

## Review

Is there a future for the continued development of the chemistry of small cage C<sub>2</sub>B<sub>4</sub>-carborane? A historical perspectiveNarayan S. Hosmane<sup>a,\*</sup>, John A. Maguire<sup>b</sup><sup>a</sup> Department of Chemistry and Biochemistry, Northern Illinois University, DeKalb, IL 60115, USA<sup>b</sup> Department of Chemistry, Southern Methodist University, Dallas, TX 75275, USA

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Dedicated to Professor Sheldon G. Shore on the occasion of his 70th birthday.

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**Abstract**

The organometallic chemistry of the small-cage *nido*-C<sub>2</sub>B<sub>4</sub>-carborane ligands is unique and offers potential advantages over both the larger-cage C<sub>2</sub>B<sub>9</sub> and cyclopentadienide systems. However, the study of the chemistry of this ligand system has been limited by the difficulties inherent in their large scale preparation. Initially, the carboranes were produced in limited quantities from the high temperature pyrolysis of gas phase alkyne–pentaborane(9) mixtures, usually in the presence of an amine catalyst. Synthetic methods have evolved so that it is now possible to produce multi-gram quantities of the trimethylsilyl-substituted carbons adjacent, *nido*-2-(SiMe<sub>3</sub>)<sub>3</sub>-(R)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> (R = SiMe<sub>3</sub>, H, or an alkyl group). Efficient methods have also been developed for the conversion of these compounds into the corresponding carbons apart, *nido*-2,4-C<sub>2</sub>B<sub>4</sub>-carborane isomers and for changing the cage carbon substituents. One of the greatest assets in fostering the study of these systems was the almost limitless supply of the pentaborane(9) precursor, supplied free-of-charge from an extensive government surplus. That source is no longer available nor is there a commercial source to take its place. These considerations have led us to review the history of the development of the methods used in the preparation of the small cage carboranes and to speculate on the future of the study of these most interesting ligands. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* History of carboranes; C<sub>2</sub>B<sub>4</sub>-cage; Small cage carborane; Metallocarborane; Pentaborane

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**1. Introduction**

The organometallic chemistry of the carborane ligands normally involves the substitution of a metal or a metal group for one or more B–H vertices in a carborane cage [1,2]. Although a number of carborane cages have formed the basis for such compounds, the majority of the complexes involve the coordination of a metal group with the electron density on the open C<sub>2</sub>B<sub>3</sub> faces of the *nido*-carboranes, [R<sub>2</sub>C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>]<sup>2-</sup> or [R<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>]<sup>2-</sup> (R = H or a cage carbon substituent). Because of the interests of the authors, this discussion will be centered

on the smaller, C<sub>2</sub>B<sub>4</sub>, carborane cages. There are two different placements of the atoms in the C<sub>2</sub>B<sub>3</sub> open face, one in which the two carbon atoms occupy adjacent positions (the 2,3-C<sub>2</sub>B<sub>4</sub> or carbons adjacent isomer) and another in which the two carbons are separated by a boron atom (the 2,4-C<sub>2</sub>B<sub>4</sub> or carbons apart isomer). Fig. 1 shows the surfaces of the occupied high energy molecular orbitals (MOs) of the dianions of these carboranes that extend above the open face of the carborane and are the most involved in carborane–metal bonding. These MOs are quite similar to the primary metal-binding MOs in the cyclopentadienide anion, [R<sub>5</sub>C<sub>5</sub>]<sup>-</sup> (Cp\*). This similarity has been exploited since the middle 1960s [3,4] to generate a number of half- and full-sandwich metallocarboranes that parallel the more familiar metal–Cp compounds.

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Main-group [2,5], d-block [2,6,7] and f-block [2,8,9] metals have been incorporated into these cages. Although the similarities between the Cp and carborane system are useful synthetic guides, there are some significant differences between the two ligand systems. Fig. 1 shows that the two highest energy occupied MOs in the carboranes are more polarized towards the boron atoms than the carbons, with the carbon  $\pi$ -electron density being concentrated in the lower energy MOs that approximate the symmetric  $a_2$  of the Cp system. In the 2,3- $C_2B_4$  carborane this low energy MO is almost devoid of boron character, while in the 2,4- $C_2B_4$  isomer the electron density is more evenly distributed. Therefore, in addition to the expected Cp-like  $\eta^5$ -bonding, one finds numerous examples of decreased hapticity by the carborane, arising from a slippage of the metal group away from the centroidal position above the bonding face. Slippage distortions

