

# A STUDY OF REDUCTIVE CAGE-OPENING PROCESS WITH CONCOMITANT METALATION OF THE RESULTING CARBORANE LIGAND

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## ABSTRACT:

An overview of the syntheses, structures, and reactivity of the compounds formed by the incorporation of a number of d- and f-block metals into C<sub>2</sub>B<sub>4</sub>- and C<sub>2</sub>B<sub>9</sub>-carborane cages have been presented. In addition, the development of a safe, bench-scale preparation of the toxic and commercially unavailable polyhedral borane synthon, namely pentaborane(9), has also been described. Thus, this report discusses the latest developments leading to a systematic synthetic approach to a number of carborane precursors and the subsequent reaction chemistry in the formation of a number of “carbons-apart” metallocarboranes.

**KEYWORDS:** Reductive, Cage-Opening Process, Metalation, Carborane Ligand, structures, pentaborane

## INTRODUCTION

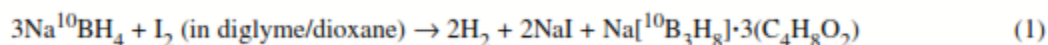
There has been extensive research reported on the chemical and structural properties of the metallocarboranes in the pentagonal bipyramidal (MC<sub>2</sub>B<sub>4</sub>) and the icosahedral (MC<sub>2</sub>B<sub>9</sub>) cage systems [1]. These complexes are generally synthesized by the reaction of the mono- or dianions of the nido-C<sub>2</sub>B<sub>4</sub> or C<sub>2</sub>B<sub>9</sub> carboranes with suitable metal reagents. Much of the emphasis for

these studies comes from the fact that the two nido-carboranes have 6  $\pi$ -electrons delocalized on a C<sub>2</sub>B<sub>3</sub> open pentagonal face that are very similar to the primary metal-bonding orbitals of the cyclopentadienide ligand, [C<sub>5</sub>H<sub>5</sub>]<sup>-</sup>. Our research in this area has involved synthetic, structural, reactivity, and theoretical studies on the full and half-sandwich metallocarboranes derived from the interactions of [nido-2-(SiMe<sub>3</sub>)-n-(R)-2,nC<sub>2</sub>B<sub>4</sub>H<sub>4</sub>] <sup>2-</sup> [n = 3, 4; R = SiMe<sub>3</sub>, n-Bu, t-Bu, Me, H] with main group [2], d-group, [3] and f-group metals [4]. One of the greatest factors in promoting the study of the small-cage C<sub>2</sub>B<sub>4</sub> carborane systems was the almost limitless supply of the pentaborane(9) (B<sub>5</sub>H<sub>9</sub>), obtained from an extensive U.S. government surplus, which can then be reacted with a suitable alkyne to form the carborane. At present, that source is no longer available, nor is there a commercial source to take its place [5]. In order for research to continue in this area, a new, convenient, and safe method of producing the pentaborane(9) must be developed. Ideally, what is desired is a one-pot method of generating pentaborane(9) from a readily available starting material, such as NaBH<sub>4</sub>, which could then further react with the appropriate alkyne to generate, in situ, the corresponding small-cage carborane. Therefore, a significant effort was made to investigate an alternative, safe, and convenient method of producing pentaborane(9) starting from readily available boric acid. Although the production of carborane from NaBH<sub>4</sub>, without the isolation of pentaborane, was not yet fully accomplished, the pentaborane synthesis by oxidative cage fusion of [B<sub>3</sub>H<sub>8</sub>]<sup>-</sup> anion was exemplified as the first step toward reaching the desired synthetic goal. In search for alternative carborane ligands, we embarked on the construction of C(cage)-appended alkyl- and silylamido- and alkyloxy-derivatives of the larger C<sub>2</sub>B<sub>9</sub>-cage systems and to investigate their reactivity toward group 4 and group 14 metals to prepare metallocarboranes with new geometries as potential catalysts or their precursors. In addition, a new methodology for the reductive cage opening of the closocarboranes with in situ metalation to form the corresponding stable half- or full-sandwich metallocarborane species were explored.

