

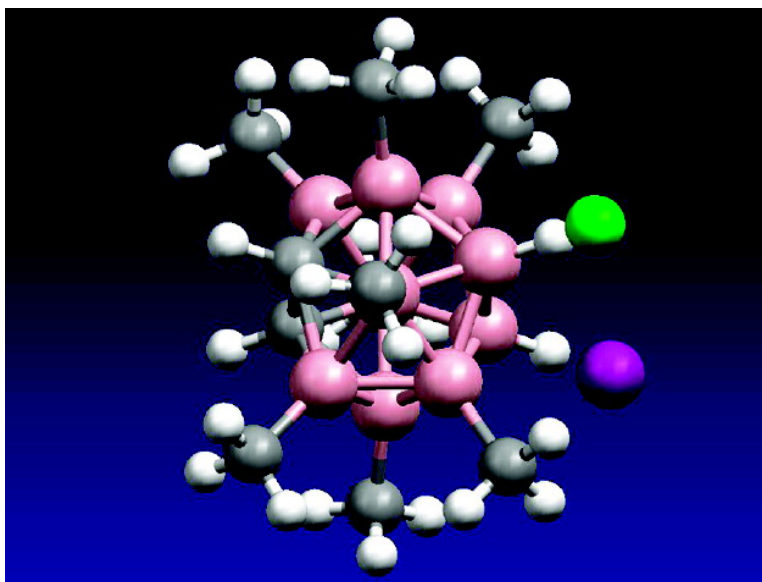
Communication

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## Are Methyl Groups Electron-Donating or Electron-Withdrawing in Boron Clusters? Permethylation of *o*-Carborane

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The concept that methyl groups attached to carbon atoms, heteroatoms, or  $\pi$ -electron systems are electron donors (+I) is widely accepted in organic chemistry. This idea is also assumed in boron cluster chemistry, most probably as a consequence of the many common reactions in both areas.<sup>1</sup> However, we show in this paper through partial methylation on *o*-carborane (**1**, see Figure 1), supported by theoretical calculations, that the methyl groups, contrary to the common belief, are electron-withdrawing (-I) in boron clusters. This result should not be strange, however, taking into account the difference in electronegativity between C (2.5) and B (2.0). In the past decade, much effort has been dedicated to the alkylation or peralkylation of *closo*-borates, the monocarborane anion, and the dicarbaboranes.<sup>2,3</sup> Good success has been obtained with anionic clusters, but much less with the dicarbaboranes.<sup>1</sup>

This parallels the rates of cluster halogenation, which decrease in the order  $[\text{B}_{12}\text{H}_{12}]^{2-} > [\text{CB}_{11}\text{H}_{12}]^- > \text{C}_2\text{B}_{10}\text{H}_{12}$ .<sup>4</sup> The halogenation rate decreases with a diminishing cluster charge. Zakharkin et al.<sup>5a</sup> and Plešek et al.<sup>5b</sup> independently had interpreted the sequential partial alkylation in **1** as a process that follows the decreasing electron density of the boron atoms. In **1** this sequence correlates with the distance to the cluster carbon atoms. The farthest from the carbon boron atoms and the richest in electron density are B(8,9,10,12); the closest are B(3,6), which are poorer in electron density. Therefore, positions B(8,9,10,12)<sup>6</sup> should be the first to be attacked by electrophiles.<sup>7</sup>

Hawthorne et al. have achieved maximum methylation starting from *o*-carborane (**1**) to get 4,5,7,8,9,10,11,12-Me<sub>8</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>4</sub> (**2**).<sup>3g</sup> Methylation at B(3,6) was not observed. Following the halogenation trend indicated before, if methyl groups were +I, electrophilic attack would be enhanced as electronic charge on the cluster was building up and B(3,6) would be methylated. The non-methylation of B(3,6) led us to believe that Me groups in boron clusters were not electron-donating. We have examined Mulliken charges on boron methyl-substituted *o*-carborane clusters at the B3LYP/6-31G\* level of theory<sup>8</sup> on **1**,<sup>9</sup> 3,6-Me<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (**3**), and 3-Me-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> (**4**). No noticeable changes are found when comparing the HOMO, HOMO-1, and HOMO-2 molecular orbitals of **1**, **3**, and **4**. A distinguishing value between **1**, **3**, and **4** concerns cluster-only total charge (CTC).<sup>10</sup> This becomes more positive for higher numbers of Me groups on boron atoms, each Me group increasing the CTC by approximately 0.18 unit.<sup>11</sup> Considering that the CTC for **1** is -0.766, for **2** it would be near +0.67 if the process was cumulative. Indeed this is the case, as this value compares well with +0.769 for **2**, as displayed in Table 1. The situation would be reversed if the Me group had been +I.

