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Carboranes Other than $C_2B_{10}H_{12}$

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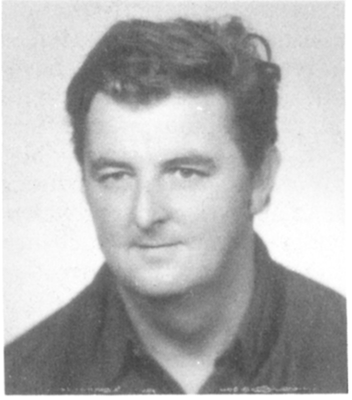

Bohumil Štíbr, born in 1940 at Slany, Town of Hops, Czechoslovakia, graduated in Inorganic Chemistry at the Institute of Chemical Technology in Pardubice in 1962. He has been active in the area of cluster boron chemistry in the Institute of Inorganic Chemistry of the Czechoslovak Academy of Sciences since 1963, especially in the area of carborane and heteroborane chemistry. His present position is Principal Research Fellow. In 1972 he worked for six months with M. F. Hawthorne (University of California, Los Angeles) in the area of metallacarborane chemistry, and for six months in 1989 with N. N. Greenwood and J. D. Kennedy (University of Leeds, UK) as a Royal Society Fellow in the area of metallacarborane and heteroborane clusters. He is a founding member of the Anglo-Czech Polyhedral Collaboration (ACPC) in the above area, which began in 1987.

I. Introduction

Carboranes are a class of carbon-containing polyhedral boron-cluster compounds that have been known since the 1960s[1,2] as a relatively younger subdiscipline of boron cluster chemistry.[3] Earlier pioneering work in this area and later experimental extensions of carborane chemistry[1] have shown that carbon and boron atoms are virtually interchangeable within wide, but well-defined limits.[1,2–7] Thus, carboranes are generally defined as boron cluster compounds with one or more polyhedral boron vertices replaced by carbon.

In most cases known so far, the presence of cage carbon centers usually enhances chemical stability of carboranes in comparison with equivalent borane structures. The ingenious recognition by Hawthorne in 1965[8] that carboranes with open polyhedral structures can act as polyhapto ligands to form extremely stable sandwich-type complexes with transition metals has also initiated a vast area of metallacarborane chemistry[6] (for more recent reviews see refs 7f,g, 9–10, for example), with structures and bonding principles that have influenced so much the recent development of organometallic and inorganic-cluster chemistry.[4]

The extreme stability of many carborane compounds has also led to intensive studies by industrial research groups aimed at developing novel carborane-based polymers designed for special uses.[1] Much of the recent practical interest has also been derived from the relatively broad chemical flexibility of carborane compounds toward modifications with "biologically active" organic substituents, leading to compounds targeted for use in neutron capture therapy (see refs 12, 13 for example).

The presence of carbon atoms in an electron-deficient deltahedral moiety also dictates novel structural features never encountered in comparable polyborane chemistry. In particular are the open-structured carboranes of the nido and arachno classes that are increasingly attracting the attention of both experimental and theoretical chemists. The differences outlined above immediately engender novel reaction principles applicable to both the skeletal and exoskeletal reaction spheres. Taking these and related factors into account, carborane chemistry offers an immense chemical and structural diversity, well comparable to that of organic chemistry. The former chemistry, being much younger and much more underdeveloped in comparison with the latter, is expected to provide chemists with still unsuspected reaction and structural principles, especially in conjunction with metallacarborane and inorganic cluster chemistry.

The aim of this review is to cover carborane chemistry since approximately 1980, when the last comprehensive review appeared.[5] The reader should also note that many partial reviews relating to general carborane chemistry have appeared that included the work of individual groups,[7,11,14–18] brief annual reviews,[19,20] or specialized structural[21,22] aspects. Organic carborane derivatives were reviewed by Koester[23] to reflect the state-of-the-art up to approximately 1984. The recent chemistry of the twelve-vertex $C_2B_{10}H_{12}$ carboranes is exempted from this review since it is discussed in another contribution to this issue, although some nido compounds of this class will be mentioned in the context of the chemistry of smaller-cage carborane systems.

Inspection of the literature over the reviewed period (approximately 1980 to early 1991) suggests that dominating trends in the carborane area have been the

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development of simple, rational synthetic strategies for the preparation of the known carboranes, detailed studies of exoskeletal reactivity leading to designed syntheses, and detailed structural studies using NMR and X-ray diffraction techniques. Less frequently have been made attempts to synthesize structurally novel carborane-cage systems through many new reaction principles, such as metal-promoted cluster condensation,[14-16] regiospecific cluster degradation and cage-growth reactions,[18] have been developed to demonstrate the immense versatility of such synthetic approaches.

The carborane area, especially that of smaller-cage systems, has also attracted the attention of several groups of theoretical chemists who have justified the experimentally obtained structural data via various methods of quantum chemistry at different computational levels. Of these the most valuable are the computations directly related to "real" experimental results and high-level ab initio calculations which probe subtle details of cluster geometries which are not always available from direct structural investigations.

This review deals with the chemistry of individual compounds sequenced approximately according to the cage size and the number of cage carbon atoms. However, the author is aware of the inconveniences that such an approach can bring, especially in discussing general synthetic principles and strategies, and has tried to keep these to a minimum. In the process of compiling this review, it became also apparent that the numbering conventions for carborane molecules were sometimes not consistent from author to author, particularly in structural work. The author, although being aware of the complex five-part descriptor nomenclature system[24] suggested for unambiguous, structurally definitive description of deltahedral structures, has opted for the usual closo, nido, and arachno convention used in much of the original literature. Where difficulties arise, the reader is advised to consult the general numbering schemes used in structures I–XXIV (section II below) and other structural drawings. A brief survey of recent theoretical work that is related to the general bonding and structural aspects of carborane chemistry has also been incorporated.

The author hopes that not only will boron cluster chemists find in this review, in conjunction with other reviews of this issue, basic synthetic and structural interrelations intrinsic to carborane species but also some inspiration for their work.

II. General and Theoretical Considerations

Polyhedral carborane cluster structures may be regarded as being based on {BH} and {CH} units held together by multicenter bonding. Alternatively, carborane structures can be derived from those of equivalent borane types via notional replacement of one or more $\{BH^-\}$ units by the equivalent number of isolobal[25] {CH} groups. Taking the earlier reported electron count and cluster arguments[26] into consideration, we can define a basic prototype (BP) (see refs 7b, 27 for example) of a given n-vertex polyborane cluster as a compound having only n exoskeletal hydrogen atoms. Thus we arrive to a series of $[B_nH_n]^{c-}$ anions which represent a basic set of closo ($c = 2$), nido ($c = 4$), arachno ($c = 6$), and hypho ($c = 8$) borane anions with $n + (c/2)$ skeletal bond pairs.

An isolobal replacement by x {CH} units as outlined above then generates a series of carborane BP's of the general formula $[C_xB_{n-x}H_n]^{x-c}$. For instance, in the case of tetracarbaboranes ($x = 4$) this approach leads to a series of $[closo\text{-}C_4B_{n-4}H_n]^{2+}$, $[nido\text{-}C_4B_{n-4}H_n]^0$ (neutral species), $[arachno\text{-}C_4B_{n-4}H_n]^{2-}$, and $[hypho\text{-}C_4B_{n-4}H_n]^{4-}$ tetracarbaborane BP's. This approach also readily suggests that a formal replacement of *all* boron vertices (n = x) engenders "nonclassical" carbocationic compounds.[7e]

There is one more consequence of this formalism to be briefly mentioned that consists in a formal, sequential addition of protons (see refs 7b, 11c, 28 for example), which does not change the total number of cage electrons, to any of the $[C_xB_{n-x}H_n]^{x-c}$ BP's. As an example, for the nine-vertex series of *nido*-dicarbaboranes ($n = 9$, $x = 2$, and $c = 4$), this formalism leads to compounds $[C_2B_9H_{11}]^{2-}$, $[C_2B_9H_{12}]^-$, and $C_2B_9H_{13}$; some positional isomers of these are already known. It should also be noted that the "extra protons" thus added are typically accommodated in the open part of a given structure (see refs 27b,d for example). Several authors have recently used EHMO,[29] MNDO, and ab initio[30-32] calculations to rationalize the positions of bridging protons in existing boranes and carboranes or of protons added to boranes in real or hypothetical situations.

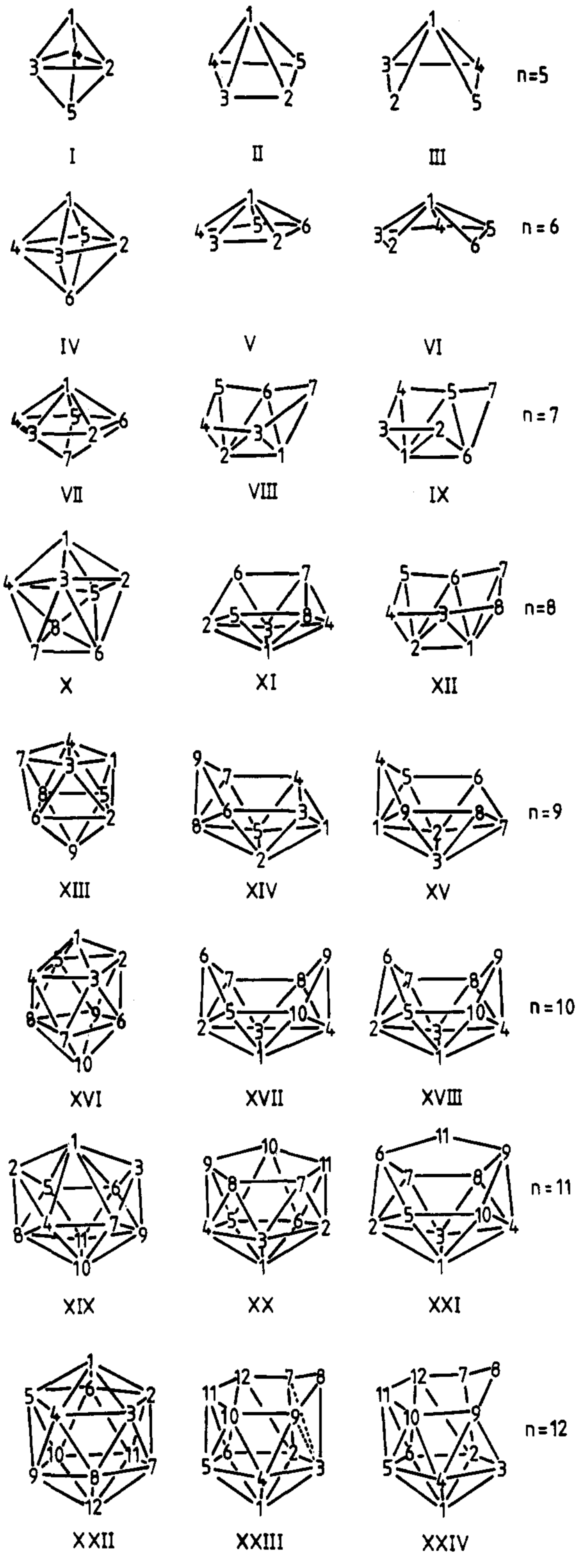
The principal architectural feature intrinsic to carboranes is a closed deltahedral (fully triangulated) framework of closo ($n + 1$ skeletal electron pairs) compounds [general structures I, IV, VII, X, XIII, XIX, and XXII (Chart 1)] from which nido ($n + 2$), arachno ($n + 3$), and hypho ($n + 4$) compounds can be derived by formally removing one, two, and three vertices of higher cage connectivity, respectively.[11c,d,26]

This concept is seen from the general structures I–XXIV (Chart 1). For instance, the removal of the vertex 1 from the closo six-vertex structure IV immediately generates the five-vertex nido structure II and, generally, removal of x vertices from the $n + x$ structure leads to n-vertex nido to hypho structures, when x = 1, 2, and 3, respectively. Application of this formal procedure (the "debor principle") leads, for instance, to the general nido (II, V, VIII, XI, XIV, XVII, XX, and XXIII) and arachno (III, VI, IX, XII, XV, XVIII, XXI, and XXIV) structures which are indeed adopted by almost all carborane species dealt with in this paper. A modified CNPR (Coordination Number Pattern Recognition) and fragment systematics for the nido carboranes has recently appeared.[11c]

As discussed in more detail in previous work,[1-6] the deltahedral constitution of borane and carborane cluster compounds is a direct consequence of the involvement of the three-center, two-electron bonding dictated by boron's electron deficiency. In this respect, no attempt is made to portray the structures in terms of localized two-center, two-electron bonds. Unless otherwise stated, the structures presented in this review will be drawn in terms of the usual "ball and stick" descriptions that should only indicate bonding connectivities within individual cages. (Black circles indicate carbon; small black circles extra protons; and white circles denote boron positions. Terminal hydrogens are omitted for clarity.)

The reader should be reminded that each cage boron and carbon contributes three atomic orbitals and two

CHART 1



and three electrons, respectively, to the cluster bonding proper, while the fourth orbital is used for exoskeletal two-electron, two-center bonding. Thus, the combination of Lipscomb's topological theory[3] and the polyhedral skeletal electron pair theory (PSEPT)[11c,26b,d] yields the basic relation ($n + (c/2) = s + t + x + y$) between the number of skeletal electron pairs [($n + (c/2)$)] and the usual *styx* symbols (s = number of bridging hydrogens, t = number of two-electron three-center bonds, y = number of two-electron, two-center bonds, and x = number of $\{BH_2\}$ units) defined by Lipscomb,[3] where c = 2, 4, 6, and 8 for closo, nido, arachno, and hypho compounds, respectively.

Over the period reviewed, the Lipscomb's topological theory[3] and the PSEPT concept, as simple and ingenious concepts usually are, have been extended into many areas, such as nonconventional borane, metallaborane, and inorganic-cluster chemistry.[33] Another extension has been suggested by Chinese theoreticians.[34] With increasing cluster symmetry and cluster size the original localized-bond treatments[3] become less adequate and molecular orbital descriptions are then generally held to be more suitable. A brief summary of the recently developed methods related to carborane chemistry might help the reader to get a basic orientation in this field.

Dewar and McKee[35] reported MNDO calculations on some of the known monocarbaboranes, *nido*-2-CB_5H_9 and [*closo*-1-$CB_{11}H_{12}]^-$, *closo*-dicarbaboranes $C_2B_{n-2}B_n$ (n = 5–12), *nido*-dicarbaboranes $C_2B_{n-2}H_{n+2}$ (n = 6, 9–11), $[C_2B_9H_{12}]^-$, and $[C_2B_9H_{11}]^{2-}$, and the $C_3B_3H_7$ tricarbaborane. On the basis of MO calculations Jemmis[36,37] proposed a "six-electron rule" to substantiate the previously recognized fact that carbon atoms usually tend to adopt the least connected positions in carborane structures.[11c,26a,c] Stabilities of selected *closo*-carborane isomers were correlated with the orbital overlap preferences of {BH} and {CH} cluster units. Whereas the latter group was found to prefer bonding to three or four-membered boron rings, the former prefers five-membered rings.

EHMO calculations of carborane stabilities based on topological charge stabilization (TCS) considerations, reported by Ott and Gimarc,[38] predicted a qualitative ordering of stabilities of positional isomers among various classes of *closo*-$C_2B_{n-2}H_n$ (for n = 5–12) carboranes. The TCS rule states that the positions of cluster carbons in a structure are related to the distribution of atomic charges that are determined by connectivity or topology for an isoelectronic, isostructural, and homoatomic reference system.

The AM1 calculations reported by Dewar[39] are an improvement upon the MNDO method because the latter overestimates the repulsive interactions between atoms. The systems studied included a range of small monocarba- and dicarbaborane cages CB_5H_7, CB_5H_9, $C_2B_3H_5$, and $C_2B_4H_6$. Of general relevance and applicability to carborane chemistry are the recent EHMO calculations by Wade et al.,[27] who included a wide range of basic prototype compounds of the closo to arachno series, and predicted relative stabilities and isomer preferences. A number of calculations aimed at rationalizing the endo bridging hydrogen positions in nido and arachno boron-cage systems[27b] and explaining the long-established observation[7b,26a,c] that no hydrogen bridges are allowed between carbon and boron and why the $\{CH_2\}$ group is preferred in arachno carborane systems have been reported and are of special theoretical significance for carborane chemistry.