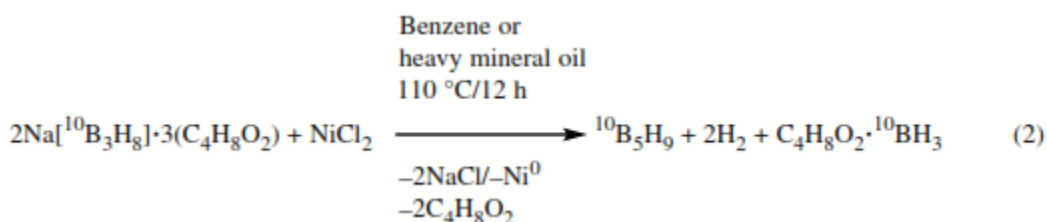
### **Synthesis of 10B-enriched pentaborane(9) from boric acid and its conversion to nido-10B10H14 and anti-10B18H22**

Pentaborane(9) has already been proven to be an important synthon for a number of higher polyhedral borane cages, including [B<sub>9</sub>H<sub>14</sub>]<sup>-</sup> [6], [B<sub>11</sub>H<sub>14</sub>]<sup>-</sup> [7], [B<sub>12</sub>H<sub>12</sub>]<sup>2-</sup>, and other cage-expanded borane anions, [8] and the neutral decaborane, B<sub>10</sub>H<sub>14</sub> [9]. The corresponding

$^{10}\text{B}$ -enriched species are the precursors for a number of potential boron drugs for use in the clinical trials using boron neutron capture therapy (BNCT). Since there is no commercial source available for any of these species with the exception of the most expensive  $^{10}\text{B}^{10}\text{H}_{14}$  [10], a convenient synthesis for hitherto unisolated  $^{10}\text{B}$ -enriched pentaborane(9) has an obvious appeal. It is this incentive that led us to explore alternative routes to  $^{10}\text{B}$ -enriched polyhedral boranes starting from readily available boric acid,  $\text{H}_3\text{BO}_3$ . Specifically, the  $^{10}\text{B}$ -enriched boric acid,  $\text{H}_3\text{BO}_3$ , was converted to the corresponding sodium borohydride,  $\text{Na}^{10}\text{BH}_4$ , in essentially quantitative yields, by using slightly modified literature methods that involve the formation of butyl borate,  $(n\text{-OBu})_3\text{B}$ , first and then reacting it with  $\text{NaH}$  in mineral oil at  $250\text{ }^\circ\text{C}$  [11,12]. The subsequent oxidation reaction of  $\text{Na}^{10}\text{BH}_4$  with  $\text{I}_2$  in diglyme, followed by the addition of dioxane during the purification step, gave the dioxane-complexed sodium salt of octahydrotriborate ( $-1$ ),  $\text{Na}[\text{B}_3\text{H}_8] \cdot 3(\text{C}_4\text{H}_8\text{O}_2)$ , in almost quantitative yields (see eq. 1) [13].

