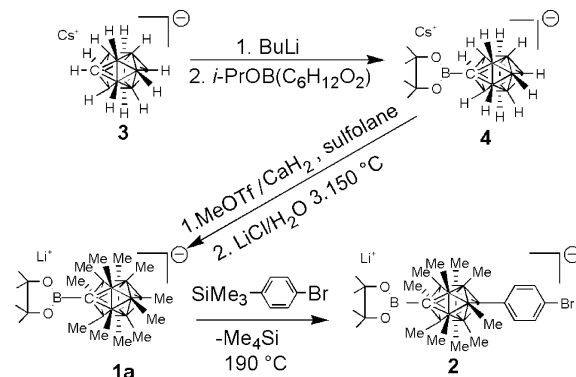
Highly methylated derivatives of the anion **3** arylated in positions 1 and 12 are of interest as precursors to charged and/or radical-containing rodlike oligomers and polymers reminiscent of earlier neutral closed-shell structures<sup>1,2</sup> based on *p*-dicarbadodecaborane. A compound of this general type containing a single unalkylated carborate anion has recently been reported,<sup>3</sup> but for our purposes permethylation<sup>4</sup> of the borate anion cage is desirable to stabilize the oxidized neutral radical<sup>5</sup> form and to minimize anion–cation interactions.<sup>6–8</sup>

Although 1-aryl derivatives of **3** are presently accessible by three different routes (Brelloch's<sup>9</sup> reaction,<sup>3,10</sup> phenylcarbene insertion,<sup>11,12</sup> and Negishi<sup>13</sup> coupling<sup>14</sup>) and 12-aryl derivatives are accessible from 12-iodinated **3** by Kumada<sup>15</sup> coupling,<sup>16</sup> we found that their subsequent methylation yields complex mixtures since both the boron cage and the aryl group react. When the methyl substituents were introduced before the aryl, the subsequent Kumada coupling in position 12 failed, possibly due to steric hindrance.

The present approach to permethylated aryl derivatives of **3** has been inspired by Heřmánek's mechanistic concept of electrophile-induced nucleophilic substitution<sup>17</sup> and prompted by two types of observation: (i) Density functional theory calculations<sup>18</sup> suggest that charge-compensated carborane ylides CB<sub>11</sub>R<sub>11</sub> with eleven ligands, a negative charge on the cage, and a positively charged carbonium or boronium center at the 12th vertex are viable reaction intermediates, and experimental support for this is beginning to accumulate. Thus, attempts to generate R<sub>3</sub>Si<sup>+</sup> or (CH<sub>3</sub>)<sub>3</sub>C<sup>+</sup> in the presence of CB<sub>11</sub>Me<sub>12</sub><sup>−</sup> result in a transfer of the methyl group in position 12 to silicon or carbon with formation of a carborane that reacts as expected for the boronium ylide CB<sub>11</sub>Me<sub>11</sub> methylated in positions 1–11,<sup>18</sup> and the exposure of 1-(BrCH<sub>2</sub>CH<sub>2</sub>)CB<sub>11</sub>Me<sub>11</sub><sup>−</sup> to solvolytic conditions yields ethylene and products expected from the carbonium ylide CB<sub>11</sub>Me<sub>11</sub> methylated in positions 2–12.<sup>19</sup> (ii) The lithium cation in LiCB<sub>11</sub>Me<sub>12</sub> is a strong Lewis acid catalyst, while the catalytic activity of other alkali metal cations, if any, is much weaker.<sup>20</sup>

We have therefore examined reactions of CB<sub>11</sub>Me<sub>12</sub><sup>−</sup> and HCB<sub>11</sub>Me<sub>11</sub><sup>−</sup> with benzene and other arenes. Indeed, in the lithium salts, multiple substitutions of methyl with aryl groups start to take place above ~100 °C, whereas the cesium salts are inert. The reactivity of **1a** is lower. Heating to 190 °C is required, and single

Scheme 1



substitution in position 12 dominates. The difference is attributed to partial deactivation of Li<sup>+</sup> by coordination with the oxygen atoms of the dioxaborole ring of **1a**. In the presence of the efficient Li<sup>+</sup> sequestering agent, 12-crown-4, no products were detectable from **1a** even after 4 days at 190 °C. An attempt to suppress the formation of positional isomers on the arene by the use of the ipso-directing trimethylsilyl substituent was successful in that the reaction of **1a** with *p*-bromotrimethylsilylbenzene provided a single major product **2** in a useful yield (Scheme 1). The SiMe<sub>4</sub> byproduct was identified by GC/MS and <sup>1</sup>H NMR.