Stone[40,41] has outlined the theoretical basis for the tensor surface harmonic (TSH) concept which is of general applicability to all closed cluster systems. The method yields a general proof of the electron-counting rules for boron cluster compounds and similar transition metal cluster compounds. It also substantiates the common preference for triangulated polyhedral structures. This theory has been generalized for nido and arachno cages[42] and extended to allow quantitative assessment of MO energy levels in various boron-cluster compounds[43-46] including closo carboranes, metallaboron, and inorganic cages.[47-49]

Another useful approach to the theoretical treatment of metallic clusters, which is generally applicable to carborane compounds, is Teo's topological electron-counting (TEC) theory.[50-52] This is based on Euler's theorem and the effective atomic number (EAN) rule and has been used to predict electron counts for a wide range of polyhedral clusters. The TEC theory was generalized[53] and its arguments were merged with those of the PSEPT by Teo[54] and Mingos.[55]

The application of the graph theory by King[56-58] to the area of polyhedral systems has proved of general interest. Among other aspects, this topological and group-theoretical approach was used to distinguish between inherently rigid clusters and those for which one or more diamond–square–diamond (DSD) rearrangement processes[59] are possible. This was done on the basis of purely geometrical arguments. An interesting approach to cage energetics and rearrangement mechanisms in boron-cage species has been reported by Fuller and Kepert,[60,61] who used a simple relation between bond energy and internuclear distances. The bonding in closed borane structures (n = 5–12) is considered to be a function of the sum of possible $n(n-2)/2$ interboron interactions.

A considerable amount of theoretical work has been reported on cluster-rearrangement processes. Usually variations of the Lipscomb's DSD concept[59] seem to offer the most acceptable explanations although other alternatives have been suggested. Theoretical aspects of carborane rearrangement (DSD) mechanisms have been recently reviewed by Gimarc and Ott.[62] Stone and Wales[63] applied the TSH concept to cluster rearrangements in boranes to show that this theory can provide very simple selection rules for distinguishing between symmetry-allowed or symmetry-forbidden processes. Wales and Mingos[11d,64] have extended and generalized this appraoch for many metallaborane and inorganic clusters.

In carborane chemistry, NMR spectroscopy is the most widely used experimental method for structure investigation in the carborane area. A very useful chapter by Kennedy[65a] on boron NMR, with emphasis on polyhedral-boron-containing species, has appeared in an important textbook which seems destined to become a standard reference work in multinuclear NMR for chemists. Heřmánek et al.[17,65b] and Teixidor[66] have defined and reviewed empirical rules for predicting $\delta(^{11}B)$ chemical shift values which are of general significance for ^{11}B NMR signal assignments within a broad variety of closed and open borane/carborane clusters. The rules are based on various effects including those related to hybridization,[65] bridging hydrogens,[65] *endo*- and *exo*-cluster substituents, coordination number,[65,66] cluster shape,[66] and antipodal atoms.[65] These predictive rules have partially lost their value since the introduction of the novel two dimensional NMR techniques, such as $[^{11}B-^{11}B]$-COSY[67-69] and $[^{1}H-^{1}H]$-COSY[70] spectroscopy. These techniques usually allow unambiguous ^1H and ^{11}B signal assignments for most borane and carborane compounds. Boron-11 NMR shifts have also been the subject of various quantum chemical treatments, such as INDO,[71] Fenske-Hall,[72] and IGLO[73] calculations. A mechanism of the antipodal effect[65] has been recently postulated on the basis of an analysis of the calculated electron densities[74] and substantiated by the Fenske-Hall MO treatment.[72]

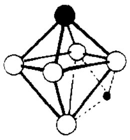
Onak et al.[75] correlated the aromatic-solvent-induced ^1H NMR shifts (ASIS effect) observed for a series of *closo*-dicarbaboranes (n = 3–10) to PRDDO-derived hydrogen charges (Q). Linear correlations between $\Delta\tau$ and Q markedly improve when nearest-neighbor cage hydrogen effects are considered. From these relationships a procedure was developed to obtain the hydrogen charges from $\Delta\tau$ values only. The same group[76] correlated the magnitude of $^1J(^{11}B-^1H)$ values for individual boron atoms in *closo*-carboranes (n = 5–12) with both the number of adjacent cage carbon atoms and cage "umbrella" angles (θ). These latter contribute significantly to changes in the observed $^1J(^{11}B-^1H)$ value. A good agreement between predicted and experimental values of coupling constants was achieved for nonfluxional carboranes. Williams et al.[7,77] reported a useful correlation between ^{13}C and ^{11}B NMR shift values for boron hydrides and corresponding nonclassical carbocationic compounds. Dolanský et al.[78] correlated electronic structures and ^{11}B NMR shifts for selected nine-vertex mono- and dicarbaboranes with parameters obtained from STO-3G and CNDO/2 calculations.

III. Monocarbaboranes

Monocarbaboranes, compounds of the general formulas *closo*-$CB_{n-1}H_{n+1}$, *nido*-$CB_{n-1}H_{n+3}$, and *arachno*-$CB_{n-1}H_{n+5}$ for neutral compounds, are still a less explored area of carborane chemistry, but many examples of new smaller-cage types of monocarbaboranes have been reported over the last decade. Typical synthetic routes are based either on methods involving one-carbon insertion into a borane moiety or, more commonly, on diverse variants of boron- or carbon-degradation reactions.

1. Small Monocarbaboranes

The smallest cage monocarbaborane that has been isolated is *closo*-1-CB_5H_7 (1),[1] and it is surprising that the deprotonated form, the parent [*closo*-1-CB_5H_6]$^-$ anion (2), has not yet been reported. Brint and Sangchakr[32] have carried out comparative MNDO calculations on 2 and the isoelectronic borane and thiaborane systems $[B_6H_6]^{2-}$ and SB_5H_5. No new chemistry of 1 has been discussed in the recent literature, perhaps due to the difficulties associated with its preparation. A theoretical study by McKee[79] has appeared, describing hydrogen scrambling reactions for 1. Barrier lengths were calculated at the MP2/6-31G* level on 3-21G optimized geometries and were corrected for differences in zero-point energy. The extra hydrogen in structure 1 was predicted to migrate in the vicinity of boron atoms with a barrier of 14.8 kcal/mol. In contrast to the results of the earlier reviewed[5] electron diffraction study, which found the extra hydrogen almost perfectly face bridging, calculations at the HF/3-21G level point to the hydrogen bridging between two borons [B(2,3) or B(2,6)] and only weakly interacting with the third boron. Brint et al.[30] have calculated the geometry of *closo*-1-CB_5H_7 at the MNDO-6-80 level and found a good agreement with the experimental bond lengths.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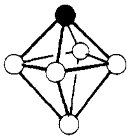
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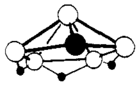
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More recent chemistry has been associated with that of the nido congener of the above compounds, *nido*-2-CB_5H_9 (**3**). DeKock and Jasperse[31] used MNDO calculations to estimate the proton affinities for **3** and predicted carbon protonation. Sneddon et al.[80,81] isolated a mixture of the positional isomers of **3**, 2-R′-3-RCH_2-2-CB_5H_7 and 2-R′-4-RCH_2-2-CB_5H_7 from the thermolysis at 355 °C of *cis*-2-RCH=C(R′)-B_5H_8 compounds (derivatives of *nido*-B_5H_9, see structure II, R,R′ = Me,Me; H,Me; or Me,H). The mechanistic study unequivocally points to the cage-boron addition to the α-carbon of the alkene. Thus the α-carbon is incorporated into the cage, while the β-carbon forms an RCH_2 group.

$$RCH{=}C(R')B_5H_8 \rightarrow R'\text{-}RCH_2CB_5H_7 \qquad (1)$$

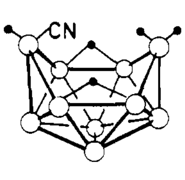
2. Eight- to Eleven-Vertex Monocarbaboranes

The traditional source for this class of monocarbaboranes is the $[6\text{-NC-}arachno\text{-}B_{10}H_{13}]^{2-}$ anion[82] (**4**) which, according to the recently reported X-ray diffraction study,[83] displays a unique endo configuration of the CN group. This arrangement accounts for the observed direct insertion of the CN carbon into the cage on protonation with hydrochloric acid[84] which produces 7-H_3N-*nido*-7-$CB_{10}H_{12}$ (structure **5**, L = H_3N) and 6-H_3N-*nido*-6-CB_9H_{11} (structure **6**, L = H_3N):

$$[B_{10}H_{13}CN]^{2-} + 2H^+ \rightarrow H_3NCB_{10}H_{12} \qquad (2)$$

$$[B_{10}H_{13}CN]^{2-} + 2H_3O^+ + H_2O \rightarrow H_3NCB_9H_{11} + B(OH)_3 + 2H_2 \qquad (3)$$

Equations 2 and 3 suggest that the latter reaction is accompanied by partial cluster degradation, evidently due to hydrolytic removal of the B(9) vertex in structure **4**. The ratio of **5** and **6**, resulting from reactions 2 and 3 seems to be primarily controlled by temperature and acid concentration.[84] Both compounds **5** and **6** (L = H_3N) were separated by tedious chromatographical procedures[84-86] as their *N*-methyl derivatives until a more efficient method was developed.[87] This method relies on the sharply different reaction rates of the amminates **5** and **6** with acetone. The predominant product, 6-Me_2C=NH-*nido*-6-CB_9H_{11}, is then easily separable from unreacted **5**. The *N*-isopropylidene group can be smoothly removed to regenerate the above mentioned H_3N derivative of **6**. Reactions at the nitrogen center led to the isolation of the $[6\text{-}H_2N\text{-}nido\text{-}6\text{-}CB_9H_{11}]^-$ anion and 6-Me_2S-*nido*-6-CB_9H_{11} (both of structure **6**).[87]



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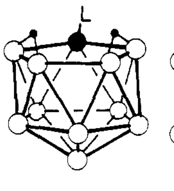

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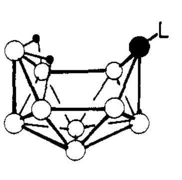

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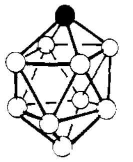
The trimethylamine derivative of **6** has been used recently to prepare the $[closo\text{-}1\text{-}CB_9H_{10}]^-$ anion (structure **7**) by treatment with excess piperidine (70°, 3 days)[88] in 68% yield:

$$Me_3NCB_9H_{11} + \text{pipe.} \rightarrow Me_3N + [\text{pipe.H}]^+[CB_9H_{10}]^- \qquad (4)$$

The reaction, eq 4, represents a straightforward nido to closo conversion and is a convenient alternative to the previously reported[84a,b] method of Knoth. A structural study[88] of **7** made on the ionic compound $[(\eta^5\text{-}C_5Me_5)_2Ir_2Cl_3]^+[1\text{-}CB_9H_{10}]^-$ led to the following mean cage distances: C(1)–B 155.5, B–B(upper belt) 182.0, B–B(interbelt) 179.5, B–B(lower belt) 185.9, and B(10)–B 162.5 pm; the B(7)–B(8) distance was found to be considerably longer at 191.7 (37) pm than the equivalent bond length in the isoelectronic $[B_{10}H_{10}]^{2-}$ anion,[89] which is indicative of a partial cage opening, a phenomenon often encountered in metallaborane chemistry. Anion **7** was also used by Russian workers for the preparation of a series of salts with a variety of miscellaneous countercations that included those of alkali metals[90] and complex cations of Co(II) and Ni(II) (complexed by benzoylhydrazine and (*m*-nitrobenzoyl)hydrazine).[91,92]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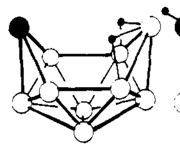
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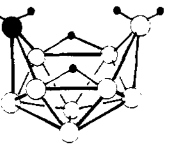
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Of key importance for the synthesis of nine- and ten-vertex species of the monocarbaborane family is the high-yield (80%) preparation of the parent $[nido\text{-}6\text{-}CB_9H_{12}]^-$ anion (**8**)[84c] from the reaction between **6** (L = Me_3N) and sodium metal in liquid ammonia (eqs 5 and 6).

$$Me_3NCB_9H_{11} + 3e^- \rightarrow Me_3N + [CB_9H_{10}]^{3-} + \tfrac{1}{2}H_2 \qquad (5)$$

$$[CB_9H_{10}]^{3-} + 2H_2O \rightarrow [CB_9H_{12}]^- + 2OH^- \qquad (6)$$

Anion **8** (trimethylammonium salt) was found to react almost quantitatively with sodium in liquid ammonia in a straightforward nido → closo conversion leading to the isolation of the $[arachno\text{-}6\text{-}CB_9H_{14}]^-$ anion (**9**),[93,94] an analogue of the prototype borane anion $[B_{10}H_{14}]^{2-}$ (see schematic structure XVIII):

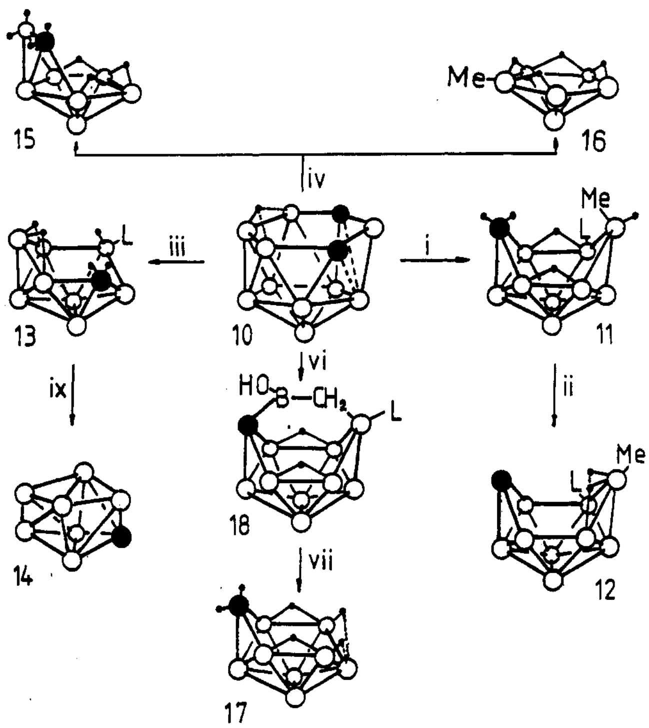
$$[CB_9H_{12}]^- + 2e^- \rightarrow [CB_9H_{12}]^{3-} \qquad (7)$$

$$[CB_9H_{12}]^{3-} + 2H_2O \rightarrow [CB_9H_{14}]^- + 2OH^- \qquad (8)$$

It should be noted that the trianions involved in eqs 5 and 7 are proposed intermediates based on the stoichiometry of these reactions but neither has been isolated so far.

A conceptually different and efficient route to nine- and ten-vertex compounds of the monocarbaborane family is outlined in Scheme 1. All reactions in Scheme 1 are based on selective removal of a defined number of boron vertices together with one cage carbon atom from the $[nido\text{-}7,9\text{-}C_2B_{10}H_{13}]^-$ anion[95-98] (structure **10**

SCHEME 1



in Scheme 1). The structure of this anion has been determined by using X-ray methods[97] and in solution by using NMR.[98] Treatment of anion **10** in aqueous THF with trimethylamine[95,99a] (path i in Scheme 1) resulted in the isolation of 9(*endo*)-Me-8-Me$_3$N-*arachno*-6-CB$_9$H$_{12}$ (structure **11** in Scheme 1). This compound is an asymmetrically substituted ligand derivative of the parent anion (**9**) with the *endo*-Me group generated from one of the skeletal carbons in structure **10** upon hydrolytic degradation of the B(8) vertex:

$$[C_2B_{10}H_{13}]^- + H_3O^+ + 2H_2O + Me_3N \rightarrow Me_3N{\cdot}CH_3CB_9H_{12} + B(OH)_3 + H_2 \tag{9}$$

A straightforward arachno → nido conversion was observed in the reaction of **11** with acetone in the presence of potassium carbonate (path ii in Scheme 1).[95,99a] This generated the nido analogue of **11**, 9-Me-8-Me$_3$N-*nido*-6-CB$_9$H$_{10}$ (structure **12** in Scheme 1) in high yield (85%):

$$Me_3N{\cdot}MeCB_9H_{12} + Me_2CO \rightarrow Me_2CHOH + Me_3N{\cdot}MeCB_9H_{10} \tag{10}$$

The molecular structure of a structurally similar compound, the [8-HO-9-Me-*nido*-6-CB$_9$H$_{10}$]$^-$ anion (8,9-disubstituted derivative of **8**), was determined by X-ray diffraction[99b] on its PPh^{4+} salt [selected bond distances: C(6)–B(5) 152.0 (6), C(6)–B(7) 152.8 (5), B(5)–B(10) 189.5 (6), B(7)–B(8) 1.962 (5), B(8)–B(9) 179.1 (5), and B(9)–B(10) 178.5 (6) pm].