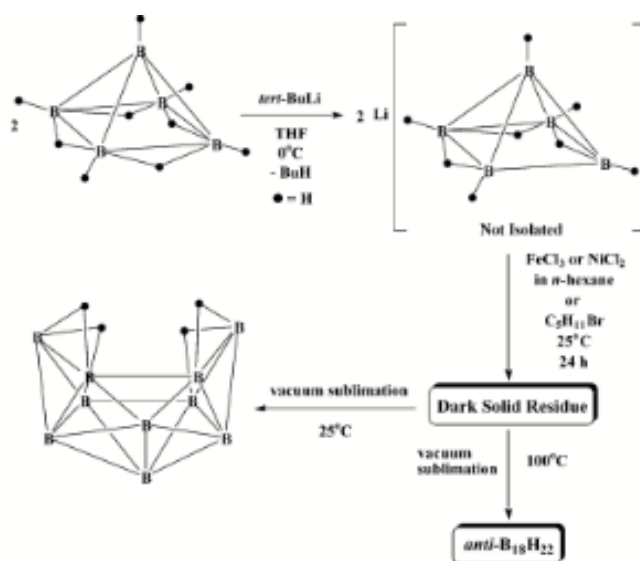


Treatment of  $\text{Na}[\text{B}_3\text{H}_8] \cdot 3(\text{C}_4\text{H}_8\text{O}_2)$  with  $\text{NiCl}_2$  in anhydrous benzene or heavy mineral oil at  $110\text{ }^\circ\text{C}$  (see eq. 2) gave the corresponding  $^{10}\text{B}_5\text{H}_9$  as the first isolated  $^{10}\text{B}$ -enriched pentaborane(9) in a laboratory environment [14]. Although there have been a number of other methods for the preparation of natural  $\text{B}_5\text{H}_9$ , the reaction written in eq. 2 is by far the most convenient and straightforward method of choice to date.



Since the  $^{10}\text{B}$ -enriched pentaborane is the only borane product of high volatility, its safe production, easy isolation, and storage in heavy mineral oil make this method most attractive to not only those who work with small-cage ( $\text{C}_2\text{B}_4$ ) carboranes and metallocarboranes, but also to the laboratories that did not have the access to this material previously. Nonetheless,  $^{10}\text{B}$ -enriched decaborane,  $^{10}\text{B}^{10}\text{H}_{14}$ , is the key chemical in preparing almost all of the C(cage)-substituted bio-boron molecules that are being investigated as boron drugs for BNCT clinical

trials in the United States and the world. This incentive led us to investigate an alternative route for the synthesis of 10B10H14, from 10B5H9 that can be prepared as described above. Although the synthetic methodology is identical to that used for anti-10B18H22 except for the oxidizing agent (Scheme 1), the room-temperature, high-vacuum sublimation of the product, instead of heating it to 100 °C, produced pure 10B10H14 in over 50 % yield. The conversion of natural pentaborane(9) to decaborane(14) has been previously demonstrated by Brewer and Grimes using the iron(II)- and iron(III) chloride-mediated cage fusion reactions. Thus, this work constitutes the first systematic synthetic approach to pentaborane(9) and decaborane(14) of both natural and 10B-enriched analogs and to their cage-expanded neutral and anionic borane species.