leading to  $\eta^3$ -bonding are quite common in the carbons adjacent metallacarboranes, being found in many of the heavier Group 13 and 14 metallacarboranes [2b], as well as in the later transition metal carborane complexes [10]. Two general types of  $\eta^2$ -bonding are found, one in which a metal group formally replaces a bridged H in a B–H–B three-center bond [11,12], and another found in certain carbons apart metallacarboranes, such as 1-(2,2'- $C_8H_6N_4$ )-1-( $t-C_4H_9$ )-1-Ga-2,4-(SiMe<sub>3</sub>)<sub>2</sub>-2,4- $C_2B_4H_4$ , in which the metal is additionally coordinated with a base molecule [13]. Enhanced slip distortions of a metal group on coordination with a base is a common feature of the Lewis acid–base properties of the  $MC_2B_4$  metallacarboranes; in all cases the slippage is away from the cage carbons [2].

An inspection of Fig. 1 reveals significant electron density on the terminal hydrogens. Thus, these terminal hydrogens play a significant role in determining the structures of many of the metallacarboranes. Specifically, the compounds exhibit a propensity to form dimers, or more extended polymeric chains, that are held together by M–H–B bridges [2,5,7–9]. The anionic metallacarboranes also tend to bond cationic groups through a series of M–H–B bridges [7,9]. In addition to the effects caused by the distribution of electron density in the carborane cages, two other factors are of importance in defining the uniqueness of the carborane ligands. One is charge and the other is the presence of an apical B–H unit, opposite from the bonding face of the ligand. The dinegative charges on the carborane ligands tend to stabilize higher metal oxidation states than do the univalent Cp ligands. For example in the heavier Group 14 metallacarboranes, half-sandwich complexes have the metals in their +2 state, while the +4 oxidation states are found in the full-sandwich complexes [2,15,16]. It is also possible to remove the apical B–H unit, by a so-called decapitation reaction, and replace it with a metal group, leading to a number of multi-decker organometallic compounds that have greater stabilities than their Cp analogues. Grimes and his coworkers [6d,17] have explored this chemistry in depth.

Despite the inherent interest and versatility of the small cage metallacarboranes, their chemistry has not been as extensively studied as the Cp complexes, or as their larger cage analogues. Part of the problem has been the difficulty in synthesizing and handling the small-cage *nido*-carborane ligands.

## 2. Syntheses and characterization

### 2.1. *nido*-2,3-(RC)<sub>2</sub>B<sub>4</sub>H<sub>6</sub>

The syntheses of neutral *nido*-2,3-(RC)<sub>2</sub>B<sub>4</sub>H<sub>6</sub> and anionic [*nido*-2,4-(RC)<sub>2</sub>B<sub>4</sub>H<sub>4</sub>]<sup>n-</sup> ( $n = 1, 2$ ) ligands has evolved over the past 40 years to where they can now be made in the multi-gram quantities required for the