Acid-promoted degradation of **10** in the presence of Lewis bases as in eq 11 (path iii in Scheme 1) resulted in the degradation of one carbon and two boron vertices from structure **10**, with the formation of a series of nine-vertex ligand derivatives of the 6(*exo*)-L-*arachno*-4-CB$_8$H$_{12}$ type (structure **13** in Scheme 1, L = Me$_3$N, Me$_2$S, urotropine, and py; yields 20–60%):[95,99a]

$$[C_2B_{10}H_{13}]^- + H_3O^+ + 4H_2O + L \rightarrow LCB_8H_{12} + B(OH)_3 + CH_3B(OH)_2 + 2H_2 \tag{11}$$

These compounds are structurally similar and isoelectronic to arachno dicarbaboranes of the C$_2$B$_7$H$_{13}$ series (structures **59** and **60** in section IV).

The action of sodium hydride on **13** (L = Me$_3$N) in THF at 60 °C (path ix in Scheme 1) resulted in the formation of the first representative of the eight-vertex closo series of monocarbaboranes, the [1-*closo*-CB$_7$H$_8$]$^-$ anion[95] (structure **14** in Scheme 1) (yield 60%). This was found to exhibit fluxional NMR behavior in solution within a wide temperature range[95] as does its borane-prototype congener [*closo*-B$_8$H$_8$]$^{2-}$.[100]

Another result of the degradation reactions of **10** is the formation of the first eight-vertex *arachno*-monocarbaborane 4-CB$_7$H$_{13}$ (structure **15** in Scheme 1) and the earlier reported[101] 2-Me-*nido*-B$_6$H$_9$ (structure **16** in Scheme 1) borane upon acidification of **10** with dilute hydrochloric acid (path iv in Scheme 1).[95] The ultimate product **16** is probably formed by degradation of the B(5) boron from the cage of **15**.

$$[C_2B_{10}H_{13}]^- + H_3O^+ + 7H_2O \rightarrow CB_7H_{13} + CB_3B(OH)_2 + 2B(OH)_3 + 3H_2 \tag{12}$$

$$[C_2B_{10}H_{13}]^- + H_3O^+ + 10H_2O \rightarrow CH_3B_6H_9 + CH_3B(OH)_2 + 3B(OH)_3 + 5H_2 \tag{13}$$

Scheme 1 (paths vi and vii) also shows another useful variation of a [C$_2$B$_{10}$H$_{13}$]$^-$-based synthesis of lower-cage monocarbaborane systems. This reaction sequence is a convenient preparation of the parent nine-vertex *arachno*-monocarbaborane 4-CB$_8$H$_{14}$ (structure **17** in Scheme 1) (yield ca. 50%, based on the starting *o*-carborane). The reaction of anion **10** with dimethyl sulfide and concentrated hydrochloric acid initially produces the unique compound μ-6,9-[B(OH)CH$_2$]-9-Me$_2$S-*arachno*-6-CB$_9$H$_{11}$ (structure **18** in Scheme 1) as an isolable intermediate:[102]

$$[C_2B_{10}H_{13}]^- + H_3O^+ + Me_2S \rightarrow Me_2SB(OH)CH_2CB_9H_{11} + H_2 \tag{14}$$

$$Me_2SB(OH)CH_2CB_9H_{11} + 4H_2O \rightarrow CB_8H_{14} + CH_3B(OH)_2 + B(OH)_3 + Me_2S + 2H_2 \tag{15}$$

Compound **18** then undergoes rapid hydrolytic degradation (eq 15) to give carborane **17** as a sole product.[102] Moreover, this carborane can be converted in 90% yield into [*nido*-6-CB$_9$H$_{12}$]$^-$, by the action of sodium tetrahydroborate in boiling THF:[102]

$$CB_8H_{14} + BH_4^- \rightarrow [CB_9H_{12}]^- \tag{16}$$

The reaction sequence according to eqs 14–16 is a new and safe synthetic route to nine- and ten-vertex monocarbaboranes from the commercially available *o*-carborane or at least a good alternative to the previously reported[84c] synthesis of compounds **17** and **8**. Reaction 17 (80% yield), which is in fact a reverse process of reaction 16, is promoted by ferric chloride.[84c]

$$[CB_9H_{12}]^- + H_3O^+ + 2H_2O \rightarrow CB_8H_{14} + B(OH)_3 + 2H_2 \tag{17}$$

Howarth et al.[103] have measured the two-dimensional NMR spectra of 4-CB$_8$H$_{14}$ and its anion, [4-CB$_8$H$_{13}$]$^-$ (structure **19**), to confirm the original signal assignments[84c] and to assign all ^{1}H NMR resonances of the cluster {BH} units in both compounds. The former compound is known to lose dihydrogen upon thermo-

TABLE 1. Monocarbaboranes with 6–10 Cage Atoms

compound	structure	measured data	ref(s)
2-Me-3-Et-2-CB_5H_7	3	^1H, ^{11}B, MS	80, 81
2-Me-4-Et-2-CB_5H_7	3	^1H, ^{11}B, MS	80, 81
2-Et-2-CB_5H_8	3	^1H, ^{11}B, MS	80, 81
4-Et-2-CB_5H_8	3	^1H, ^{11}B, MS	80, 81
$[1\text{-}CB_7H_8]^-$	14	^1H, ^{11}B	95, 99a
4-CB_7H_{13}	15	^1H, ^{11}B,[a] MS	95
6(exo)-L-4-CB_8H_{12}[b]	11	^1H,[a] ^{11}B,[a] MS	95, 99a
1-CB_8H_{12}	20	^1H,[a] ^{11}B,[a] MS	84c, 104
4-CB_8H_{14}	17	^1H,[a] ^{11}B,[a] MS	84c, 103
$[1\text{-}CB_9H_{10}]^-$	7	^1H, ^{11}B, XR	95, 99a
$[6\text{-}CB_9H_{12}]^-$	8	^1H, ^{11}B[a]	84c, 87
6-L-CB_9H_{11}[c]	6	^1H, ^{11}B,[a] MS	84c, 87
6-Me-8-Me_3N-6-CB_9H_{10}	12	^1H,[a] ^{11}B,[a] MS, mp	95, 99
$[6\text{-}CB_9H_{14}]^-$	9	^1H, ^{11}B,[a] MS	93, 94
$[6\text{-Me-8-HO-6-}CB_9H_{10}]^-$	9	^1H,[a] ^{11}B,[a] XR	99
6-Me-8-Me_3N-6-CB_9H_{12}	11	^1H,[a] ^{11}B,[a] MS, mp	95, 99a

[a] 2-D measurements. [b] L = Me_3N, Me_2S, Py. [c] L = H_3N, Me_3N, $Me_2C{=}NH$, Me_2S, and NH_2^-.

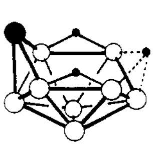
TABLE 2. Compounds of the Eleven-Vertex L-*nido*-7-$CB_{10}H_{11}X$ Type (Cage Structure 5)

compound [X, L]	measured data	ref(s)
H, 7-H_3N	mp, ^1H, ^{11}B, R_F	105
H, 7-Me_3N	^1H, ^{11}B, R_F	105
H, 7-$Me_2C{=}NH$	mp, ^1H, ^{11}B, R_F, IR	105
H, 7-$(CH_2)_5C{=}NH$	mp, ^1H, ^{11}B, R_F, IR	105
H, 7-$PhC(PhCH_2){=}NH$	mp, ^1H, ^{11}B, R_F, IR	105
H, 7-Me_2S	mp, ^1H, ^{11}B, R_F, IR	105
H, 7-$(CH_2)_6N_4$	mp, ^1H, ^{11}B, R_F	105
H, 7-$HOCONH_2$	mp, ^1H, ^{11}B, R_F, IR	105
H, 7-$MeCONH_2$	mp, ^1H, ^{11}B, R_F, IR	105
H, 7-$PhCONH_2$	mp, ^1H, ^{11}B, TLC, IR	105
H, $[7\text{-}NH_2]^-$	^{11}B	105
8-C_6H_{11}, 7-$^tBuNH_2$, 2-Me_2S	mp, ^1H, ^{11}B, IR, XR	106
H, 8-Me_2S	mp, ^1H, ^{11}B,[a] IR	107
H, 8-PPh_3	mp, ^1H, ^{11}B,[a] IR, XR	107
7-$(Me_3Si)_2CH$, 8-Me_2S	mp, ^1H, ^{11}B,[a] IR	108
7-$(Me_3Si)_2CH$, 8-PPh_3	mp, ^1H, ^{11}B,[a] IR	109

[a] 2-D measurements.

lysis at 350 °C and to generate *nido*-1-CB_8H_{12} (**20**),[84c] whose structure and its relation to the binary borane anion $[nido\text{-}B_9H_{12}]^-$ (schematic structure XIV) has been confirmed unambiguously by [^{11}B–^{11}B]-COSY NMR spectroscopy.[104]

Selected compounds of the six- to ten-vertex series of monocarbaboranes are listed in Table 1.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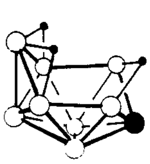
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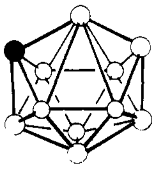
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The eleven-vertex series of monocarbaboranes is represented by the parent anions $[closo\text{-}2\text{-}CB_{10}H_{11}]^-$ (**21**) and $[nido\text{-}7\text{-}CB_{10}H_{13}]^-$ (**22**) reviewed earlier.[1,2,5] The usual synthesis of these monocarbaboranes starts from 7-ligand derivatives of anion **22**, 7-L-*nido*-7-$CB_{10}H_{12}$ (**5**) (L = H_3N and Me_3N), which are accessible from *nido*-$B_{10}H_{14}$ as in eq 2[84] or from the reaction of decaborane with isonitriles.[85]

The author's group[105] has employed the H_3N derivative of **5** to prepare a series of compounds of the same type by using various chemical modifications of the exoskeletal H_3N group. These reactions afforded compounds with modified ligands on the carbon vertex in structure **5** (L = $Me_2C{=}NH$, $(CH_2)_5C{=}NH$, $PhCH_2(PhCH{=})N$, Me_2S, urotropine, $HOCOCH_2NH_2$, $MeCONH_2$, $PhCONH_2$), with yields varying from 11 to 92%. These "organic-like" reactions demonstrate chemical flexibility of the exoskeletal H_3N group for designed syntheses of compounds for targeted research. Measured properties for individual compounds of the eleven-vertex nido series are summarized in Table 2. Boron-substituted compounds of the general *nido*-7-L-7-$CB_{10}H_{12}$ type are available from boron-substituted precursors derived from both {*nido*-B_{10}} and {*nido*-CB_{10}} cage systems. Thus, 2-Me_2S-7-$^tBuNH_2$-8-(cyclohexyl)-*nido*-7-$CB_{10}H_{10}$ was prepared[106] by a variation of the original isocyanide synthesis.[85] The structural details of this compound were determined by X-ray crystallography, as shown in Figure 1.

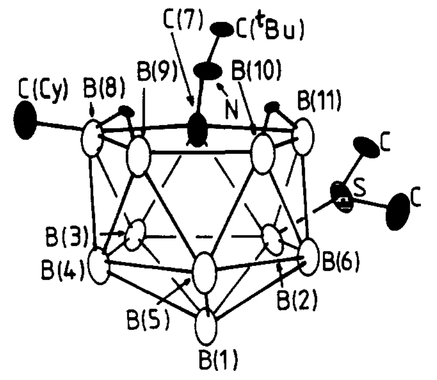


Figure 1. Schematic representation of the 2-Me_2S-7-$^tBuNH_2$-8-C_6H_{11}-*nido*-7-$CB_{10}H_{10}$ structure.[106] Selected mean exocage distances were B(2)–S 188.9 (9), mean S–C(Me) 179.9, C(7)–N 147.3 (9), and N–C(^{t}Bu) 149.8 (9) pm. For mean cage distances see Table 3.

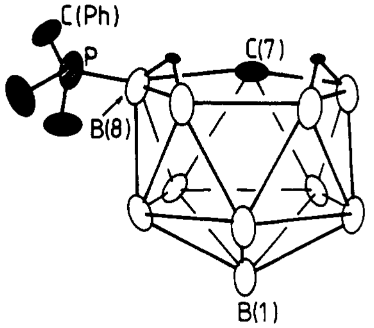
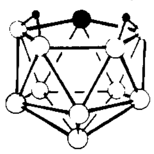


Figure 2. Simplified representation of the structure of 8-PPh_3-*nido*-7-$CB_{10}H_{12}$ (**23**). Selected exocluster bond distances were[107] B(8)–P 194.8 (4), P–C(Ph) 180.3, and C–C(Ph) 137.6 pm. For numbering see Figure 1 and for mean cage distances Table 3.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Another positional isomer of the same series, 8-Me_2S-*nido*-7-$CB_{10}H_{12}$ (see the PPh_3 analogue **23** in Figure 2), was prepared[107] from the reaction between $[7\text{-}CB_{10}H_{13}]^-$ and dimethyl sulfide in the presence of concentrated sulfuric acid:

$$[CB_{10}H_{13}]^- + Me_2S + H^+ \rightarrow Me_2SCB_{10}H_{12} + H_2 \tag{18}$$

The dimethyl sulfide derivative was converted to 8-

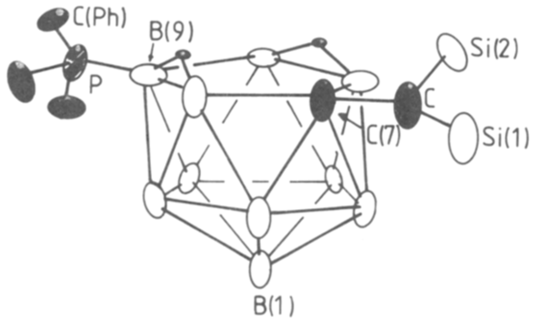


Figure 3. Schematic drawing of the molecular structure of 7-$(Me_3Si)_2CH$-9-PPh_3-*nido*-7-$CB_{10}H_{11}$ (**24**). Selected exocage distances were[109] B(9)–P 192.8 (5), C(7)–C 156.2 (7), mean C–Si 189.6, and C(Me)–Si 186.8 pm. For numbering see Figure 1 and for cage distances Table 3.

TABLE 3. Comparison of Mean Cage Distances (pm) for Structurally Determined Eleven-Vertex Nido Compounds of the {L-7-$CB_{10}H_{11}$X} Type (Cage Structure 5)

distance	L X	2-Me_2S-7-$NH_2{}^tBu$ 8-C_6H_{11}[a]	8-PPh_3[b]	9-PPh_3- 7-$(Me_3Si)_2CH$[c]
B(1)–B		177.1	174.5	176.8
B–B (lower belt)		175.8	177.5	176.7
B–B (interbelt)		178.2	176.6	178.0
C–B (interbelt)		171.1	170.1	170.0
C–B (open face)		167.4	163.5	165.6
B–B (bridge)		187.2	184.6	187.1
B(9)–B(10)		187.8	185.9	186.8

[a] From ref 106. [b] From ref 107. [c] From ref 109.

PPh_3-*nido*-7-$CB_{10}H_{12}$ (**23**) by refluxing with triphenylphosphine in benzene (80% yield).[107] The simplified molecular structure of **23**, as determined by X-ray diffraction, is depicted in Figure 2.