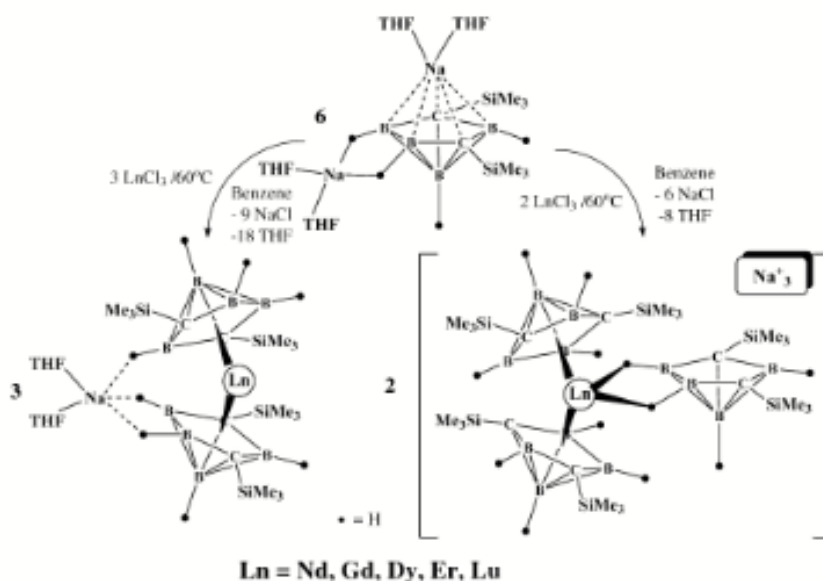


**Scheme 1 Synthesis of nido10B10H14 and anti-10B18H22 from 10B5H9.**

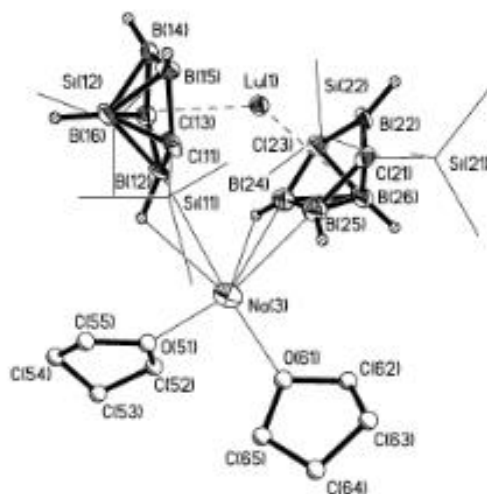
### **Reductive cage-opening process with concomitant metalation of the resulting carborane ligand: A novel route to metallacarborane synthesis**

The two-electron reductive cage opening of the closo-carboranes, in both the C<sub>2</sub>B<sub>10</sub> and C<sub>2</sub>B<sub>4</sub> cage systems, have been well documented in the literature. In all cases, the use of naphthalene, as the electron-transfer reagent, along with an alkali metal was essential for the reaction to begin and then proceed irreversibly to form the corresponding thermodynamically stable dianionic nido-cages in which the cage carbons are always separated by a boron atom. The use of naphthalene in the traditional two-electron reductive cage-opening reactions has several

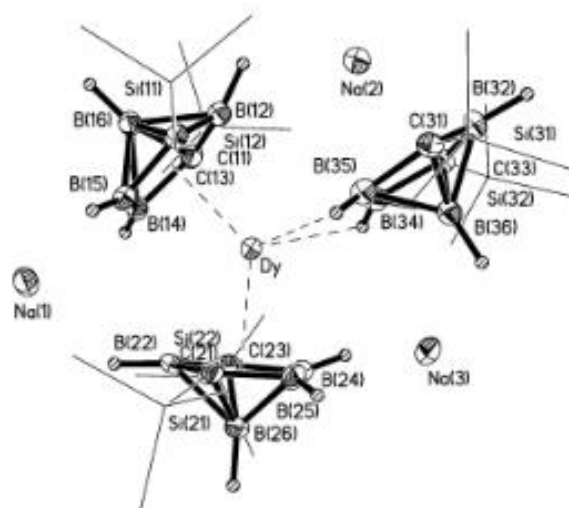
disadvantages. It introduces an additional reagent that must be removed from the reaction mixture before the nido-carborane products can be reacted further. In addition, naphthalene also has a tendency to cocrystallize with any product or to substitute for terminal B–H hydrogen, which often interferes with the reactivity of these dianionic ligands. The subsequent metalations of these ligands, in the conventional synthetic procedure, shown in Scheme 2, produce metallacarboranes of different geometries depending on the ratios of reactants involved. The structures of the representative compounds are depicted in Figs. 1 and 2.