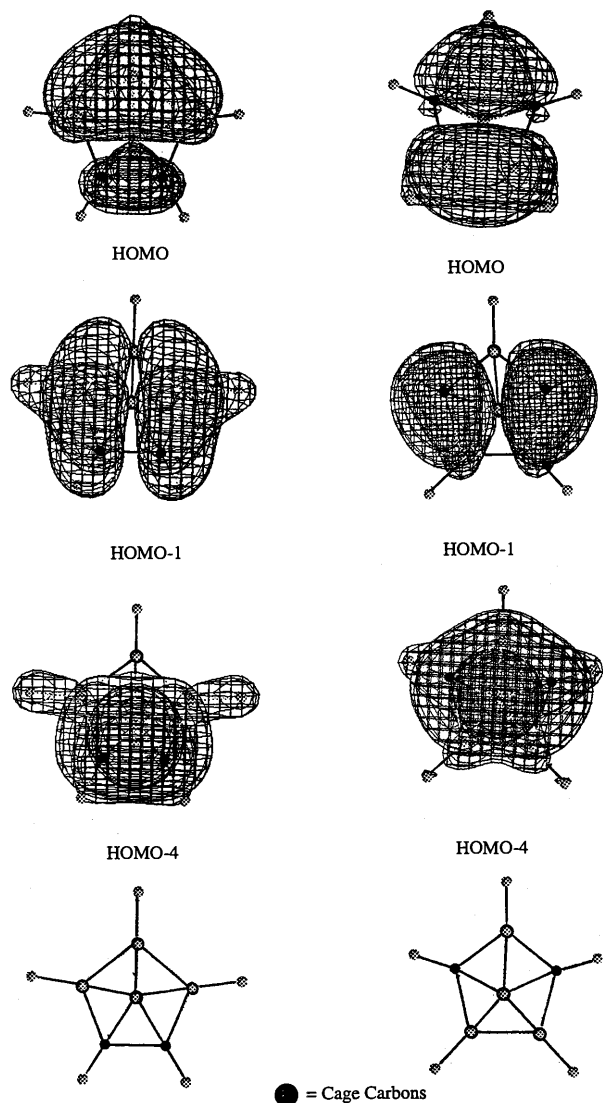
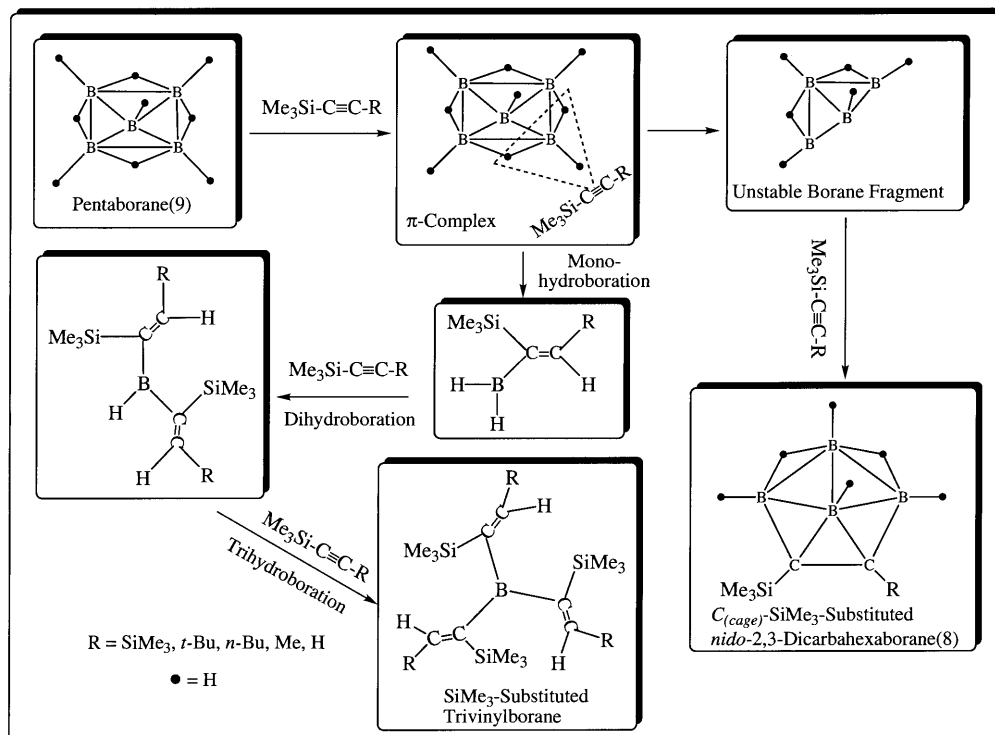
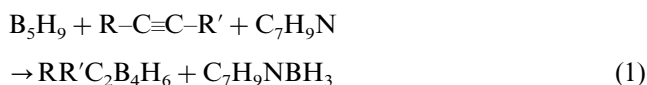


Fig. 1. Primary metal binding orbitals of the [*nido*-2,3- $C_2B_4H_6$ ]<sup>2-</sup> and [*nido*-2,4- $C_2B_4H_6$ ]<sup>2-</sup> dianions as viewed from above their open faces.

Scheme 1. Synthesis of derivatives of *nido*-2,3-dicarbahexaborane(8) and trivinylborane.

systematic study. In 1962, Onak, Williams and Weiss [18] reported the syntheses of a series of alkyl-substituted *nido*-2-(R)-3-(R')-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> (R = H, R' = CH<sub>3</sub>, C<sub>3</sub>H<sub>7</sub>; R = CH<sub>3</sub>; R' = CH<sub>3</sub>) carboranes from the room temperature (r.t.) reaction of B<sub>5</sub>H<sub>9</sub> with a series of substituted alkynes in the presence of 2,6-dimethylpyridine, as shown in Eq. (1). However, the yields were limited by a competing reaction of the base with the pentaborane to give a (BH)<sub>x</sub> polymer