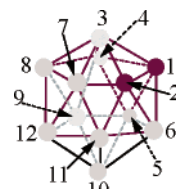


Figure 1. Vertex numbering in 1,2-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>, *o*-carborane (**1**).

Table 1. Calculated Mulliken Charges with B3LYP/6-31G\* on Some Methylated *o*-Carborane Derivatives

B3LYP/6-31G*	1	2	3	5(H,H)
C1	-0.331	-0.375	-0.354	-0.401
C2	-0.331	-0.378	-0.354	-0.399
B3	0.017	-0.064	<b>0.245</b>	<b>0.149</b>
B4	0.002	<b>0.210</b>	-0.008	<b>0.234</b>
B5	0.002	<b>0.212</b>	-0.008	<b>0.214</b>
B6	0.017	-0.068	<b>0.245</b>	<b>0.151</b>
B7	0.002	<b>0.210</b>	-0.008	<b>0.218</b>
B8	-0.012	<b>0.254</b>	-0.006	<b>0.306</b>
B9	-0.061	<b>0.146</b>	-0.067	-0.127
B10	-0.012	<b>0.259</b>	-0.006	<b>0.312</b>
B11	0.002	<b>0.221</b>	-0.008	<b>0.216</b>
B12	-0.061	<b>0.142</b>	-0.067	-0.126
cluster-only total charge (CTC)	<b>-0.766</b>	<b>0.769</b>	<b>-0.396</b>	<b>0.747</b>

Methyl groups on boron are -I in electron-deficient boron cages. This interpretation explains "anomalies" in boron cluster chemistry as had been suggested in the stabilization of tetra-decker metal-lacarboranes.<sup>12</sup> In agreement with the -I character of B-Me is the <sup>11</sup>B NMR of methyl-substituted boron clusters. If methyl groups were +I, an upfield resonance shift would be expected on the alkyl-substituted boron atom with regard to the parent unsubstituted cluster. But this is not the case. With no exception, chemical shifts for B-C in clusters are shifted to lower field,<sup>3a,c,e,g,i</sup> as happens for B-F, B-Cl, and B-Br.<sup>13</sup> The same explanation is valid for the <sup>1</sup>H and <sup>13</sup>C NMR of methyl-substituted boron clusters. For Me (-I) groups connected to boron, the proton and carbon resonances should become more shielded and should be found at higher field.<sup>3d,g,h</sup> Indeed this is the case, and B-CH<sub>3</sub> resonances at -2.9 ppm are observed, for instance, in **2**.<sup>3g</sup>

Further evidence is found in the intermolecular Sn...H<sub>3</sub>C, M...H<sub>3</sub>C (M = Ge, Sn, Pb), Zr...H<sub>3</sub>C, and Ag...H<sub>3</sub>C interactions observed in [*n*-Bu<sub>3</sub>Sn][CB<sub>11</sub>Me<sub>12</sub>],<sup>14a</sup> [Me<sub>3</sub>M][CB<sub>11</sub>Me<sub>12</sub>] (M = Ge, Sn, Pb),<sup>14b</sup> [ZrCp<sub>2</sub>Me][CB<sub>11</sub>HMe<sub>11</sub>],<sup>14c</sup> and [Ag(HCB<sub>11</sub>Me<sub>11</sub>)-(PPh<sub>3</sub>)]<sup>14d</sup> that can be explained on the basis of the Me electron enrichment in B-Me.

From the cumulative and large CTC value for **2**, it may appear that boron permethylation in **1** is severely hampered due to the -I effect of Me. We have also shown that CTC values are comparable for different isomers. To prove the relevance of cumulative CTC in the permethylation process, we decided to use **3**<sup>15</sup> as starting material, as it is complementary to **2** in terms of Me substituents.

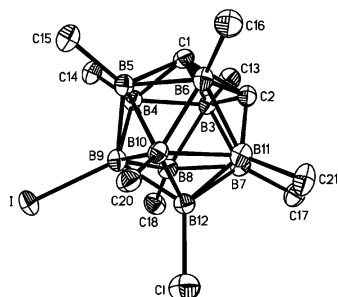
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**Figure 2.** Perspective view of 9-X-12-Y-3,4,5,6,7,8,10,11-(CH<sub>3</sub>)<sub>8</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>2</sub> (X, Y = I, Cl) with 30% ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å): C(1)–C(2) 1.632(4), B(9)–I 2.159(4), B(12)–Cl 1.816(4), B–C<sub>Me</sub> 1.561(5)–1.649(5).