**Scheme 2 Conventional synthetic route for lanthanacarboranes**



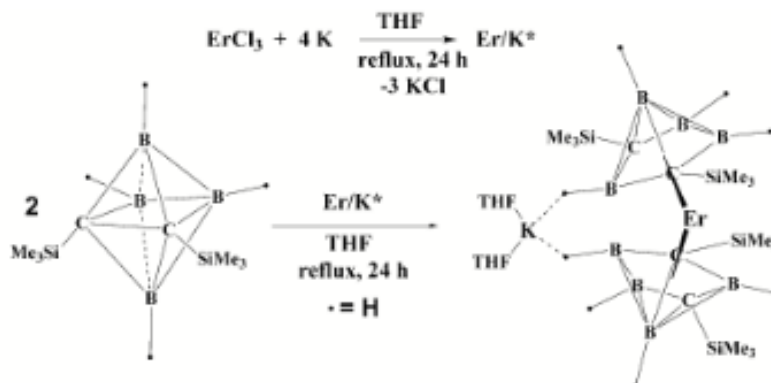
**Fig. 1 Lutetiacarborane sandwich**



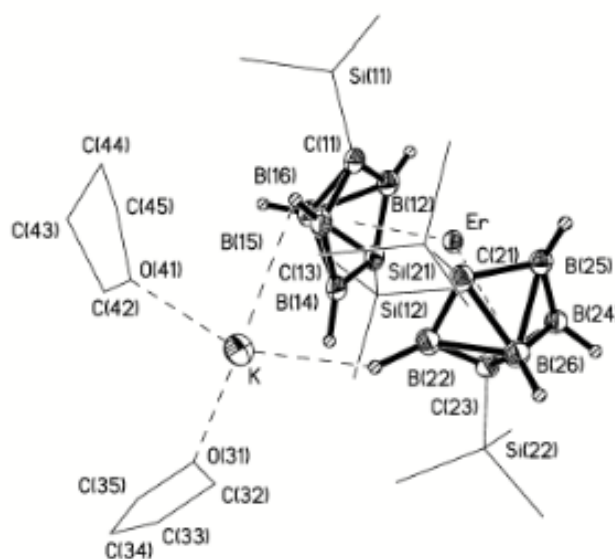
**Fig. 2 Dysprosacarborane sandwich**

The inability of the closo-carboranes to undergo reduction in the absence of naphthalene led us to question whether such carboranes could be reductively opened by the in situ generation of reactive metal atoms whose cations are good coordinators of the carborane. To explore this possibility, anhydrous  $\text{ErCl}_3$  was reacted with 4 equiv of freshly cut potassium metal, under refluxing conditions in THF, to produce what we believe to be an active erbium metal alloy of the form of  $\text{Er}/\text{K}^*$  (Scheme 3). The alloy was immediately treated with the closo-carborane, 1,2-(SiMe<sub>3</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>, which after refluxing overnight with constant stirring, produced a light-orange crystalline solid, identified as the “carbons apart” erbacarborane sandwich, 2,2',4,4'-(SiMe<sub>3</sub>)<sub>4</sub>-3,6'-[( $\mu$ -H)<sub>2</sub>K(THF)<sub>2</sub>]-1,1'-commo-Er( $\eta^5$ -2,4-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>)<sub>2</sub>, in 82 % yield (see Scheme 3). It is important to note that, under the same reaction conditions, neither the Er nor K metal alone nor the one generated in situ by reacting K with  $\text{ErCl}_3$  in 3:1 ratio, underwent reductive cage opening; in both cases the closo-carborane precursor was recovered unchanged. Although the Na/Hg alloy has been widely used in coupling reactions of many organometallic species, there have been no reports of its use either in the reductive cage-opening of the carboranes or in the synthesis of mercuracarborane complexes. Therefore, the reaction shown in Scheme 3 is an unprecedented example of a new reductive cage-opening process that should

prove applicable to the closo-carboranes in both the icosahedral and subicosahedral cage systems, and lead to the formation of hitherto unknown metallocarborane species.