A new route to monocarbaboranes of the {*nido*-7-CB_{10}} type is provided by the reaction of decaborane(14) and bis(trimethylsilyl)acetylene in boiling benzene[108] in the presence of dimethyl sulfide (eq 19). This leads to 9-Me_2S-7-$(Me_3Si)_2CH$-*nido*-7-$CB_{10}H_{11}$ (see similar structure **24** in Figure 3) (28% yield) and 5-Me_2S-6-[$(Me_3Si)_2C{=}CH$]-*nido*-$B_{10}H_{11}$ (21%). While the latter compound is a product of hydroboration at the B(6) site of the decaborane cage (schematic structure XVII), the former is apparently formed by direct one-carbon insertion into the area of the cage defined by the B-(5,6,9,10) atoms in structure XVII.

$$(Me_3Si)_2C_2 + B_{10}H_{14} + Me_2S \rightarrow Me_2S{\cdot}(Me_3Si)_2CHCB_{10}H_{11} + H_2 \quad (19)$$

$$R_2C_2 + B_{10}H_{12}{\cdot}(SMe_2)_2 \rightarrow R_2C_2B_{10}H_{10} + 2Me_2S + H_2 \quad (20)$$

The reaction depicted in eq 19 contrasts with the long-established[1,2,5] two-carbon insertion process (eq 20) leading to twelve-vertex dicarbaboranes. Inspection of the former equation also indicates that the carbon insertion is accompanied by the $\alpha \rightarrow \beta$ migration of the silyl substituent along the C=C bond of the primary hydroboration intermediate. Ligand exchange between the Me_2S derivative and triphenylphosphine yielded the corresponding 9-PPh_3-7-$(Me_3Si)_2CH$-*nido*-7-$CB_{10}H_{11}$ analogue (**24**) (80% yield),[109] the X-ray structure of which is outlined in Figure 3. Bond distances for structurally determined compounds of the {*nido*-L-7-$CB_{10}H_{12}$} type are in Table 3.

In the light of previous[5] and recent[110] review work, compounds of the {*nido*-L-7-CB_{10}} type are used exclusively to generate monocarbaboranes of the eleven-vertex closo series, typified by the [*closo*-2-$CB_{10}H_{11}$]$^-$ anion (**21**), by reaction with suitable reagents which result in the net removal of two cage electrons. Recent work in this area represents a continuation of this strategy and has brought another useful synthetic variation.

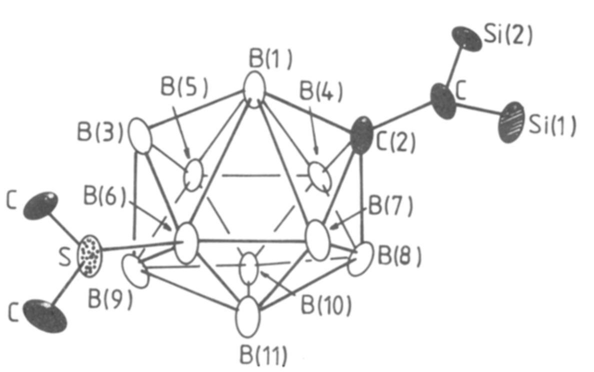


Figure 4. Simplified molecular structure of 2-$(Me_3Si)_2CH$-6-Me_2S-*closo*-2-$CB_{10}H_9$ (**25**).[108] Selected exocage bond lengths were B(6)–S 189.5 (5), mean C(Me)–S 177.9, C(2)–C 153.2, and mean C(Me)–Si 185.4 pm. For cage distances see Table 4.

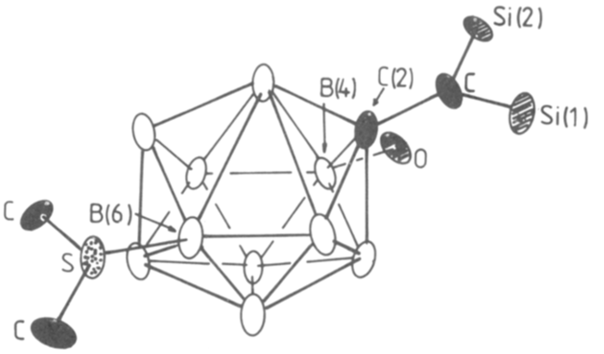


Figure 5. Schematic representation of the X-ray structure of 2-$(Me_3Si)_2CH$-4-HO-6-Me_2S-*closo*-2-$CB_{10}H_9$ (**26**).[108] Selected exocage bond lengths are B(6)–S 189.4 (4), B(4)–O 138.4 (5), C–C(2) 154.2 (4), C–Si 190.1 (4), and mean C(Me)–Si 186.3 (5) pm. For numbering see Figure 4 and for cage distances Table 4.

Two groups[18,107] have modified the preparation of the parent anion **21** by treatment of 8-Me_2S-*nido*-7-$CB_{10}H_{12}$ with basic reagents. The best result has been achieved by sodium hydride:[107]

$$Me_2SCB_{10}H_{12} + H^- \rightarrow [CB_{10}H_{11}]^- + Me_2S + H_2 \quad (21)$$

Reaction 21 represents a straightforward nido → closo conversion accompanied by expulsion of Me_2S. Thermal dehydrogenation of 8-Me_2S-7-$CB_{10}H_{12}$ in boiling toluene afforded 4-Me_2S-*closo*-2-$CB_{10}H_{10}$,[107] a 4-substituted derivative of **21**. A similar thermal treatment of the 9-Me_2S-7-$(Me_3Si)_2CH$-7-$CB_{10}H_{11}$ derivative afforded[108] 6-Me_2S-2-$(Me_3Si)_2CH$-*closo*-2-$CB_{10}H_9$ (**25**), i.e. 2,6-disubstituted derivative of **21**. A 4-hydroxy derivative of the last compound, 4-HO-6-Me_2S-2-$(Me_3Si)_2$-2-$CB_{10}H_8$ (**26**), was obtained as a minor product from the thermolysis reaction in the solid state. A variation of the reaction represented in eq 21 was observed with 9-Me_2S-7-$(Me_3Si)_2CH$-7-$CB_{10}H_{11}$ and NaH (or $LiBHEt_3$) in THF. The product was a silylated derivative of **21**, the [2-$(Me_3Si)_2CH$-2-$CB_{10}H_{10}$]$^-$ anion (**27**), which was isolated as Cs^+, Li^+, Na^+, and $[Cp_2Co]^+$ salts.[108] Structures of the closo compounds **25**–**27** have been analyzed by X-ray crystallography and, simplified, they are depicted in Figures 4–6.

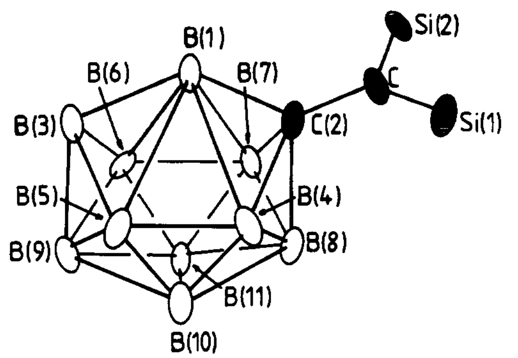


Figure 6. Schematic drawing of the X-ray structure of $[Cp_2Co]^+[2\text{-}(Me_3Si)_2CH\text{-}\textit{closo}\text{-}2\text{-}CB_{10}H_{10}]^-$ (**27**). Selected mean exocage bond distances are[108] C–C(2) 154.0 (6), mean C–Si 190.3, and mean C(Me)–Si 185.5 pm. For cage distances see Table 4.

TABLE 4. Mean Cage Bond Distances (pm) for Crystallographically Determined Derivatives of the Eleven-Vertex *closo*-{2-CB_{10}} Type (Data from Ref 108)

	compound		
	25[a]	**26**[b]	**27**[c]
C(2)–B(1)	164.6 (5)	165.6 (6)	164.1 (8)
C(2)–B(4,5)	159.2	157.6	159.2
C(2)–B(8)	169.3 (6)	170.3 (6)	168.2 (7)
B(1)–B(3)	174.7 (3)	177.5 (6)	170.4 (9)
B(1)–B(6,7)	198.6	199.7	203.0
B(8)–B	176.5	178.1	178.1
B(9)–B	177.0	176.3	175.4
B(10)–B(11)	181.8 (7)	180.6 (6)	179.5 (9)
B(4,5)–B(10,11)	176.6	178.2 (6)	177.2
B(6,7)–B(10,11)	175.7	175.4	176.2
B(4 or 5)–B(7 or 6)	164.7	165.2	164.5

[a] Data for $2\text{-}(Me_3Si)_2CH\text{-}6\text{-}Me_2S\text{-}\textit{closo}\text{-}2\text{-}CB_{10}H_9$. [b] Data for $2\text{-}(Me_3Si)_2CH\text{-}4\text{-}HO\text{-}6\text{-}Me_2S\text{-}\textit{closo}\text{-}2\text{-}CB_{10}H_8$. [c] Data for $[Cp_2Co]^+[2\text{-}(Me_3Si)_2CH\text{-}\textit{closo}\text{-}2\text{-}CB_{10}H_{10}]^-$.

TABLE 5. Monocarbaborane Compounds of the Eleven-Vertex L-*closo*-2-$CB_{10}H_9X$ Type

X	L	structure	measured data	ref(s)
H	H^-	21	^1H, ^{11}B, IR, UV, DTA	11, 112
H	$4\text{-}Me_2S$	21-type	^1H, ^{11}B, MS	107
$2\text{-}(Me_3Si)_2CH$	$6\text{-}Me_2S$	25	^1H, ^{11}B, MS, XR	108
$2\text{-}(Me_3Si)_2CH$ 4-HO	$6\text{-}Me_2S$	26	^1H, ^{11}B, MS, XR	108
$2\text{-}(Me_3Si)_2CH$	H^-	27	^1H, ^{11}B, XR	108

Kuznetsov et al.[111,112] have extended the cationic chemistry of **21** by isolating salts with various countercations [including all alkali metals, R_4N^+ (R = Me, Et, and ^{n}Bu), and PPh_4^+] and determined some of their properties. Selected compounds of the eleven-vertex series of monocarbaboranes are in Tables 2 and 5, and selected mean bond distances for structurally determined compounds are in Tables 3 and 4.

3. Twelve-Vertex Monocarbaboranes

TABLE 6. Comparison of Mean Cage Bond Distances (pm) for Crystallographically Determined Compounds of the {*closo*-1-CB_{11}} Type (Cage Structures 29 and 30)

	29[a]	**29**[b]	**30**[c]	**30**[d]
C(1)–B	170.1	169.8	172.3	172.3
B–B (upper belt)	177.3	175.7	178.1	177.0
B–B (interbelt)	178.3	175.3	176.5	175.4
B–B (lower belt)	178.6	178.3	177.6	176.4
B(12)–B	177.6	177.0	177.6	176.8

[a] Data for $AgCB_{11}H_{12}$ from ref 113. [b] Data for $Fe(TPP)CB_{11}H_{12}$ from ref 115. [c] Data for $1\text{-}Me_3N\text{-}1\text{-}CB_{11}H_{11}$ from ref 127. [d] Data for $NMe_4^+[1\text{-}Me_2N\text{-}1\text{-}CB_{11}H_{11}]^-$ from ref 129.

Compounds of the twelve-vertex closo family, represented by the parent $[\textit{closo}\text{-}1\text{-}CB_{11}H_{12}]^-$ anion (**28**), have been extensively studied in recent times. Structural work has been reported for a variety of compounds that contain **28** as the main cluster constituent. Reed's group has found this anion to be the least coordinating of ligands for the complexation of transition metals, such as Ag and Fe. The complexes included $[(\eta^1\text{-}C_6H_6)Ag(\textit{closo}\text{-}1\text{-}CB_{11}H_{12})]\cdot C_6H_6$,[113] $[Fe(TPP)(\textit{closo}\text{-}1\text{-}CB_{11}H_{12})]\cdot C_7H_8$,[114,115] $[Ir(CO)(PPh_3)_2Ag(\textit{closo}\text{-}1\text{-}CB_{11}H_{12})]$,[116,117] and $[Cp(CO)_2FeCB_{11}H_{12}]$,[117] all of which were structurally characterized via X-ray diffraction studies. The complexes contain a σ-bonded carborane anion with a common $[M\text{-}H\text{-}B_{11}CH_{11}]$ structural motif (**29**), whose intrinsic feature is the M-H-B(12) bridging group (for selected bond distances of some structurally determined compounds of the {*closo*-CB_{11}} type, see Table 6).

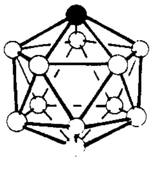
Kuznetsov et al.[118–122] have extended the cation-modification approach to the chemistry of **28** in order to isolate a series of salts with alkali metals and cobalt and nickel cations complexed by (*m*-nitrobenzoyl)-hydrazine, 2,2′-bipyridine, and *o*-phenanthroline. They characterized these salts by DTA, IR spectra, and elemental analyses.

The author's group has developed an alternative synthetic route to the compounds of the {*closo*-1-CB_{11}} series, based on cluster-expansion reactions between the 7-L-*nido*-7-$CB_{10}H_{12}$ (L = H_3N and Me_3N) compounds and triethylamine borane at elevated temperatures (180–200 °C). Variations of this method have generated compounds of the 1-L-*closo*-1-$CB_{11}H_{11}$ type (**30**) (L = H_3N and Me_2NH),[123–125] both of which can be methylated to give $1\text{-}Me_3N\text{-}1\text{-}CB_{11}H_{11}$. As documented by ^{10}B-tracer studies,[126] the reaction is site-selective, in agreement with a clean insertion of one boron vertex into the open pentagonal face of the {*nido*-CB_{10}}-type cage (**5** or **22**). Thus, reactions of $[\textit{nido}\text{-}7\text{-}CB_{10}H_{13}]^-$ and $7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_{12}$ with $Et_3N^{10}BH_3$ produced $[\textit{closo}\text{-}1\text{-}CB_{11}H_{12}]^-$ and $[1\text{-}Me_3N\text{-}\textit{closo}\text{-}CB_{11}H_{11}]$ compounds regiospecifically labeled by ^{10}B at the B(2) position.[126] However, the same reaction with $8\text{-}PhCH_2\text{-}7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_{11}$ results in the rearrangement of the benzyl substituent to yield $1\text{-}Me_3N\text{-}7\text{-}PhCH_2\text{-}1\text{-}CB_{11}H_{10}$.[126]

Useful variants of the capping reaction described above are the direct formation of the parent $[1\text{-}CB_{11}H_{12}]^-$ anion by the treatment of $8\text{-}Me_2S\text{-}\textit{nido}\text{-}7\text{-}CB_{10}H_{12}$ with $^nBu_3P\cdot BH_3$[107] and the thermal-decomposition reaction (eq 22).[126] This reaction, combined with the

$$[BH_2(NMe_3)_2]^+[7\text{-}CB_{10}H_{13}]^- \rightarrow Me_3N\text{-}1\text{-}CB_{11}H_{11} + Me_3N + 2H_2 \quad (22)$$

electrophilic substitution of **28** by treatment with H_2NSO_3H,[126] yields all three possible B-substituted isomeric derivatives of the L-*closo*-1-$CB_{11}H_{11}$ type, 2-, 7-, and $12\text{-}Me_3N\text{-}1\text{-}CB_{11}H_{11}$.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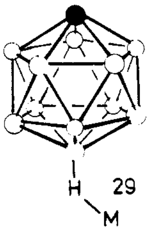

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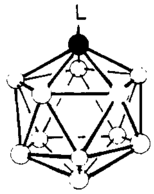

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TABLE 7. Substituted Derivatives of the $[closo\text{-}1\text{-}CB_{11}H_{12}]^-$ Anion (Cage Structure 28)

substituent(s)	measured data	ref(s)
H^- (parent)	^1H, ^{11}B, IR, DTA	112–122
1-H_2N	^1H, ^{11}B, R_F	125
1-MeHN	^1H, ^{11}B, R_F	124
1-O-HC═NMe	^1H, ^{11}B, IR, R_F	124
1-Ph(O)C═NMe	^1H, ^{11}B, IR, R_F	124
1-HO	^1H, ^{11}B, R_F	125
1-MeO	^1H, ^{11}B, R_F	125
7,8,9,10,11,12-D_6	^1H, ^{11}B, R_F	125
7,8,9,10,12-Cl_5	^1H, ^{11}B, R_F	125
7,8,9,10,11,12-Cl_6	^1H, ^{11}B, R_F	125
7,8,9,10,11,12-Br_6	^1H, ^{11}B, R_F	125
12-I	^1H, ^{11}B, R_F	125
7,12-I_2	^1H, ^{11}B, R_F	125
1-HS,1-MeS	^1H, ^{11}B, R_F	125

TABLE 8. Compounds of the L-*closo*-1-$CB_{11}H_{11}$ Type

L	measured data	ref(s)
1-H_3N	^1H, ^{11}B, MS, R_F	125
1-MeH_2N	^1H, ^{11}B, MS, R_F	123
1-Me_2HN	^1H, ^{11}B, MS, R_F	123, 124
1-Me_3N	^1H, ^{11}B, MS, R_F, XR	123–125
1-Me_3N-7-$PhCH_2$	^1H, ^{11}B, MS, R_F, mp	126
7-Me_3N	^1H, ^{11}B, MS, R_F	125
1-MeEtHN	^1H, ^{11}B, MS, R_F	125
1-HO—HC═NMe	^1H, ^{11}B, MS, R_F, IR	125
1-Ph(HO)C═NMe	^1H, ^{11}B, IR, MS, R_F	125
1-Me_2S	^1H, ^{11}B, IR, MS, R_F	125
12-Me_2S	^1H, ^{11}B, IR, MS, R_F	125
12-$(MeS)_2CH_2$	^1H, ^{11}B, IR, MS, R_F	125
1-, 7-, and 12-Me_3N	^1H, ^{11}B, MS, R_F	126

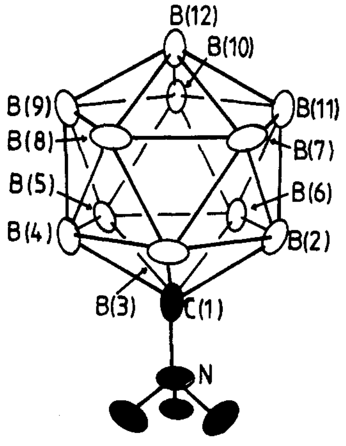


Figure 7. Schematic drawing of the X-ray structure of 1-Me_3N-*closo*-1-$CB_{11}H_{11}$ (**30**). Selected mean exocage bond lengths were[127] C(1)–N 154.7 (1) and C(Me)–N 151.2 pm, the mean angle about the N atom being 110.17°. For selected cage distances see Table 6.