The methylation procedure on **3** is similar to that for **2**.<sup>3g</sup> Treatment of **3** with MeI/AlCl<sub>3</sub> at reflux for 2 days produces **5**, whose <sup>11</sup>B NMR spectrum indicates a mixture of species. The <sup>11</sup>B{<sup>1</sup>H} NMR spectrum was practically identical, suggesting that all or most of the BH's had been substituted. The <sup>1</sup>H NMR spectrum confirmed this observation. The carborane C–H region between 2.6 and 4.6 ppm was very informative. Resonances due to C–H (in ppm with relative areas in parentheses) were observed at 4.47 (2.97), 3.16 (1), 2.99 (1), 3.04 (5), 2.94 (5), 2.77 (2.65), and 2.74 (2.65). This indicates that four dominant species, one of them being symmetrical, are formed in this reaction. The most abundant compound displays its cluster C–H's at 3.04 and 2.94 ppm, the second in importance at 2.77 and 2.74 ppm, the third at 4.47 ppm (this being most probably symmetrical), and the least abundant at 3.16 and 2.99 ppm. The abundances would be approximately 49%, 26%, 15%, and 10%.

Suitable colorless crystals were obtained from hexane. The crystal structure of **5**<sup>16</sup> indicates that octa boron methyl substitution of the C<sub>2</sub>B<sub>10</sub> icosahedron at positions 3, 4, 5, 6, 7, 8, 10, and 11 has taken place. As for **2**, there are only eight Me groups on the cluster. The remaining positions, B(9) and B(12), are each partially occupied by halogen and hydrogen atoms. Site occupation parameters (SOP) for I and H, connected to B(9), are 0.707(3) and 0.293(3), respectively, while the position at B(12) is partially occupied by Cl (SOP = 0.566(5)) and H(12) (SOP = 0.434(5)). The crystal's components are concordant with the average composition of the solid studied by NMR. It is made of four compounds corresponding to 9-X-12-Y-3,4,5,6,7,8,10,11-Me<sub>8</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>2</sub>, named **5**(I,Cl), **5**(I,H), **5**(H,H), and **5**(H,Cl) depending on the nature of X and Y, and with an overall formula 9-I<sub>0.707</sub>H<sub>0.293</sub>-12-Cl<sub>0.566</sub>H<sub>0.434</sub>-3,4,5,6,7,8,10,11-Me<sub>8</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>2</sub> (**5**).<sup>17</sup> X-ray structural analysis has permitted us to identify the species in solution; in order of abundance they are **5**(I,Cl) > **5**(I,H) > **5**(H,H) > **5**(H,Cl) (Figure 2).

The existence of three species with H in the 9,12 positions, **5**(I,H), **5**(H,H), and **5**(H,Cl), while all other B positions are methyl substituted could induce one to reason that positions 9 and 12 are not the first to suffer electrophilic attack in **3**. To discard this possibility, a careful time monitoring of the methylation reaction by <sup>11</sup>B NMR has permitted us to find a synthetic procedure for 3,6,8,9,10,12-Me<sub>6</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>6</sub> in 68% yield. This experiment proves that B(9) and B(12) are among the first four boron positions to be methylated. There is no evidence indicating at which stage of the methylation process the attack by other nucleophiles to the B(9)–Me and B(12)–Me groups takes place, but what seems clear from this work is that the cluster evolves to remove the high load of positive charge by incorporating groups that either are less electron-withdrawing or that, by back-donation, can refill the cluster of electron density. Substitution of antipodal to cluster carbon B–Me group by nucleophiles had been observed earlier in methyl derivatives of [CB<sub>11</sub>Me<sub>12</sub>]<sup>–</sup>.<sup>18</sup>

The main conclusion of this work is that methyl groups are electron-withdrawing when bonded to boron in boron clusters. For the particular case of neutral carboranes, methyl substitution produces a build-up of positive charge that prevents permethylation. Most probably this conclusion can be extended to any substituent generating B–C bonds.

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**Supporting Information Available:** Table of Mulliken charges on related boron methylated *o*-carborane derivatives; computational chemistry and theoretical methods; tables showing examples of methyl deshielding effect on boron in <sup>11</sup>B NMR for *o*-, *m*-, and *p*-dicarboranes; monoanionic and dianionic species; crystallographic data; and experimental preparation of **5** (PDF, CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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