**Scheme 3 Reductive cage-opening with concomitant metalation of the carborane ligand**

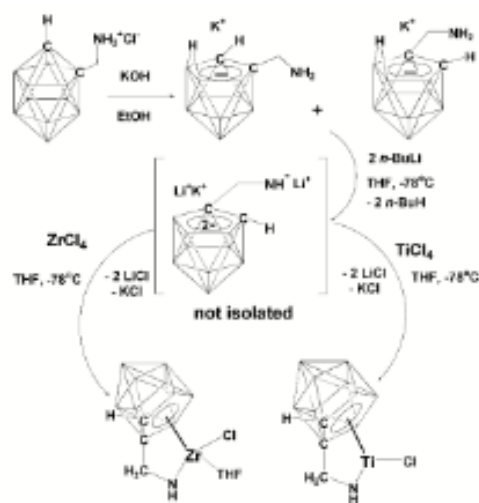


**Fig. 3 Erbacarborane sandwich**

### Chemistry of half-sandwich, constrained-geometry C<sub>2</sub>B<sub>9</sub>-metallocarboranes

The potential applications of functionalized carborane clusters in catalytic organic reactions have resulted in the reports of the syntheses and reactivities of a number of new metallocarboranes. Our preliminary research in this area has shown that the trianionic ligand [nido-7-(CH<sub>2</sub>NH)-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] <sup>3-</sup>, prepared from the reaction of [nido-7-(CH<sub>2</sub>NH<sub>2</sub>)-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>] – with 2 equiv

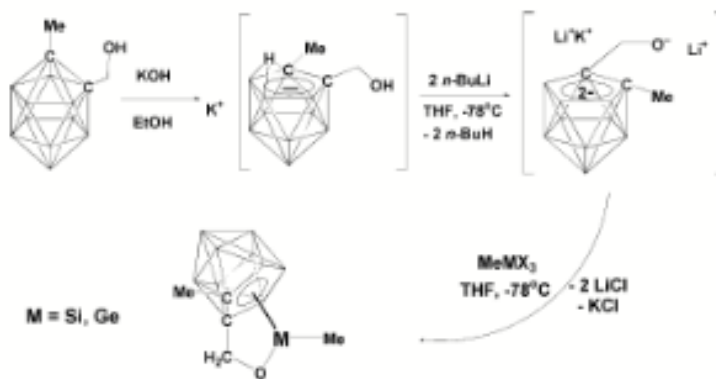
of  $n\text{-BuLi}$ , reacts with  $\text{MCl}_4$  ( $\text{M} = \text{Ti}, \text{Zr}$ ) to give the corresponding half-sandwich metallocarboranes (Scheme 4). Nevertheless, there have been a handful of reports in which the appended moiety forms either a coordinate covalent bond or another delocalized  $\pi$ -bond with the metal atom exo-polyhedrally, and none demonstrated the additional stabilization of the metal by sigma bonding to the C(cage)-appended moiety. Therefore, our results are the first examples of half-sandwiched group 4 metallocarboranes in which the nitrogen atom of the exo-polyhedral C(cage)-alkylamido unit is  $\eta^1(\text{sigma})$ -bonded to the metal that is complexed with the open C2B3-bonding face of the carborane ligand (Scheme 4). These observations suggested the possibility of using other constrained-geometry ligands, such as the ansa-alkylloxocarborane, to prepare a series of C(cage)-appended half-sandwich alkylloxometallicarboranes (Scheme 5).



**Scheme 4 Synthetic scheme for ansa-alkylamidometallicarboranes**

Thus, the in situ generated trianionic ligand was further reacted with anhydrous  $\text{MeMCl}_3$  ( $\text{M} = \text{Si}, \text{Ge}$ ), followed by recrystallization from a toluene/heptane solution to form the corresponding half-sandwich group 14 metallocarboranes,  $\text{closo-1-M(Me)-2-(1-}\eta^1(\sigma)\text{-OCH}_2\text{)-3-Me-}\eta^5\text{-2,3-C}_2\text{B}_9\text{H}_9$  [ $\text{M} = \text{Si}, \text{Ge}$ ], in 48 and 56 % yields, respectively. The NMR spectra, IR spectra, and the microanalytical data for these species confirmed their formulations as shown in Scheme 5. The reactivities of these constrained-geometry metallocarboranes, especially of the group 4 metals, toward olefinic substrates are currently underway in our laboratories.