Compounds of the 1-L-*closo*-1-$CB_{11}H_{11}$ type (**30**) (L = H_3N and Me_2NH) have been used to isolate a broad range of further ligand-derivatives of the same family (L = $[MeHN]^-$, MeH_2N, HO—HC═NMe, $[O\text{—}HC\text{═}NMe]^-$, MeEtHN, Ph(HO)C═NMe, $[Ph(O)C\text{═}NMe]^-$, Me_2S, HO^-, and MeO^-) on reactions of the exoskeletal amine group[124,125] (for other data see Tables 7 and 8). A detailed insight into the structures of compounds of this class has been provided by X-ray diffraction studies on 1-Me_3N-1-$CB_{11}H_{11}$[127,128] (Figure 7) and the $[1\text{-}Me_2N\text{-}1\text{-}CB_{11}H_{11}]^-$ anion[129] (Figure 8). Selected interatomic distances for some structurally determined compounds of the {*closo*-1-CB_{11}} type are in Table 6.

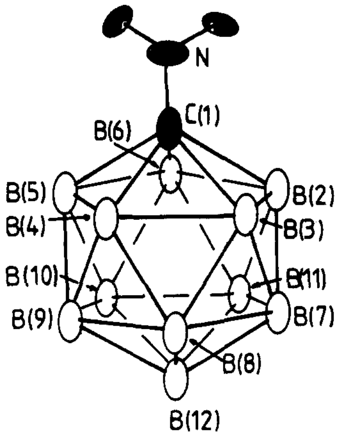


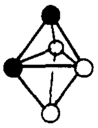
Figure 8. Schematic representation of the X-ray structure of NMe_4^+ $[1\text{-}Me_2N\text{-}closo\text{-}1\text{-}CB_{11}H_{11}]^-$ (deprotonized **30**).[129] The mean bond angle about the N atom at 112° indicates an almost regular sp^3 disposition of N–C bonds with no substantial donation of the lone electron pair on the nitrogen center to the cage. For cage bond lengths see Table 6.

IV. Dicarbaboranes

The chemistry of dicarbaboranes, i.e. of compounds of general formulas *closo*-$C_2B_{n-2}H_n$, *nido*-$C_2B_{n-2}H_{n+2}$, *arachno*-$C_2B_{n-2}H_{n+4}$, and *hypho*-$C_2B_{n-2}H_{n+6}$ for neutral species, is the oldest and most investigated area of carborane chemistry. This class of compounds is generally available from carbon cluster-expansion reactions, most typically from the reactions of alkynes with various borane substrates,[1,2,5] from boron-degradation procedures[18] involving larger-cage carborane species, or alternatively from metal-promoted cluster condensation reactions.[15] The smallest-cage dicarbaboranes ever isolated are the two isomeric five-vertex $C_2B_3H_5$ compounds while the largest ones are the isomeric $C_2B_{10}H_{12}$ carboranes (excluding coupled-cage or conjuncto species).

1. Small Dicarbaboranes

Much of the recent chemistry of the small dicarbaboranes (n = 5–7) has concerned the previously reported[1,2,5] compounds 1,2- and 1,5-*closo*-$C_2B_3H_5$ (**31** and **32**), 1,2- and 1,6-*closo*-$C_2B_4H_6$ (**33** and **34**), 2,3- and 2,4-*closo*-$C_2B_5H_7$ (**35** and **36**), and some nido structured species, such as 1,2-$C_2B_3H_7$ (**37**), 2,3-$C_2B_4H_8$ (**38**), and the $[2,4\text{-}C_2B_4H_7]^-$ anion (**39**). Indeed, most of the chemistry has been derived from compounds **31**, **36**, and **38**, evidently due to their relative availability. It is interesting to note that small-sized *arachno*- and *hypho*-carboranes have not yet been prepared.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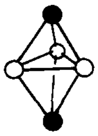
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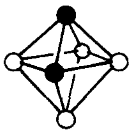
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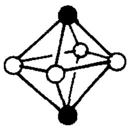
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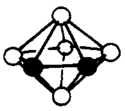
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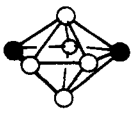
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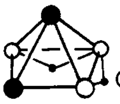
Most of the chemistry of this field has been in two areas: exopolyhedral substitution reactions (for a partial review, see refs 7d and 11e,f) and the designed syntheses of metalladicarbaborane clusters (for recent review, see ref 16). Except for the innovative work based on metal-promoted cluster condensation reactions,[15] relatively little attention has been paid to the development of novel skeletal chemistry of small carboranes.



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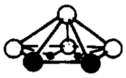

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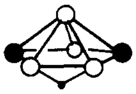

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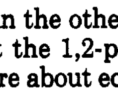
The small size of these compounds has attracted considerable attention from theoretical chemists. Gimarc and Ott[130] have investigated the DSD rearrangement mechanism for the $C_2B_3H_5$ carborane system at the EHMO level to show that the rearrangements of this type[59] are blocked by HOMO/LUMO crossing, indicating that these processes face a very high activation energy barrier. It was suggested that the closo five-vertex dicarbaborane isomers should be stereochemically rigid. The same result was achieved by the THS[63] and ab initio[131a] calculations, the latter indicating a HOMO/LUMO crossing of ca. 80 kcal mol^{-1}. A mechanism based on the rotation of two equatorial atoms (2 and 3) about an axis in the equatorial plane and a new cyclopentene-like structure **40** with three unsaturated boron centers for the 1,2-isomer were also considered.[131a] Relative energies have been calculated for the $C_2B_3H_5$, $C_2B_3H_4Me$, and $C_2B_3H_2F_3$ systems in the isomeric forms 1,5-trigonal bipyramidal (closo), 1,2-planar, 1,2-trigonal bipyramidal (closo), 2,3-square pyramidal, 1,3-planar, and 2,3-trigonal bipyramidal (closo). The 1,5-closo form, **32**, was found considerably more stable than the other structures, for $C_2B_3H_5$ and $C_2B_3H_4Me$, but the 1,2-planar and 1,5-trigonal bipyramidal forms are about equally stable for $C_2B_3H_2F_3$.[131b]



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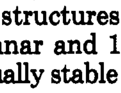

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Semenov calculated electronic structures and localized MO's for 1,5-$C_2B_3H_5$ and 1,2- and 1,6-$C_2B_4H_6$,[132-134] and McKee[135] carried out ab initio calculations on the rearrangement mechanisms in the $C_2B_4H_6$ and $C_2B_5H_7$ dicarbaborane systems. McKee[136] has also carried out ab initio calculations on the cage (nido) (**38**) and chair hexagonal (**41**) forms of $C_2B_4H_8$ at the MP2/6-31G* + ZPC/3-21G level and found that the **41** form was 56.5 kcal mol^{-1} higher in energy than the usual structure **38**. Whelan and Brint reported[137] geometry-optimized ab initio calculations at the STO-3G level on the molecules 2,3- and 1,6-$C_2B_4H_6$ and [2,3- and 1,6-$C_2B_4H_7]^+$ and found good agreement between the experimental and calculated proton affinities. The site of protonation is determined by the distribution of the HOMO and is predictable on symmetry grounds. Similar calculations by DeKock and Jasperse[31] at the MNDO and selected ab initio 3-21G levels predicted carbon protonation for 1,5-$C_2B_3H_5$ and B–B edge protonation for 1,6-$C_2B_4H_6$ and 2,4-$C_2B_5H_7$, from calculated proton affinities.

TABLE 9. Substituted Derivatives of *closo*-1,5-$C_2B_3H_5$ (Cage Structure 32)

substituent(s)[a]	measured data	ref(s)
1,5-Me_2-2,3,4-Et_3	^{11}B, ^{13}C	143
1,2,3,4,5-Et_5	^{11}B, ^{13}C	143
2-R	^1H, ^{11}B, MS, IR	144
2,3,4-R_3	^1H, ^{11}B, MS, IR	144
2-R^1	^1H, ^{11}B, MS, IR	144
2-R^2	^1H, ^{11}B, MS, IR	144
2-R^3	^1H, ^{11}B, MS, IR	144
2-R^4	^1H, ^{11}B, MS, IR, R, PES, R_υ	145–147
2,3-$(R^4)_2$	^1H, ^{11}B, MS, IR, PES, R_υ	145, 146
1-R^4	^1H, ^{11}B, MS, IR, R_υ	146
1,2-$(R^4)_2$	^1H, ^{11}B, MS, IR, R_υ	146
2-R^4-3-R^5	^1H, ^{11}B, MS, IR, R_υ	146
2-R^6	^1H, ^{11}B, MS, IR, R_υ	146

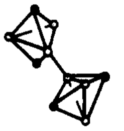
[a] R = *cis*-2-but-2-enyl; R^1 = 2-but-1-enyl; R^2 = *trans*-1-but-1-enyl; R^3 = ethenyl; R^4 = 2′-[1′,5′-$C_2B_3H_4$]; R^5 = 1′-[1′,5′-$C_2B_3H_4$]; R^6 = 2′-[1′,6′-$C_2B_4H_5$].

Dixon[138] has actually measured proton affinities for 1,6-$C_2B_4H_6$ (208 ± 4 kcal mol^{-1}) and 2,4-$C_2B_5H_7$ (173 ± 1 kcal mol^{-1}) by using pulsed ion cyclotron resonance (ICR) methods combined with bracketing techniques. Gal'chenko et al. have determined standard enthalpies of combustion and vaporization for both compounds.[139] Other authors have considered the bonding within 1,2- and 1,6-$C_2B_4H_6$ by using the Roby projection density method.[140] The general pentagonal pyramidal (structure VI) cage skeletal rearrangement was considered by Huttner et al.,[141] who suggested a "tandem isomerisation mechanism" via a trigonal prismatic intermediate. Ab initio calculations by McKee[142] at the HF/3-21 level were aimed at studying the interaction of the *closo*- and *nido*-carboranes $C_2B_3H_5$ and $C_2B_3H_7$ with ammonia. The hypothetical *nido*-$C_2B_3H_5$·NH_3 adduct was found to be less stable than the corresponding arachno species $C_2B_3H_7$·NH_3.

Koester and Wrackmeyer[143] report $\delta(^{11}B)$ and $\delta(^{13}C)$ NMR shift values and some $^1J(^{11}B-^{13}C)$ and $^1J(^{11}B-^{11}B)$ coupling constants for a series of selected pentaalkyl derivatives of **32**, of the general formula 1,5-R_2'-2,3,4-R_3-1,5-C_2B_3 (for individual compounds see Table 9).

Alkylation of the small carboranes *closo*-1,5-$C_2B_3H_5$, -1,6-$C_2B_4H_6$, and -2,4-$C_2B_5H_7$, and *nido*-2,3-$C_2B_4H_8$ by alkynes (acetylene or 1- or 2-butyne), catalyzed by complexes of the general formula $[(RC_2R')Co_2(CO)_6]$ (R, R′ = H, Me, or Et), yielded a series of the corresponding boron-substituted alkenyl (RHC=CR′—) carboranes (for individual compounds see Tables 9–12). The degree of substitution can be controlled by varying the reaction conditions, and products have been obtained, ranging from single substitution at only one boron site to complete substitution at all boron positions. The overall reaction corresponds to a catalyzed BH addition of the carborane to the alkyne in a cis fashion. Internal alkynes were found to be more reactive than terminal and 1-butyne was found to give predominantly Markovnikov addition.[144]

The coupled compounds 2:2′-[1,5-$C_2B_3H_4$][1′,5′-$C_2B_3H_4$] (**42**) and 2:2′,3′:2″-[1,5-$C_2B_3H_4$][1′,5′-$C_2B_3H_3$][1″,5″-$C_2B_3H_4$] (**43**) have been prepared from the pyrolysis of **32**.[145] The structures **42** and **43** have been explored using the MNDO quantum chemical approach. The experimental and calculated results clearly show that both of these conjuncto species are coupled by exopolyhedral B–B bonds and demonstrate that, with respect to rotation, **42** possesses a single stable conformation of D_{2d} symmetry resulting from a π-type interaction across the exopolyhedral B–B bond.[145]



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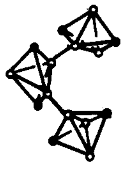

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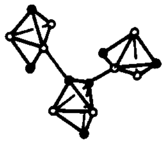
Under similar conditions, Astheimer and Sneddon[146] isolated **42**, **43**, and a number of previously unknown low-yield products that included a boron–carbon linked compound 1:2′-[1,5-$C_2B_3H_4$][1′,5′-$C_2B_3H_4$] (**44**) together with two boron–carbon- and boron–boron-linked species, 2:2″,1′:2″-[1,5-$C_2B_3H_4$][1′,5′-$C_2B_3H_3$][1″,5″-$C_2B_3H_4$] (**45**) and 2:2′,3′:1″-[1,5-$C_2B_3H_4$][1′,5′-$C_2B_3H_3$][1″,5″-$C_2B_3H_4$] (**46**). The pyrolysis of 1,6-$C_2B_4H_6$ did not give any linked products; however, the copyrolysis with 1,5-$C_2B_3H_5$ was found to give a coupled, mixed-cage carborane 2:2′-[1,5-$C_2B_3H_4$][1′,6′-$C_2B_4H_6$] (**47**) in 65% yield. Later, the same group substantially improved the synthetic route to compound **42** and also isolated 2:2′-[1,6-$C_2B_4H_5$][1′,6′-$C_2B_4H_5$] (**48**) in quantitative yields via platinum(II) dibromide-catalyzed dehydrocoupling reactions of the corresponding carboranes **32** and **34**.[147] Sneddon et al.[148] have used high-resolution ^{10}B and ^{11}B NMR to determine the details of boron–boron coupling along the intercage B–B bonding vector in the coupled-cage derivatives of **32** and in the previously reported[149] conjuncto derivatives of **36**.