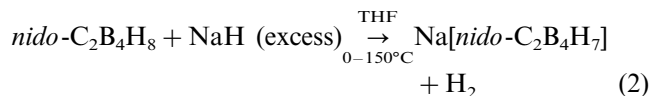


which had been described earlier by Burg [19]. Much higher overall yields were obtained by the gas phase pyrolysis of alkyne-B<sub>5</sub>H<sub>9</sub> mixtures. For example, the yield of the propyne-B<sub>5</sub>H<sub>9</sub> reaction was increased from 8.4 at r.t. to 54% at 175°C [19a]. In general, it was found that increasing alkyl substitution on the alkyne led to increasing yields of the carborane; the reaction with acetylene (R = R' = H) gave only 7% yield at r.t. [19a]. Even though adjusting the experimental conditions could increase the yields, the absolute quantity of the carborane was severely limited by the restrictions inherent in a gas-phase reaction. An enhancement in the absolute amounts of obtainable product was described in 1979 by Hosmane and Grimes [20]. Their procedure was similar to that described in Eq. (1) except that a stronger base, such as (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>N was used. The yields were acceptable (> 50%), but the main advantage was that they were bench-scale reactions in

which multi-grams of product could be obtained. When a sulfide base, such as (CH<sub>3</sub>)<sub>2</sub>S, was used in place of the amine bases, the yield was slightly increased but the reaction times were greatly extended [20]. This became the method of choice for preparing alkyl-substituted *nido*-carboranes, interestingly, when C<sub>2</sub>H<sub>2</sub> was the alkyne, no carborane product was formed with either (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>N or (CH<sub>3</sub>)<sub>2</sub>S [20]. High temperature pyrolysis of B<sub>5</sub>H<sub>9</sub>-C<sub>2</sub>H<sub>2</sub> mixtures still remained the best synthetic route to the unsubstituted *nido*-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>. In 1985, Hosmane and coworkers reported a high-yield, multi-gram synthesis of the trimethylsilyl-substituted carboranes, of the form 2-(Si(CH<sub>3</sub>)<sub>3</sub>)-3-(R)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> (R = Si(CH<sub>3</sub>)<sub>3</sub>, CH<sub>3</sub>, and H), from the reaction of the particular R-C≡C-SiMe<sub>3</sub> with B<sub>5</sub>H<sub>9</sub> in a stainless steel cylinder in the absence of either solvent or base [21]. At r.t. the yields of the carboranes ranged from 82 for R = CH<sub>3</sub> to 96% for R = H, based on the B<sub>5</sub>H<sub>9</sub> consumed; at 135°C, the yields were somewhat lower, ranging from 73 for R = Si(CH<sub>3</sub>)<sub>3</sub> to 14% for R = H, but the reactions were much faster. While this method is the most efficient in terms of carborane formed from pentaborane consumed, it is expensive in terms of the alkyne. One mole of trivinyl borane is produced for each mole of carborane formed, as shown in Scheme 1. Since the alkyne is more readily available than is the pentaborane(9), this has become the method of choice for the syntheses of all the *nido*-2-(SiMe<sub>3</sub>)-3-(R)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> carborane derivatives. Overall it is more efficient to prepare the bis(trimethylsilyl)-substituted

carborane and to replace the  $\text{Si}(\text{CH}_3)_3$  groups with other substituents than to use a different alkyne.

The neutral *nido*-2,3-(RC) $_2\text{B}_4\text{H}_6$  (R = H or a cage carbon substituent) carboranes have two bridging hydrogens, one or both of which are removed on metallation. While the first main group metallacarboranes in the small cage system were obtained from the gas phase reaction of the neutral  $\text{C}_2\text{B}_4\text{H}_8$  with the metal alkyls,  $(\text{CH}_3)_3\text{Ga}$  or  $(\text{CH}_3)_3\text{In}$ , to give the corresponding 1- $\text{CH}_3$ -1-M-2,3- $\text{C}_2\text{B}_4\text{H}_6$  (M = Ga, In) [4b], it was found that prior deprotonation of the carborane to give the mono- or di-anion produced higher yields and cleaner products. The first proton is conveniently removed by reaction of the neutral carborane with NaH (see Eq. (2)) [1,22]. However, neither an excess of the NaH base



nor the use of a stronger base, such as KH, led to the removal of the second proton [22b]. On the other hand, bases such as BuLi react quantitatively with the monoanion to give the  $\text{Na}^+\text{-Li}^+$  salt of the dianion [14]. The stoichiometry of Eq. (2) seems more a function of its heterogeneous nature, rather than a difference in relative base strengths. The solid-state structure of the monosodium compound of the bis(trimethylsilyl)-substituted carborane was found to be a network of  $[(\text{THF})\text{Na}^+]_2[2,3\text{-}(\text{SiMe}_3)_2\text{-2,3-C}_2\text{B}_4\text{H}_5]_2$  dimers that were layered symmetrically on top of one another [23]. Each  $(\text{THF})\text{Na}^+$  unit occupied the apical position