Complete assignment of the <sup>1</sup>H, <sup>13</sup>C, and <sup>11</sup>B NMR spectra of **1**, **2** and **4** required the use of gHSQC,<sup>21</sup> gHMBC,<sup>22</sup> gHMBC,<sup>23</sup> and 2-D <sup>11</sup>B–<sup>11</sup>B COSY<sup>24</sup> (Supporting Information). The structure of **2** was further secured by a single-crystal X-ray diffraction analysis (Figure 1). The accommodation of the relatively hindered dioxaborolyl and aryl substituents is of interest. Their planes are both aligned nearly exactly at 90° to the planes of the boron pentagons B(2–6) and B(7–11). The projection of the OBO plane into the former pentagon makes an angle of 4° with one of its edges, the projection of the aryl plane into the latter pentagon makes an angle of 7° with one of its edges, and the dihedral angle between the two

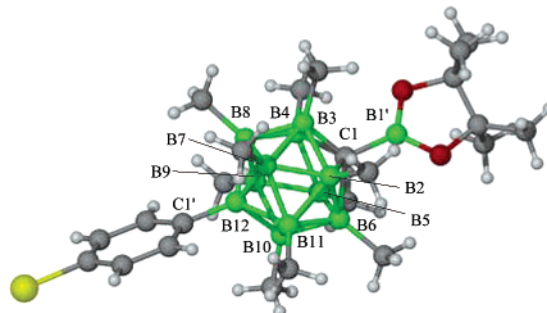


Figure 1. Single-crystal X-ray diffraction structure of the anion in [Na(H<sub>2</sub>O)(CH<sub>3</sub>CN)]<sup>+</sup>[1-(C<sub>6</sub>H<sub>12</sub>O<sub>2</sub>)B-12-(4'-Br-C<sub>6</sub>H<sub>4</sub>)-CB<sub>11</sub>Me<sub>10</sub>]<sup>−</sup>.

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substituent planes is 52°. This suggests that minima in the 10-fold barrier for the rotation of a planar substituent in the free anion occur when its plane is parallel to one of the edges of the proximate pentagon of boron atoms. The length of the B12–C1' bond to the phenyl substituent is the same as those to the methyl carbons (1.59–1.60 Å); otherwise, the bond lengths and valence angles in **2** are unexceptional.

The scope and mechanism of this Li<sup>+</sup>-induced B-arylation reaction are presently under examination. The formal  $\sigma$ -bond metathesis probably starts with an electrophilic complexation of the Li<sup>+</sup> cation to the carbon of the methyl group in position 12, most likely backside as in the reported<sup>7,8,25</sup> complexation of other metal cations. This could activate the B–C bond toward true  $\sigma$ -bond metathesis with the aromatic Si–C bond to form new B–C and Si–C bonds (similar B–C bond forming metathesis with aromatic C–H bonds is known for some transition metal containing structures<sup>26</sup>). Alternatively, it could lead to an S<sub>E</sub>2 substitution on the methyl carbon, generating CH<sub>3</sub>Li and the boronium ylide 1-(C<sub>6</sub>H<sub>12</sub>O<sub>2</sub>)B–CB<sub>11</sub>Me<sub>10</sub> with a missing ligand and a cationic center in position 12, which could then react with the trimethylsilylated arene by insertion into the Si–C bond, with a transition-state geometry suggested by Figure 1, or perform an electrophilic aromatic substitution in the ipso position via a much more hindered transition state. Either way, a subsequent attack by CH<sub>3</sub>Li on the silicon center would lead to the observed products and recovery of the Li<sup>+</sup> catalyst.

**Acknowledgment.** This work was supported by DARPA/ONR (N-00014-01-10726), the National Science Foundation (CHE-0140478 and CHE-0131003), and the Ministry of Education of the Czech Republic (LN00A028). We are grateful to Mr. Michal Valášek for technical assistance and to Dr. Richard Shoemaker for the recording and analysis of the NMR spectra.

**Supporting Information Available:** Experimental details for the synthesis of **2** (PDF) and its X-ray diffraction analysis (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA0387857