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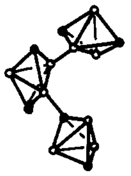

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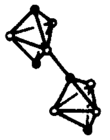

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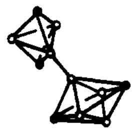

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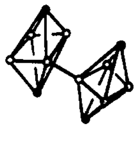

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DeKock et al.[150] reported MO and bond energy calculations which probed the changes that occurred when *arachno*-B_4H_{10} reacts with acetylene to form hydrogen and the two isomeric six-vertex *closo*-carboranes **33** and **34**. Bragin et al.[151] reported the vibrational spectra of 1,6-$C_2B_4H_6$ and assigned the vibrational fundamentals in the IR and Raman spectra. Hosmane et al.[152] prepared the 1,2-bis(trimethylsilyl) derivative of *closo*-1,2-$C_2B_4H_6$, 1,2-$(Me_3Si)_2$-1,2-$C_2B_4H_4$, in quantitative yield via oxidative removal of the {Sn} vertex from the [2,3-$(Me_3Si)_2$-*closo*-1,2,3-$SnC_2B_4H_4$] stannadicarbaborane, with stoichiometric amounts of either $PtCl_4$ or $PtCl_2$ at room temperature:

$$2(Me_3Si)_2SnC_2B_4H_4 + PtCl_4 \rightarrow Pt^0 + 2(Me_3Si)_2C_2B_4H_4 + 2SnCl_2 \quad (23)$$

$$(Me_3Si)_2SnC_2B_4H_4 + PtCl_2 \rightarrow Pt^0 + (Me_3Si)_2C_2B_4H_4 + SnCl_2 \quad (24)$$

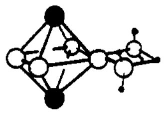
TABLE 10. Substituted Derivatives of *closo*-1,6-$C_2B_4H_6$ (Cage Structure 34)

substituent(s)[a]	measured data	ref(s)
R[b]	^1H, ^{11}B, MS, IR	144
2-R^1	^1H, ^{11}B, MS, IR	147
2-Cl	^1H, ^{11}B, MS	153, 155
2,4-Cl_2	^1H, ^{11}B, MS	153, 155
2,3,4,5-Cl_4	^1H, ^{11}B, ^{13}C, IR	167
2-Br	^1H, ^{11}B	155
2,4-Br_2	^1H, ^{11}B	155
2-Br_2B	^1H, ^{11}B	154
2,2-[B_2H_5]	^1H, ^{11}B,[c] MS	156

[a] R = *cis*-2-but-2-enyl; R^1 = 2′-[1′,6′-$C_2B_4H_6$]. [b] All possible mono- to tetrasubstituted B-alkyl compounds. [c] Inclusive of [^{11}B–^{11}B]-COSY measurements.

A variety of boron substitution reactions of *closo*-1,6-$C_2B_4H_6$ was reported by Onak et al.[153–155] Fehlner et al.[72] have calculated ^{11}B NMR shifts for this compound and its halo derivatives, 2-X-1,6-$C_2B_4H_5$ (X = F, Cl, and Br), using the Fenske–Hall MO method. Some of the measured properties of the substituted derivatives of *closo*-1,6-$C_2B_4H_6$ are summarized in Table 10.

An important platinum(II) dibromide-catalyzed cage growth reaction between 1,6-$C_2B_4H_6$ and excess diborane (48 h, room temperature) in decane,[156] followed by repeated vacuum fractionation of the reaction products, yielded a cage-coupled carborane 2:1′,2-[1,6-$C_2B_4H_5$][B_2H_5] (**49**). This compound is, however, unstable at 40 °C and reconverts to **34** and diborane. Inspired by this work, McKee,[157] using ab initio calculations, investigated the structure and energetics of carborane- and borane-coupled cages linked together by a B–B bond or a pair of hydrogen bridges. In general, these structures were found to be only slightly perturbed from the corresponding noncoupled molecules. From model calculations of 1,6-$C_2B_4H_6$ and 1,5-$C_2B_3H_5$ reacting with {BH_3},[157] activation barriers were estimated for the exchange of terminal hydrogens between the carborane and B_2H_6. In contrast to 1,6-$C_2B_4H_6$/B_2H_6, a low barrier (ca. 10 kcal mol^{-1}) was predicted for the exchange in 1,5-$C_2B_3H_5$/B_2H_6.



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Grimes et al. reported a new bench-scale synthetic route to the substituted derivatives of **38**, consisting in the reaction between pentaborane(9) and alkynes in the presence of triethylamine:[158,159]

$$B_5H_9 + R_1C{\equiv}CR_2 \rightarrow R_1R_2C_2B_4H_6 + Et_3N{\cdot}BH_3 \quad (25)$$

The pentaborane can be generated in situ from $[B_3H_8]^-$ and HCl, and all subsequent reactions can be carried out in the same vessel. Apart from acetylene, a broad range of alkynes can be used[160–164] in reaction 25 to obtain derivatives of **38** (see Table 11), many of which have been later employed in designed syntheses of multifunctional metalladicarbaborane and -tetracarbaborane (see section V) systems.[14,16] When the open-chain dialkynes $EtC{\equiv}C(CH_2)_nC{\equiv}CEt$ (n = 4 and 6),

TABLE 11. Substituted Derivatives of *nido*-2,3-$C_2B_4H_8$ (Cage Structure 38)

substituent(s)[a]	measured data	ref(s)
1-R^1	^{1}H, ^{11}B, MS, IR, R_v	144
4-R^1	^{1}H, ^{11}B, MS, IR, R_v	144
5-R^1	^{1}H, ^{11}B, MS, IR, R_v	144
2,3-Et_2	^{1}H, ^{11}B, MS, IR	159, 160
2,3-$(PhCH_2)_2$	^{1}H, ^{11}B, MS, IR	161
2-$Ph(CH_2)_3$	^{1}H, ^{11}B, IR	162
2-R^2	^{1}H, ^{11}B, IR	163
2,3-R^2	^{1}H, ^{11}B, IR	163
2-R^3	^{1}H, ^{11}B, IR	163
2,3-R^3	^{1}H, ^{11}B, IR	163
2,3-$^nBu_2$	^{1}H, ^{11}B, ^{13}C, IR, MS	164
2,3-$(^iC_5H_{11})_2$	^{1}H, ^{11}B, ^{13}C, IR, MS	164
2,3-$(^nC_6H_{13})_2$	^{1}H, ^{11}B, ^{13}C, IR, MS	164
2,3-Ph_2	^{1}H, ^{11}B, ^{13}C, IR, MS	164
2-Me_3Si	^{1}H, ^{11}B, ^{29}Si, MS	166–169
2-Me_3Si-3-Me	^{1}H, ^{11}B, ^{29}Si, MS	166
2-$(Me_3Si)_2$	^{1}H, ^{11}B, ^{29}Si, MS	166, 167
2,3,4-Et_3	^{1}H, ^{11}B, IR, MS	172
2,3-Et_2-4-$PhCH_2$	^{1}H, ^{11}B, IR, MS	172
2,3-Et_2-4-$MeC_6H_4CH_2$	^{1}H, ^{11}B, IR, MS	172
2,3-Et_2-4-$Ph(CH_2)_3$	^{1}H, ^{11}B, IR, MS	172
2,3-$(PhCH_2)_2$-4-Me	^{1}H, ^{11}B, IR, MS	172
2,3,4-$(PhCH_2)_3$	^{1}H, ^{11}B, IR, MS	172

[a] R^1 = *cis*-2-but-2-enyl; R^2 = 1-indenylmethyl; R^3 = 9-fluorenylmethyl.

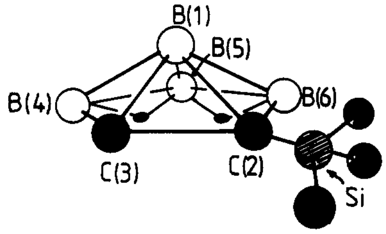


Figure 9. Representation of the GED structure of 2-Me_3Si-*nido*-2,3-$C_2B_4H_7$. Bond lengths in the basal plane of the cage were[168] C–C 146.0 (11), C–B 154.4 (8), and B–B 175.8 (16) pm, while mean distances to the B(1) apex were C–B 183.2 and B–B 172.4 pm. All C–Si distances were close to 188 pm, and the Si atom was nearly in the basal plane.

trialkyne $HC{\equiv}C(CH_2)_5C{\equiv}C(CH_2)_5C{\equiv}CH$, and the cyclic dialkynes $\overline{CH_2(CH_2)_4C{\equiv}C(CH_2)_nC{\equiv}C—}$ (n = 4–6) were used as reaction components,[165] all available C≡C units were transformed to carborane {*nido*-C_2B_4} moieties. The corresponding carborane oligomers were fully characterized by NMR, IR, and mass spectra.

Hosmane et al.[166,167] reported a high-yield reaction between silylated acetylenes, $Me_3SiC{\equiv}CR$ (R = Me_3Si, Me, or H), and pentaborane(9) which generated the corresponding disubstituted 2-Me_3Si-3-R-*nido*-2,3-$C_2B_4H_6$ at elevated temperatures. Heating liquid 2,3-$(Me_3Si)_2$-2,3-$C_2B_4H_6$ with solid $NaHF_2$ at 140 °C or with HCl resulted in partial desilylation to produce 2-Me_3Si-2,3-$C_2B_4H_7$ in 90% and 62% yields,[168] respectively. The molecular structure of this compound was determined in the gas phase by electron diffraction as presented schematically in Figure 9.

With the HCl procedure used in the preparation of the last compound, but at higher temperatures (160–170° for 4 days), the parent carborane **38** was obtained[169] in improved yields (30%) along with 2,3,4,5-Cl_4-*closo*-1,6-$C_2B_4H_2$. The area of the trimethylsilylated derivatives of **38**, inclusive of their main group metal chemistry has been recently reviewed by Hosmane and Maguire.[11f] Von Arx et al.[170] employed 2-Me_3Si-2,3-$C_2B_4H_7$ in THF at room temperature as a source of hydrogen to reduce a series of ketones to the corresponding alcohols.

Fessler et al.[171] have studied bridge deprotonation of the substituted 2,3-R,R′-2,3-$C_2B_4H_6$ (R = alkyl, arylmethyl, or phenyl; R′ = R or H) species by the hydride anion and determined the reaction rates and activation parameters as a function of individual substituents. The reaction was found to be independent of the metal hydride present and to be primarily dependent on the steric inhibition caused by the substituent. Davies et al.[172] have also found that alkylation of the $[2,3\text{-}R_2\text{-}2,3\text{-}C_2B_4H_5]^-$ ions with organic halides (R′X) proceeds in a highly regiospecific manner to generate enantiomeric 4-R′-2,3-R_2-$C_2B_4H_5$ carboranes (for individual compound see Table 11). The alkylation is proposed to proceed via bridged μ(4,5)-R′-2,3-R_2-2,3-$C_2B_4H_5$ intermediates, which rapidly rearrange to the corresponding 4-substituted compounds.

Hosmane et al. reported the syntheses of the disilylated $[2,3\text{-}(Me_3Si)_2\text{-}nido\text{-}2,3\text{-}C_2B_4H_4]^{2-}$[173] and $[2,3\text{-}(Me_3Si)_2\text{-}nido\text{-}2,3\text{-}C_2B_4H_5]^-$ anions.[174] The latter compound was structurally characterized by an X-ray diffraction study and multinuclear NMR spectra as $(C_4H_8ONa^+)_2$ $[2,3\text{-}(Me_3Si)_2\text{-}nido\text{-}2,3\text{-}C_2B_4H_5^-]_2$.

Abdou et al.[175] reported an interesting "decapitation" of the B(1) vertex in *closo*-2,4-$C_2B_5H_7$ (**36**) yielding the $[nido\text{-}2,4\text{-}C_2B_4H_7]^-$ anion (**39**). This was accomplished by prolonged action of lithium dimethylamide on **36**.

Of the "small dicarbaborane" compounds, probably the most studied has been the most accessible compound of the class, i.e. *closo*-2,4-$C_2B_5H_7$ (**36**).[1,5] Recent chemistry of its substituted derivatives has recently been reviewed by Onak.[7d,11e] This review will therefore outline only general features of the chemistry along with the most recent developments in the area.

Carborane **36** is the compound on which the first two-dimensional NMR study in the area of boron-cluster compounds was performed.[67a] Durso et al.[176] have recently used microwave techniques to determine the structure and dipole moment of 5-F-*closo*-2,4-$C_2B_5H_6$ (for structure see **36**). They found that the interboron distances are comparable with those obtained for the parent compound[1,5] and the relatively short B–F distance (133.0 (3) pm) was interpreted in terms of partial double-bond character. Previous work by Onak et al.[7d] on the electrophilic substitution reactions of **36** have generated a number of chlorinated and methylated derivatives, and more detailed studies on the preparation, thermal rearrangements, and kinetic stabilities of the substituted derivatives of **36** have now been reported.

A number of halogenated (X = Cl, Br, and I) derivatives of **36** (for individual compounds see Table 12) were prepared from reactions between **36** and the corresponding halogens with or without the $AlCl_3$ catalyst.[153,177] The $\Delta\delta(^{11}B)$ additivity constants for individual halogens and cage positions were derived.[177] Using competition studies, Nam and Onak[155] estimated the relative reactivities for *closo*-dicarbaboranes 1,6-$C_2B_4H_6$, 2,4-$C_2B_5H_7$, 1,10-$C_2B_8H_{10}$, and some of their derivatives, toward electrophilic reagents of the type $RX/AlCl_3$ (RX = MeCl, EtCl, Cl_2, and Br_2). The 2,4-$C_2B_5H_7$ carborane was found to be most reactive with alkyl substituents generally enhancing and halogen substituents decreasing the reactivity. The nature and

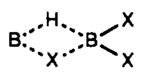
TABLE 12. Substituted Derivatives of *closo*-2,4-$C_2B_5H_7$ (Cage Structure 36)

substituent(s)[a]	measured data	ref(s)
R^b	^1H, ^{11}B, MS, IR, R_v	144
$R_2{}^b$	^1H, ^{11}B, MS, IR, R_v	148
$R_3{}^b$	^1H, ^{11}B, MS, IR, R_v	148
$R_4{}^b$	^1H, ^{11}B, MS, IR, R_v	148
1,3,5,6,7-R_5	^1H, ^{11}B, MS, IR, R_v	148
1-R^1	^{11}B, $^1J[^{11}B–^{11}B]$	148
3-R^1	^{11}B, $^1J[^{11}B–^{11}B]$	148
3-Ph	^1H, ^{11}B	154
3-R^2	^{11}B, $^1J[^{11}B–^{11}B]$	148
1- and 5-F	^1H, ^{11}B, MW	176, 179, 187, 188
3,5-F_2	^1H, ^{11}B	187, 188
Cl, Br, I^b	^1H, ^{11}B	153, 177, 155, 179, 154, 188, 190
Cl_2, Br_2, $I_2{}^b$	^1H, ^{11}B	153, 154, 155, 177, 179, 188, 190
2-Cl-4-Br	^1H, ^{11}B	155
5-Cl-6-Br	^1H, ^{11}B	179, 188
1-I-5,6-Br_2	^{11}B	179
1,7-I_2-5,6-Br_2	^{11}B	179
1,7-I_2-3,5,6-Br_3	^{11}B	179
Me^b	^1H, ^{11}B	155, 188, 189
$Me_2{}^b$	^1H, ^{11}B	155
$Me_3{}^b$	^1H, ^{11}B	155
$Me_4{}^b$	^1H, ^{11}B	155
1,3,5,6,7-Me_5	^1H, ^{11}B	155
Et^b	^1H, ^{11}B	155, 178, 185
$Et_2{}^b$	^1H, ^{11}B	155, 178, 185
1-Me-5-Et	^1H, ^{11}B	155
5-Me-6-Et	^1H, ^{11}B	155
1-Me-5,6-Et_2	^1H, ^{11}B	155
Me-Cl^b	^1H, ^{11}B	155, 191
6-Me-5-I	^1H, ^{11}B	155, 185
1-Me-5,6-Cl_2	^1H, ^{11}B	155
3-Me-5,6-Cl_2	^1H, ^{11}B	155
Cl-$Et_2{}^b$	^{11}B	178
5-[$HO(CF_3)_2C$]	^1H, ^{11}B, ^{19}F, MS, IR	182
5-[$HO(C(CF_3)_2)_2O$]	^1H, ^{11}B, ^{19}F, MS, IR	182

[a] R = *cis*-2-but-2-enyl; R^1 = 3′-[2′,4′-$C_2B_5H_6$]; R^2 = 5′-[2′,4′-$C_2B_5H_6$]. [b] All possible combinations of B-substituted derivatives.

cage position of the substituents on 2,4-$C_2B_5H_7$ appear to have little or no influence on the site of further substitution.