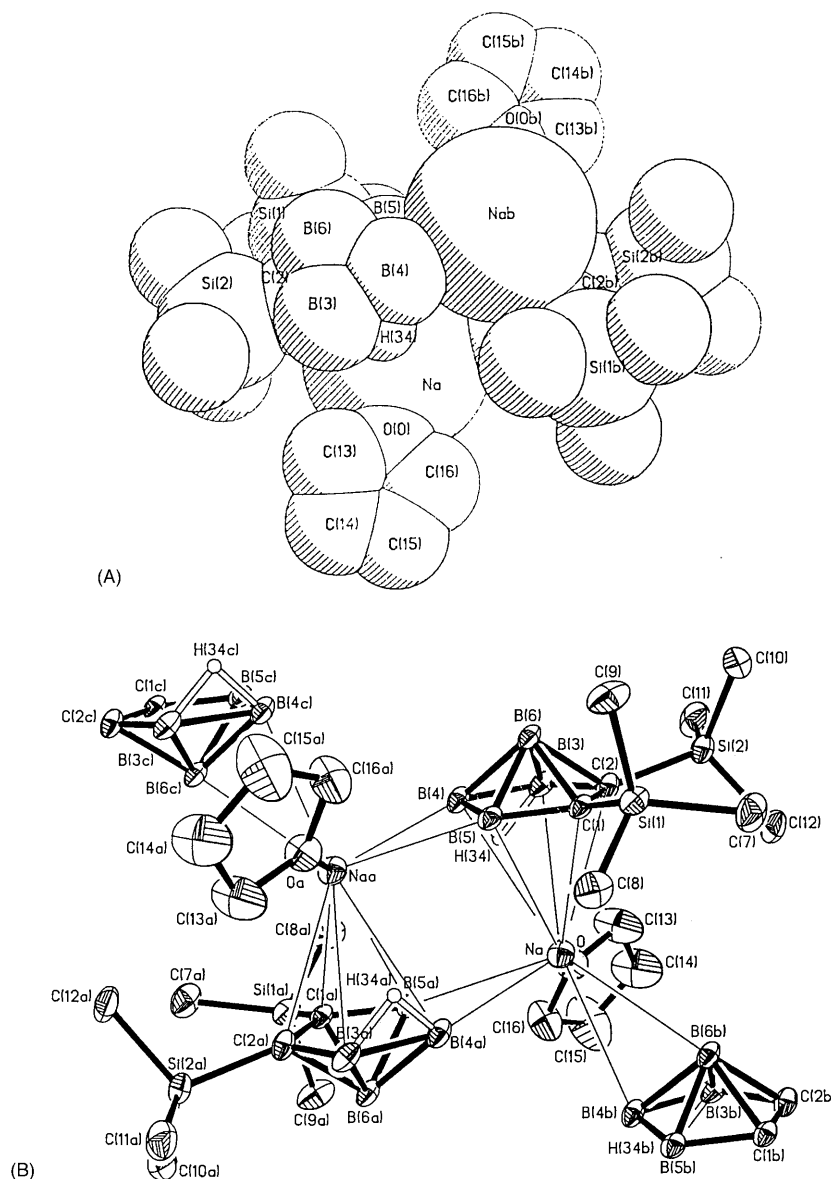


Fig. 2. Space-filling model (A) and a perspective view (B) of  $[1\text{-Na}(\text{THF})\text{-2,3-(SiMe}_3)_2\text{-2,3-C}_2\text{B}_4\text{H}_5]_2$  dimer.