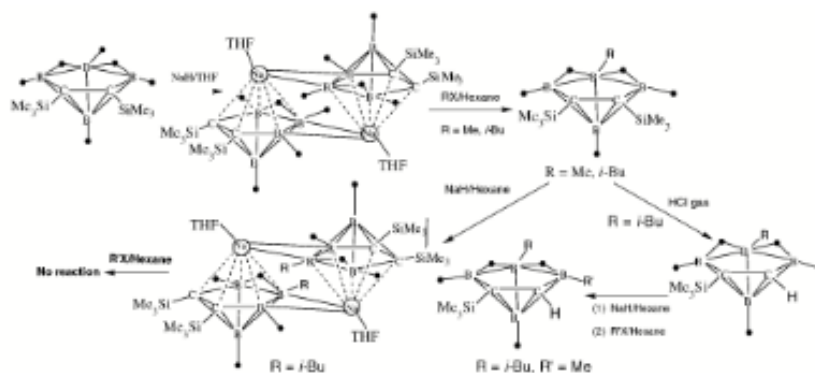




**Scheme 5 Synthetic scheme for ansa-alkyloxometallacarboranes**

### Syntheses and reactivities of B(cage)-alkyl- and silylamido-C2B4-carboranes

In order to investigate the reactivities of alkylated and polyalkylated carboranes, we have initiated a study of the regiospecific alkylation of the nido-2,3-(SiMe<sub>3</sub>)<sub>2</sub>,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> and an investigation of the chemical behavior of any B-alkylated products. The following specific questions were addressed: (1) Is it possible to systematically alkylate and/or polyalkylate carboranes having such bulky substituents as the SiMe<sub>3</sub> groups? (2) If so, what is the effect of the SiMe<sub>3</sub> groups in determining the distribution of products? (3) Could any alkylated product undergo standard deprotonation and oxidation reactions preparatory to the formation of metallacarboranes and the carbons apart analogs, respectively? And (4) how effective are the standard techniques of <sup>1</sup>H, <sup>11</sup>B, and <sup>13</sup>C NMR spectroscopy in identifying the structures of any alkylated products? Therefore, the reaction of the sodium compound of nido-2,3-(SiMe<sub>3</sub>)<sub>2</sub>,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> with the standard alkylating agents, MeI and *i*-BuBr, was carried out to produce the corresponding neutral monoalkylated carboranes, nido-5-(R)-2,3-(SiMe<sub>3</sub>)<sub>2</sub>,3-C<sub>2</sub>B<sub>4</sub>H<sub>5</sub> (R = Me and *i*-Bu) in 75 % yields, respectively (Scheme 6).



**Scheme 6 Systematic B(cage)-alkylation of the the nido-2,3-(SiMe3)2-2,3-C2B4H6**

## CONCLUSION

The alkylation reaction seems to be a general one, that leads exclusively to B(unique)-alkylated products. The alkylation reactions are presumably through an intermediate in which the incoming alkyl unit is bridged between the unique boron and one of its neighboring basal borons. The intermediate then collapses with the alkyl group migrating to the terminal position of one of the two borons, changing places with its terminal hydrogen. The difference in the directing ability of the SiMe<sub>3</sub> compared to the C-alkyl groups is most likely due to the steric bulk of the SiMe<sub>3</sub> moiety. This unique directive property of the SiMe<sub>3</sub> group was profitably exploited in the synthesis of the corresponding B(cage)-silylamido-substituted carborane derivatives. The reaction of the sodium salt of the [nido-2,3-(SiMe<sub>3</sub>)<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>5</sub>]<sup>-</sup> anion with (t-butylamido)dimethylchlorosilane, in a 1:1 ratio in THF, followed by extraction and purification, produced a new B(unique)-substituted small-cage carborane, nido-2,3-(SiMe<sub>3</sub>)<sub>2</sub>-5-[Si(Me)<sub>2</sub>NH(Me<sub>3</sub>C)]-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>5</sub> in 85 % yield.

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