Ethylation of 2,4-$C_2B_5H_7$ and 3-Cl-2,4-$C_2B_5H_6$ by $EtCl/AlCl_3$ has produced a series of 5-Et, 5,6-Et_2, 3-ClEt, and 3-$ClEt_2$ derivatives of **36** (see Table 12).[178] The action of interhalogens, ICl or IBr, in the presence of $AlCl_3$, on 2,4-$C_2B_5H_7$ and its haloderivatives was found to produce predominantly *B*-iodo products. In contrast, in the absence of the catalyst, the same reaction generates *B*-chloro and *B*-bromo derivatives, which is indicative of a different (radical type) reaction mechanism.[179] Nam and Onak[154] also reported the reactions between 2,4-$C_2B_5H_7$ and boron trihalides, BX_3 (X = Cl, Br, and I), or BPh_3 at elevated temperatures (120–270 °C). These produced 3-, 5-, and 3,5-X_2-substituted products in reasonable yields (1–52%), depending on the site of substitution. The formation of these products was suggested to involve a four-membered intermediate formulated as **50**.



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Beltram et al.[180] investigated and assigned the HeI photoelectron (PES) spectra of 5-X and 5,6-X_2 derivatives of **36** (X = Cl, Br, and I). Besides the inductive effects, π-type interactions between cluster surface (π-endo) orbitals and filled halogen p orbitals successfully account for the effects of halogen substitution on the PES of the substituted carborane. Nam et al.[181] reported several types of previously unobserved long- and short-range spin couplings in 2,4-$C_2B_5H_7$ from the resolution-enhanced proton and ^{11}B NMR spectra of a wide range of 2,4-$C_2B_5H_7$ derivatives.

Free-radical substitution of the 2,4-$C_2B_5H_7$ cage was reported by Astheimer and Sneddon[182] in the gas-phase photolysis reaction at 3000 Å with hexafluoroacetone. This resulted in the formation of both 5-[$HO(CF_3)_2C$] and 5-[$HO[C(CF_3)_2]_2O$] derivatives of **36**. Zhigach et al.[183] reported a synthesis of carbon-substituted 2,4-R_2-2,4-$C_2B_5H_5$ compounds (R = D, Me_3Si, HMe_2Si, $ClMe_2Si$, $BrMe_2Si$, $MeOMe_2Si$, and $EtOMe_2Si$) along with some oligomeric silylated compounds.

Siwapinyoyos and Onak[184,185] studied the reaction of 3- and 5-Cl-2,4-$C_2B_5H_6$ with Lewis bases (L = Me_3N and Me_3P) yielding a nido-structured $L{\cdot}ClC_2B_5H_6$ adduct. The addition of BCl_3 to this intermediate generated an ionic compound formulated as [3- or 5-L-*closo*-2,4-$C_2B_5H_6$]$^+$[BCl_4]$^-$ (see structure **35** for numbering), the net result being the elimination of chlorine from the exocage position. A similar reaction of Me_3N

$$LClC_2B_5H_6 + BCl_3 \rightarrow [LC_2B_5H_6]^+[BCl_4]^- \quad (26)$$

with the 1-Cl derivative of **36** proceeds with more difficulty, but once formed, the 1:1 adduct combines with BCl_3 to give the rearranged product [3-Me_3N-*closo*-2,4-$C_2B_5H_6$]$^+$[BCl_4]$^-$. An unusual substituent-exchange reaction was observed[186] in the study of the 5-Br-2,4-$C_2B_5H_6/Me_3N$ reaction system in dichloromethane. The $Me_3N{\cdot}$5-Br-2,4-$C_2B_5H_6$ adduct underwent quantitative Br/Cl exchange with CH_2Cl_2 to form 5-Cl-2,4-$C_2B_5H_6$ and [Me_3NCH_2Cl]$^+$$Br^-$. This last reaction, resulting in the net front displacement of bromine by chlorine by the action of trimethyl amine, has initiated a useful and unprecedent cage substituent-exchange strategy.

In an extension of this work,[187,188] a site-specific halogen exchange reaction was observed between B-haloderivatives of **36** and tetraalkylammonium halides ($NBu_4{}^+$, $NCH_2PhEt_3{}^+$) in various solvents. The exchange appears possible only when the "reagent" halide ion is smaller than the leaving exocage halide. Thus, 3-I, 5-Br, and 3,5-I_2 derivatives of **36** are quantitatively converted to the corresponding *B*-fluoro derivatives, 3-F, 5-F, and 3,5-F_2. Both 3- and 5-I-2,4-$C_2B_5H_6$ react with Br^- to give the respective 3- and 5-Br isomers. Similarly, the 5-Br isomer is converted to 5-Cl-2,4-$C_2B_5H_6$ in the presence of Cl^-. The same halide reacts also with $Me_3N{\cdot}$5,6-$Br_2C_2B_5H_5$ to give both 5-Cl-6-Br-2,4-$C_2B_5H_5$ and 5,6-Cl_2-2,4-$C_2B_5H_5$. The rate of the substitution varied, in correspondence with the expected nucleophilicity trend $F^- > Cl^- > Br^-$ in nonaqueous solvents. Another interesting Br → F exchange reaction was observed between 5-Br-2,4-$C_2B_5H_6$ or $Me_3N{\cdot}$5-Br-2,4-$C_2B_5H_6$ and Et_2NSF_3 in nonaqueous solvents.[179]

One of the best examined areas of the 2,4-$C_2B_5H_7$ chemistry are the substituent-rearrangement reactions that include a number of mono-, di-, and trisubstituted derivatives. Heating individual isomers always generates equilibrium mixtures of rearranged products (for more detailed reviews see refs 7d and 11e). The relative abundance of each isomer is dictated by the thermo-

TABLE 13. Theoretically Predicted and Experimental Stability Orders for Mono- and Disubstituted Derivatives of *closo*-2,4-$C_2B_5H_7$ (Cage Structure 36)

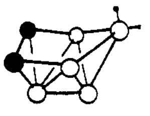
substituent(s)	predicted stabilities	experimental stabilities
B-monomethyl	3 > 5 > 1[a]	3 > 1 > 5[b]
B,*B*′-dimethyl	1, 3 > 3, 5 > 1, 7 > 1, 5 > 5, 6[a]	1, 3 > 3, 5 > 1, 7 > 1, 5 > 5, 6[c]
B-methyl-*B*′-chloro	1, 3 > 5, 3 > 3, 5 > 3, 1 > 1, 5 > 5, 6 > 1, 7 > 5, 1[a]	1, 3 > 3, 5 > 3, 1 > 5, 3 > 1, 5 > 5, 6 > 5, 1 > 7[c]
B-monoethyl	3 > 1 > 5[d]	3 > 1 > 5[e]
B,*B*′-diethyl	1, 3 > 3, 5 > 1, 7 > 1, 5 > 5, 6[d]	1, 3 > 3, 5 > 1, 7 > 1, 5 > 5, 6[e]
B-monochloro	3 > 5 > 1[a,f] 5 > 3 > 1[h]	3 > 5 > 1[c,g]
B-monobromo	3 > 5 > 1[d]	3 > 5 > 1[i]
B-monoiodo	5 > 3 > 1[d]	3 > 5 > 1[i]
B,*B*′-dichloro	3, 5 > 1, 3 > 5, 6 > 1, 5 > 1, 7[a]	3, 5 > 1, 3 > 5, 6 > 1, 5 > 1, 7[c,g]
B,*B*′-dibromo	3, 5 > 1, 3 > 5, 6 > 1, 5 > 1, 7[d]	3, 5 > 5, 6 > 1, 3 > 1, 5 > 1, 7[i]
B,*B*′-diiodo	5, 6 > 3, 5 > 1, 5 > 1, 3 > 1, 7[d]	5, 6 > 3, 5 > 1, 5 > 1, 3 > 1, 7[i]

[a] MNDO level, data from ref 192. [b] Data from ref 189. [c] Data from ref 191. [d] MNDO level, data from ref 193. [e] Data from ref 178. [f] Gaussian-86 calculations, data from ref 193. [g] Data from refs 153 and 190. [h] Gaussian-86, STO-3G level, data from ref 180. [i] Data from ref 177.

dynamic stability at a given temperature. These studies[153,177,178,189-191] produced a vast number of 2,4-$C_2B_5H_7$ derivatives (see Table 13) of varying stabilities. The experimental data were compared with results from MNDO[192,193] and ab initio calculations at different levels.[180,193] The comparison of experimental and theoretical stabilities for individual isomer sets of mono- and disubstituted compounds is outlined in Table 13. The results are consistent with a DSD type of so called "degenerate" rearrangement (without change in cage-carbon positions) which was also endorsed by ab initio SCF MO calculations by Ott et al.[194] The last workers have also predicted the expected order of stabilities for *closo*-$C_2B_5H_7$ isomers: 2,4 > 2,3 > 1,2 > 1,7.

Beck et al.[195,196] have developed a new moderate-yield (50–60%) route to 2,3-Et_2-*closo*-2,3-$C_2B_5H_5$ (cage structure **35** above) by inserting a boron vertex into the open face of *nido*-2,3-Et_2-2,3-$C_2B_4H_6$ (cage structure **38**) by reaction with Et_3NBH_3 at 140 °C. The insertion of the boron atom at the B(7) apex was confirmed by ^{10}B tracer study. 2,3-Et_2-*closo*-2,3-$C_2B_5H_5$ is also available from the reaction of Li^+[*nido*-2,3-Et_2-2,3-$C_2B_4H_5$]$^-$ with $Me_2S{\cdot}BH_3$, or alternatively, from the treatment of Na^+Li^+[2,3-Et_2-*nido*-2,3-$C_2B_4H_4$]$^{2-}$ with Me_2SBHBr_2. Reaction of the dianion with $PhBCl_2$ or $MeBBr_2$ produced the expanded B-monosubstituted compounds 1-R-2,3-Et_2-*closo*-2,3-$C_2B_5H_4$ (R = Ph and Me, respectively). Halogenation of 2,3-Et_2-2,3-$C_2B_5H_5$ with bromine at room temperature resulted in the exclusive formation of the 5-Br-2,3-Et_2 derivative. The 2,3-Et_2 derivative of **35** undergoes rearrangement to the 2,4-isomer in high yield at 350 °C.

A cage-opening reaction of 2,3-Et_2-*closo*-2,3-$C_2B_5H_5$ with 1 equiv of $LiBEt_3H$ resulted in the formation of the first seven-vertex *nido*-carborane, the [4,5-Et_2-3,4-$C_2B_4H_6$]$^-$ anion[197] (cage structure **51**). A similar type *closo* → *nido* reaction with excess trimethylphosphine[196] gave 7-Me_3P-4,5-Et_2-*nido*-4,5-$C_2B_5H_5$ (cage structure **52**, L = PMe_3). Both structures **51** and **52** contain a {BH_2} group, held to be exceptional for all *nido*-dicarbaboranes examined to date.



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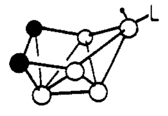

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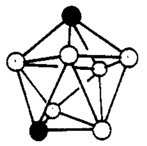
2. Eight- to Ten-Vertex Dicarbaboranes

Eight- and nine-vertex compounds include the previously reviewed[1,5] *closo*-dicarbaboranes 1,7-$C_2B_6H_8$ (**53**) and 1,7-$C_2B_7H_9$ (**54**) and the arachno-structured *nido*-3,6-$C_2B_6H_{10}$ species (**55**)[5] (general structures X, XIII, and XII, respectively).



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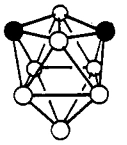

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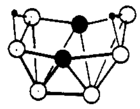

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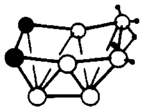
Theoretical chemists have predicted possible DSD-type rearrangement pathways for the dodecahedral (D_{2d}) and tricapped trigonal prismatric (D_{3h}) structures of **53** and **54**. Wales and Stone[63] have shown that the THS theory is very useful in rationalizing the energy barriers to skeletal rearrangement in $B_8H_8^{2-}$ (general structure X) for which a single DSD process leads to a transition state of distorted C_{2v} geometry (bicapped trigonal prism). Gimarc and Ott[198-200] report ab initio SCF MO calculations at the STO-3G level to analyze geometries and possible rearrangement pathways for all possible isomeric *closo*-$C_2B_6H_8$ and -$C_2B_7H_9$ dicarbaboranes. King[201] has used graph theory arguments to account for rearrangements in the eight- to ten-vertex systems.

O'Neill and Wade[202] have considered the bonding in nine-vertex D_{3h} (structure XIII) clusters, including $[B_9H_9]^{2-}$ and $C_2B_7H_9$ in terms of edge-bonding or antibonding characteristics of the nondegenerate tenth and eleventh MO's. Skeletal bonding was found to be strongest when there are 20 skeletal bonding electrons present. Gimarc and Ott[203] have shown that a rearrangement mechanism involving a single DSD process for $[B_9H_9]^{2-}$ or $C_2B_9H_{11}$ is forbidden by the principle of conservation of orbital symmetry but a double DSD process is allowed.

Beck and Sneddon[196] reported the formation of ethyl-substituted derivatives of **53** and **54**, 1,7-Et_2-1,7-$C_2B_6H_6$, and 1,7-Et_2-1,7-$C_2B_7H_7$, from the reaction between 2,3-Et_2-$C_2B_4H_6$ and $Et_3N{\cdot}BH_3$ at 170 °C. The author's group prepared the first representative of the eight-vertex *arachno*-dicarbaborane family, the [4,5-$C_2B_6H_{11}$]$^-$ anion (**56**), from the degradation of 1,2-$C_2B_8H_{10}$ (structure **61** below) in 5% aqueous sodium hydroxide (47% yield).[204] Another member of the eight-vertex arachno family of dicarbaboranes, the



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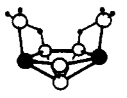

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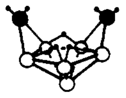


58

TABLE 14. Eight- and Nine-Vertex Dicarbaboranes

compound	cage structure	measured data	ref(s)
1,7-$Et_2C_2B_6H_6$	**53**	^{1}H, ^{11}B, MS	196
1,7-$Et_2C_2B_7H_7$	**54**	^{1}H, ^{11}B, MS	196
$[4,5\text{-}C_2B_6H_{11}]^-$	**56**	^{1}H, ^{11}B^a	204
2,4-$C_2B_6H_{12}$	**57**	^{1}H, ^{11}B, ^{13}C, MS	156
3,6-$C_2B_6H_{10}$	**55**	^{11}B	156
$[7,8\text{-}C_2B_6H_{13}]^-$	**58**	^{1}H, ^{11}B, MS	205
4,5-$C_2B_7H_{13}$^{b}	**59**	^{1}H, ^{11}B,^{a} ^{13}C, MS	206–208
4,6-$C_2B_7H_{13}$^{c}	**60**	^{1}H, ^{11}B,^{a} ^{13}C, MS	210

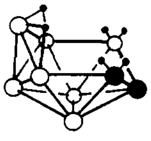
[a] 2-D measurements. [b] Inclusive of 6-halo derivatives. [c] Inclusive of 3-halo and 3,5-dihalo derivatives.

uniquely structured 2,4-$C_2B_6H_{12}$ (**57**) was isolated by Corcoran and Sneddon[156] from the platinum dibromide-catalyzed cage-growth reaction between *closo*-1,5-$C_2B_3H_5$ and diborane at room temperature. The reaction is suggested to proceed via insertion of one more boron into an unisolated coupled-cage $[1,5\text{-}C_2B_3H_4][B_2H_5]$ species. Dehydroisomerization of **57** at 65 °C leads directly to *nido*-3,6-$C_2B_6H_{10}$ dicarbaborane (**55**) and represents a new preparative route to this compound. Jelínek et al.[205] have developed a high-yield preparation of the first *hypho*-dicarbaborane, the $[7,8\text{-}C_2B_6H_{13}]^-$ anion (**58**) (so-called "helmet anion") from the degradation reaction between *arachno*-4,5-$C_2B_7H_{13}$ (structure **59** below) and an aqueous solution of the cyanide anion.