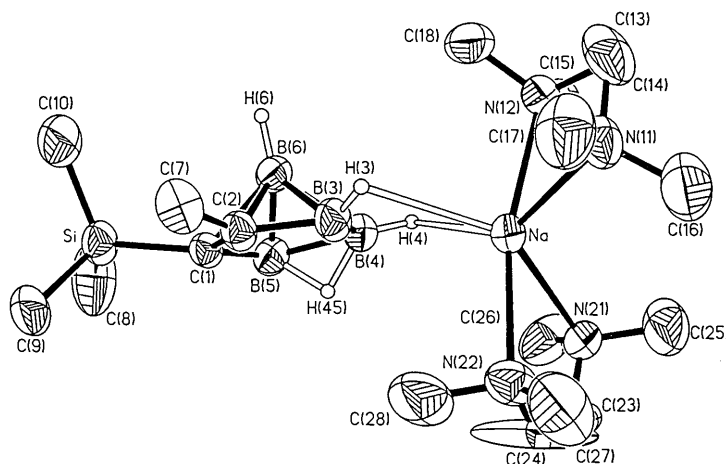


Fig. 3. Perspective view of *nido-exo*-4,5-[( $\mu$ -H)<sub>2</sub>Na(TMEDA)]-2-2-(SiMe<sub>3</sub>)-3-(Me)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>5</sub>.

above the face of the carborane, as seen in the space filling model and the ORTEP drawing shown in Fig. 2. It is apparent from the model that the second bridged hydrogen, H(34), is well-protected within the cluster and is not accessible to a solid base, such as NaH. Further support for this argument was provided by the observation that a more extensively solvated monosodium salt, *nido-exo*-4,5[( $\mu$ -H)<sub>2</sub>Na-(TMEDA)<sub>2</sub>-2-(SiMe<sub>3</sub>)-3-(Me)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>5</sub>] (see Fig. 3), in which the bridge H was uncovered, reacted readily with solid NaH to give the disodium compound [24]. Most of the full- and half-sandwich metallocarboranes in the C<sub>2</sub>B<sub>4</sub> cage systems are prepared by mixing stoichiometric quantities of either the mono- or di-anion of the particular carborane with a suitable metal halide [1,2]. These reactions are usually run in nonpolar solvents so that the driving force for the synthesis of the metallocarboranes could well be the formation of the insoluble alkali metal halides.

## 2.2. *nido*-2,4-(RC)<sub>2</sub>B<sub>4</sub>H<sub>6</sub>

The syntheses of the carbons adjacent *nido*-carboranes, which were first reported some 38 years ago [18], are fairly direct ones, involving the reaction of pentaborane(9) with a particular alkyne. Most of the research since that initial report has focused on increasing the yields and efficiency of this key reaction (*vide supra*). However, the path to the carbons apart, *nido*-2,4-C<sub>2</sub>H<sub>8</sub> family of ligands is much more circuitous. There is no direct route to this carborane, most syntheses involve the reductive opening of the corresponding *closo*-(RC)<sub>2</sub>B<sub>4</sub>H<sub>4</sub> carborane, which itself is difficult to come by. Up until 1990, most of the starting *closo*-carboranes were produced either by high energy reactions of pentaborane(9) with alkynes for short periods of time in continuous-flow systems [25], the reaction of such mixtures in silent electric discharge apparatus [26], or

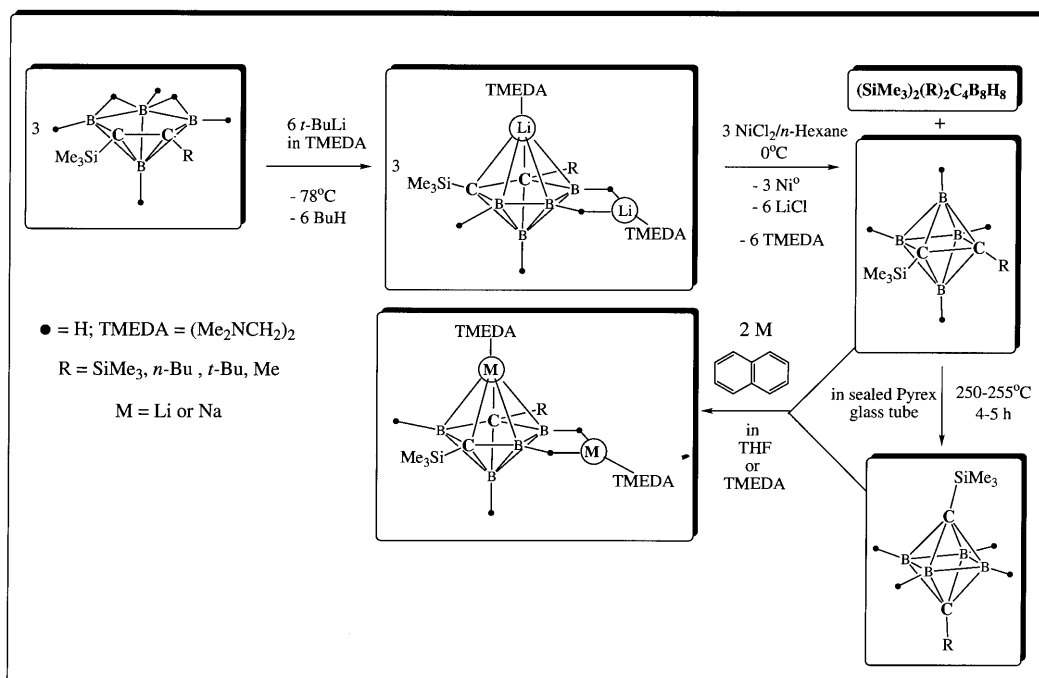
by the pyrolysis of the *nido*-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> derivatives [27]. Under the high-energy conditions of these reactions, the thermodynamically more stable 1,6-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> isomer was the major product. Lower temperature photolysis reactions had to be employed to obtain the less stable 1,2-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> compounds [28]. These are all gas-phase reactions that usually give multiple products in low-to-moderate yields and are severely limited in the total amount of product that can be obtained in a single reaction. However, a number of C- and B-substituted derivatives of the 1,6-isomer have been prepared and characterized [ld]. These *closo*-compounds can be reductively opened to give the corresponding *nido*-2,4-C<sub>2</sub>B<sub>4</sub>, (carbons apart) carboranes [31]. The exact nature of the products depends on the reducing agent used. When NaH or LiH was used with *closo*-1,6-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>, the carbons apart *nido* mono-anions, [2,4-C<sub>2</sub>B<sub>4</sub>H<sub>7</sub>]<sup>-</sup>, were produced as their Na<sup>+</sup> or Li<sup>+</sup> salts [29]. On the other hand, when trimethylamine, Me<sub>3</sub>N, was used, the charge-compensated, 5-Me<sub>3</sub>N<sup>+</sup>-*nido*-2,4-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub><sup>-</sup> was formed in about 80% yield [29,30]. This compound rearranged to the 3-Me<sub>3</sub>N<sup>+</sup>-2,4-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub><sup>-</sup> on heating or standing at r.t. in chloroform [29]. Other compounds have been used to open the *closo*-cages and their products have been characterized [ld]. Although these compounds are interesting, the limited quantities produced have precluded an exploration of their reaction chemistry. *closo*-1,6-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> has been found to react directly with organometallic compounds, such as Ni( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>, Fe(CO)<sub>5</sub>, and Co( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub> to give direct metal insertion into the C<sub>2</sub>B<sub>4</sub> cage [32]; in all cases, the carbons apart compounds were produced. When 1,6-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> was open with Na-C<sub>10</sub>H<sub>8</sub> in the presence of a Na[C<sub>5</sub>H<sub>5</sub>]-CoCl<sub>2</sub> mixture and then oxidized by O<sub>2</sub>-H<sub>2</sub>O, a number of carbons apart mixed-sandwich Cp-cobaltacarboranes were obtained, including a small amount (4%) of an interesting triple-decker compound, (2,4-C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>)Co<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> in which

two ( $\eta^5$ -two ( $\eta^5$ -two ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Co units occupy opposite faces of a carbons apart C<sub>2</sub>B<sub>3</sub> ring, presumably formed when a *nido*-2,4-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> unit lost its apical B–H group in a decapitation reaction [33].

In 1990 a high yield, multi-gram synthesis of *closo*-1,2-(SiMe<sub>3</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub> from the reaction of the stannacarborane, *closo*-1-Sn-2,3-(SiMe<sub>3</sub>)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>, with either PtCl<sub>4</sub> or PtCl<sub>2</sub> was described [34]. The yield with PtCl<sub>4</sub> was 98%, while PtCl<sub>2</sub> gave a 94% yield, based on the stannacarborane consumed [34]. Somewhat later it was found that anhydrous NiCl<sub>2</sub> would react with the unsolvated and solvated Na–Li or dilithium compounds of the *nido*-carboranes, [2-(SiMe<sub>3</sub>)<sub>2</sub>-3-(R)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>]<sub>2</sub><sup>-</sup> (R = SiMe<sub>3</sub> or Me), to produce nickel metal and the *closo*-1-(SiMe<sub>3</sub>)<sub>2</sub>-2-(R)-1,2-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub> carborane in yields ranging from 59–45% (see Scheme 2) [35]. Considering the relative costs of the starting materials, the NiCl<sub>2</sub> reactions, despite their lower yields, are normally used for producing large amounts of the C<sub>2</sub>B<sub>4</sub> *closo*-carboranes. Just as with the parent and C-alkyl *closo*-(RC)<sub>2</sub>B<sub>4</sub>H<sub>4</sub> carboranes, the trimethylsilyl-substituted *closo*-1,2-isomer can be converted to its 1,6-isomer by heating [36]. However, it is not necessary to convert to that isomer before opening to carborane, it has been shown that 1,2-(SiMe<sub>3</sub>)<sub>2</sub>-*closo*-1,2-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub> can be reductively opened to give the corresponding [2,4-(SiMe<sub>3</sub>)<sub>2</sub>-*nido*-2,4-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>]<sub>2</sub><sup>-</sup> [37]. The method outlined in Scheme 2 has been used to prepare a number of different carbons apart carborane dianions from which the corresponding metal-lacarboranes are synthesized and their coordination chemistry has been explored [2,5b,d,7b,8,14,38].

### 3. Future directions

The *nido*-C<sub>2</sub>B<sub>4</sub> carboranes are produced stepwise, with the carbons adjacent carboranes being the precursor of the carbons apart isomers. Within a particular system, the carboranes differ from one another in the nature of the substituent groups that may have replaced a terminal hydrogen, usually on the cage carbons, in the parent C<sub>2</sub>B<sub>4</sub>H<sub>8</sub> carboranes. Irrespective of the substituents, the compounds are ultimately derived from the reaction of a suitable alkyne with B<sub>5</sub>H<sub>9</sub>. Therefore, the study of the coordination chemistry of these small cage carboranes depends on the ready availability of the starting compounds; the alkynes are usually available from standard chemical supply houses, the pentaborane(9) is not. The major source of the pentaborane has been the U.S. Air Force stockpile, estimated at some 200 000 lb, that was accumulated in the 1960s when the compound was being studied as a possible jet/rocket fuel. This source is no longer available, nor is there a commercial source to take its place. Although several procedures for the synthesis of B<sub>5</sub>H<sub>9</sub> are available, they are difficult, lengthy, hazardous and only moderately efficient in terms of yields [39]. More efficient synthetic paths to the *nido*-C<sub>2</sub>B<sub>4</sub> carboranes are needed, that either do not involve the use of high energy precursors such as pentaborane or diborane, or that generate them in situ. Presently, such paths do not exist. However, Wrackmeyer and coworkers [40] have recently described the synthesis of sodium hexaethyl-2,4-dicarba-*nido*-hexaborate(1-), that is the per ethylated carbons apart the monoanion, from the reac-



Scheme 2. Syntheses of *closo*-1,2-C<sub>2</sub>B<sub>4</sub>-carborane and its conversion to *nido*-2,4-C<sub>2</sub>B<sub>4</sub>-carborane dianion.

tion of  $\text{Na}[\text{BEt}_3\text{H}]$  and 2-carba-*nido*-pentaborane(8). The pentaborane was derived from  $\text{Et}_2\text{B}-\text{C}\equiv\text{C}-\text{Me}$  [41]. In their 1979 report on the  $\text{Et}_3\text{N}$  catalyzed reaction of alkynes and  $\text{B}_5\text{H}_9$ , Hosmane and Grimes also described the synthesis of *nido*-2,3-(CMe) $_2\text{B}_4\text{H}_6$  from the reaction of  $\text{CH}_3\text{C}\equiv\text{CCH}_3$  and  $\text{Et}_4\text{N}^+\text{B}_3\text{H}_8^-$  [20]. The carborane was produced in high purity and modest yields. An alternate approach would be to try and stabilize the pentaborane so that it could be more easily handled. Cendrowski–Guillaume and Spencer reported that THF solutions of  $\text{B}_5\text{H}_9$  were greatly stabilized towards air oxidation, but reacted with 3-hexyne in the presence of triethylamine to give the corresponding *nido*-2,3-(Et) $_2$ -2,3- $\text{C}_2\text{B}_4\text{H}_6$  in ca. 74% yield [42]. Although this has promise, it still begs the question concerning the preparation of significant quantities of pentaborane(9). It may be possible to develop simpler and safer methods of preparation for the large scale preparation of the small cage carboranes. If such methods are not developed the exploration of the chemistry of these most interesting ligands will cease as the present laboratory supplies of pentaborane are consumed.

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