The author's group published an efficient synthetic route to the nine-vertex *arachno*-4,5-$C_2B_7H_{13}$ dicarbaborane (**59**) based on the reaction of the $[7,8\text{-}C_2B_9H_{12}]^-$ anion with formaldehyde in the presence of acid.[206]

$$[C_2B_9H_{12}]^- + H_3O^+ + 5H_2O + CH_2{=}O \rightarrow C_2B_7H_{13} + 2B(OH)_3 + CH_3OH + 2H_2 \quad (27)$$

The reaction (eq 27) is in agreement with the degradation of two adjacent B(9) and B(10) vertices from structure **74**; a possible reaction path was proposed from a deuterium-tracer study[207] of a wide range of deuterated derivatives of **74**. Two papers[207,208] have dealt with the revision of the structure of carborane **59**, which was for a long time held as *nido*-$C_2B_7H_{11}$. Jelínek et al.[209] reported halogenation reactions of **59** with hydrogen halides and halogens leading to 6(exo)-substituted species. The reactions were consistent with the so-called EINS (electrophile-induced nucleophilic substitution) mechanism. Similar halogenation of the isomeric 4,6-$C_2B_7H_{13}$ (**60**) species[210] have generated *mono*-(3-X) and disubstituted (3,5-X_2) derivatives of **60** (X = Cl, Br, and I). Selected compounds of the eight- and nine-vertex family of dicarbaboranes are presented in Table 14.



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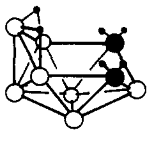
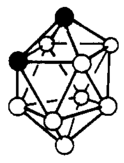


60

The ten-vertex closo series of dicarbaboranes includes the well-known isomeric 1,2-, 1,6-, and 1,10-$C_2B_8H_{10}$ compounds (structures **61**–**63**). Gimarc and Ott[198-200] have employed ab initio SCF calculations to analyze bond distances and predict total energies and the order of stabilities of the four unknown $C_2B_8H_{10}$ isomers. DSD-type rearrangement pathways among all seven isomers were also outlined. Other authors[211] reported a MNDO theoretical study of 1,10-$C_2B_8H_{10}$ to demonstrate the straightforward similarity of related structures, such as $[B_{10}H_{10}]^{2-}$, 1,10-$(N_2)_2B_{10}H_8$, and 1-SB_9H_9.



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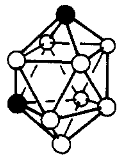

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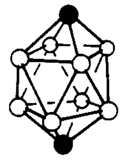


63

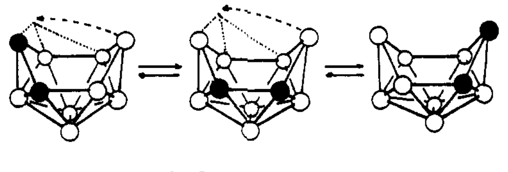
The dimethyl derivative of **61**, 1,2-Me_2-1,2-$C_2B_8H_8$, was prepared by the usual lithiation/methylation route.[212] The same species is generated in 33% yield from an interesting reaction between the coupled-cage *nido*-1:2′-$[B_5H_8]_2$ borane and 2-butyne at 60 °C in the presence of 2,6-lutidine.[213] Atavin et al.[214] determined the molecular structure of the 1,10-isomer via the gas-phase electron-diffraction technique. The bond distances were C–B 160.2 (2), B–B (tropical) 185.0 (5), and B–B (intertropical) 182.9 (4) pm. Temperature dependence of the Raman spectrum of the plastic solid 1,10-$C_2B_8H_{10}$ was measured[215] in order to investigate the phase transition–orientational–disorder properties of this compound. Nam and Onak[155] isolated the 2-Cl derivative of **63** from competitive reactions between carboranes **36** and **63** and the $Cl_2/AlCl_3$ chlorination system.

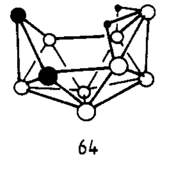
Of the nido ten-vertex dicarbaboranes the most studied is the most available compound of this family, 5,6-$C_2B_8H_{12}$ (**64**). It was converted into the levorotatory isomer in a one-way conversion reaction by using (+)-*N*-methylcamphidine (NMC) as the resolving agent:[216]

$$(\pm)\text{-}5,6\text{-}C_2B_8H_{12} + \underset{\text{solution}}{\text{NMC}} \rightleftarrows \underset{\text{solid}}{(+)\text{-}NMCH^+[(-)\text{-}5,6\text{-}C_2B_8H_{11}]^-} \xrightarrow{HCl} (-)\text{-}5,6\text{-}C_2B_8H_{12} \quad (28)$$

The reaction according to eq 28 yields only the levorotatory form on acidification of the solid diastereomer in 85% yield (based on **64**). On the other hand, once isolated, (−)-**64** is racemized on deprotonation by basic reagents. This is in agreement with fluxional behavior of the $[5,6\text{-}C_2B_8H_{11}]^-$ anion in solution. A reasonable explanation seems to be the "B(9)-vertex-flip" mechanism outlined in Scheme 2.

SCHEME 2





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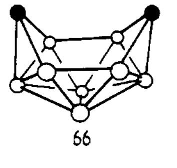


66

Shore et al.[217] reported the synthesis of the dimethyl derivative of **64** from the reaction between *arachno*-

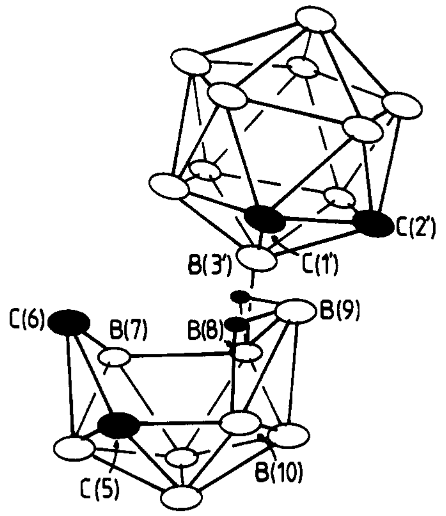


Figure 10. Simplified structure of 8:3′-[*nido*-5,6-$C_2B_8H_{11}$][*closo*-1′,2′-$C_2B_{10}H_{11}$] (**65**). Selected interatomic distances in the {*nido*-5,6-$C_2B_8H_{11}$} subunit were[220] C(5)–C(6) 145.7 (2), C(5)–B(1) 165.7 (2), C(5)–B(2) 169.2, C(5)–B(10) 175.1 (2), C(6)–B(2) 169.1 (2), C(6)–B(7) 150.8 (2), and B–B (mean) 179.3 pm.

$Et_2O{\cdot}B_9H_{13}$ and 2-butyne in diethyl ether at ambient temperature. The reaction was consistent with the removal of one {BH_3} unit from the general structure XV.

$$Et_2O{\cdot}B_9H_{13} + 4Me_2C_2 \rightarrow Me_2C_2B_8H_{10} + B(MeC{=}CC(Me)H)_3 \quad (29)$$

The author's group reported[218] the definitive assignments in the ^{11}B NMR spectrum of **64** on the basis of data from its substituted derivatives. One of the interesting derivatives of **64** is a conjuncto species 8:3′-[5,6-$C_2B_8H_{11}$][1′,2′-$C_2B_{10}H_{11}$] (**65**) which was isolated from a mild thermolysis of 7,8-$C_2B_9H_{13}$ (structure **73** below) in boiling benzene[219] (10% yield). A more detailed insight into the structure of **64** is provided by the X-ray diffraction study[220] of **65** (see Figure 10).

The structure of another nido compound of the ten-vertex carborane series, the $[6,9\text{-}C_2B_8H_{10}]^{2-}$ dianion (**66**), was definitely assigned via high-field NMR measurements[221] that confirmed gross structural similarity of **66** to the arachno congener 6,9-$C_2B_8H_{14}$ (**67**). The author's group has substantially improved the synthesis of **67** by heating **64** with sodium borohydride in ethanolic KOH.[222] The $AlCl_3$-catalyzed halogenation of **67** was found to proceed exclusively at the B(1) site[222,223] to afford a series of 1-substituted (X = Cl, Br, and I) derivatives. Of interest is the synthesis of 5-substituted haloderivatives of **67** from the reaction between **66** and anhydrous hydrogen halides:[223,224]

$$[C_2B_8H_{10}]^{2-} + 3HX \rightarrow XC_2B_8H_{13} + 2X^- \quad (30)$$

The overall mechanistic pathway of reaction 30, involving the stereoselective addition of HX to the C–B bond in **66**, was proposed on the basis of a deuterium-tracer study.[224] A variation of the reaction 30 using sulfuric acid led to the isolation of 5,5′-X-(*arachno*-6,9-$C_2B_8H_{13}$)$_2$ compounds (X = O and OSO_3O) (**68**). Of the two possible diastereomeric conformations, **68a** and **68b** (simplified structures oriented open face up), the formation of the less sterically hindered **68a** was confirmed by X-ray diffraction analysis[226] of the oxygen derivative.

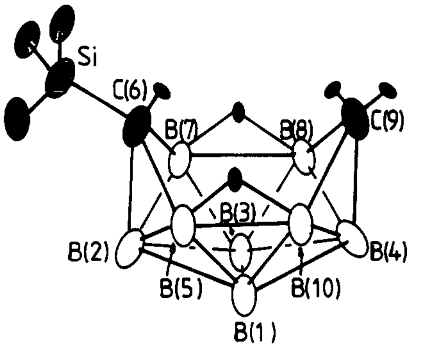


Figure 11. Schematic drawing of the molecular structure of 6(exo)-Me_3Si-*arachno*-6,9-$C_2B_8H_{13}$ (**69**). Selected exocage distances were[227] C(6)–Si 189.1 (2) and C(Me)–Si 185.2 pm. For selected cage bond distances see Table 16.

TABLE 15. Ten-Vertex Dicarbaboranes

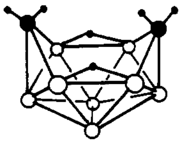
compound	cage structure	measured data	ref(s)
1,2-Me_2-1,2-$C_2B_8H_8$	**61**	^1H, ^{11}B, MS	212, 213
1,10-$C_2B_8H_{10}$[a]	**63**	GED[b]	214
$[6,9\text{-}C_2B_8H_{10}]^{2-}$	**66**	^1H, ^{11}B	221
5,6-$C_2B_8H_{12}$[c]	**64**	^{11}B	218
$[5,6\text{-}C_2B_8H_{11}]^-$	**64**[d]	^1H, ^{11}B	216a
5,6-Me_2-5,6-$C_2B_8H_{10}$	**64**	^{11}B, MS	217
6,9-$C_2B_8H_{14}$[e]	**67**	^1H, ^{11}B,[f] MS, mp	222, 223
6-Me_3Si-6,9-$C_2B_8H_{13}$	**67**	^1H, ^{11}B,[f] MS, mp	227
5,5′-X-6,9-$(C_2B_8H_{13})_2$	**68a**	^1H, ^{11}B,[f] MS, XR, mp	223–226

[a] Inclusive of the 2-Cl derivative. [b] Gas-phase electron diffraction. [c] Inclusive of the 4-, 8-, and 10-Cl and 2-Ph derivatives. [d] Deprotonized. [e] Inclusive of the 1- and 5-halo derivatives. [f] 2-D measurements.

TABLE 16. Selected Mean Cage Bond Distances (pm) for the Structurally Determined Derivatives of *arachno*-6,9-$C_2B_8H_{14}$ (Cage Structure 67)

	68[a]	69[b]
C–B(open face)	174	173.3
C–B(2 or 4)	166	164.8
B(1 or 3)–B(2 or 4)	173	173.5
B(2 or 4)–B(open face)	178	176.7
B(1)–B(3)	180	179.5
B(1 or 3)–B(open face)	179	178.9
B–B(bridging positions)	188	188.5

[a] Data for the 5,5′-O derivative from ref 226. [b] Data for the 6-(*exo*)-Me_3Si derivative from ref 227.



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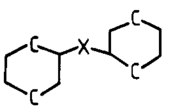
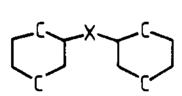


68a



68b

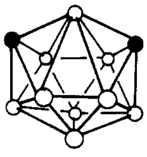
Wermer et al.[227] reported the formation of the 6-(exo)-substituted derivative of **67**, 6(*exo*)-Me_3Si-6,9-$C_2B_8H_{13}$ (structure **69** in Figure 11; for selected bond distances, see Table 16) from the cage-expansion reaction between $[2,3\text{-}(Me_3Si)_2\text{-}nido\text{-}2,3\text{-}C_2B_4H_5]^-$ (see deprotonized structure **38**) and pentaborane(9).

Measured structural data and selected cage distances for characteristic ten-vertex dicarbaborane compounds characterized over the reviewed period are in Tables 15 and 16, respectively.

3. Eleven-Vertex Dicarbaboranes

The only closo compound of this series that has been reported is the parent 2,3-$C_2B_9H_{11}$ dicarbaborane (**70**), with both cage carbons occupying the least connected cluster sites. Theoretical chemists[38,198] have calculated optimal geometries and the order of stabilities for all possible 20 $C_2B_9H_{11}$ isomers[228] and have analyzed possible DSD rearrangement pathways.

In addition to the structure of the 2,3-Me_2 derivative of **70**,[5] Leonowicz and Scholer[229] determined the molecular structure of a trisubstituted derivative, 4,7-$(HO)_2$-10-Br-2,3-$C_2B_9H_8$. The structure exhibits severe distortions from the idealized C_{2v} symmetry, evidently due to the back-donation effects from the substituents. In comparison with the 2,3-Me_2 isomer, the B(1)–B(4) distances are lengthened by 32 pm and the configuration of this cage seems to be intermediate between the closo C_{2v} structure **70** and the C_{5v} icosahedral fragment (see general structure XX).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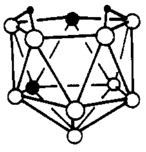
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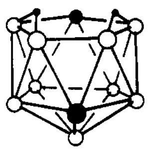
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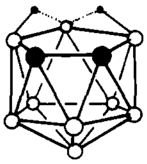
The neutral *nido*-dicarbaboranes of the eleven-vertex series (general structure XX) are represented by the isomeric species 2,7-$C_2B_9H_{13}$ (**71**) (known only as alkylated derivatives[230]), 2,9-$C_2B_9H_{13}$ (**72**), and 7,8-$C_2B_9H_{13}$ (**73**) reviewed earlier.[5] The two extra protons in these species can be accommodated without difficulties in the open pentagonal face. Formal or real removal of one proton leads to the popular "dicarbollide" anions, of which previously reported were the isomeric $[7,8\text{-}C_2B_9H_{12}]^-$ (**74**) and $[7,9\text{-}C_2B_9H_{12}]^-$ (**75**) species. The last two compounds are readily available from the well-established[1,2,5] degradation of the isomeric 1,2- and 1,7-$C_2B_{10}H_{12}$ twelve-vertex carboranes. The long standing problem of the location of the extra hydrogen in structure **74** has recently been resolved by means of high-level NMR[231,232] and X-ray[231] studies that confirmed its H(10) endo position with some coupling to the B(9) and B(11) boron sites, as indicated in **74**. The latest work[232] also points to two endo protons, H(9) and H(11), with some partial sharing to the B(10) center in structure **73**. No coupling of the extra hydrogen to the carbon atoms in structures **73**–**75** was observed in the [^{1}H–^{1}H]-COSY NMR spectra.[232] Leites et al.[233] reported the detection of this peculiar extra hydrogen in the Raman spectra of the anions **74** and **75** without structural interpretation. Shevchenko et al.[234-236] have quenched anion **74** with various ammine complexes of Co(III) and Cr(III) and determined DTA, IR, and UV properties of the isolated salts. Two groups[231,237] have calculated the MO structure of **74** and its deprotonated analogue, $[7,8\text{-}C_2B_9H_{11}]^{2-}$.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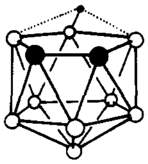
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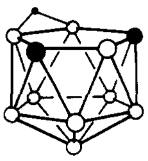
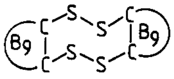

75

The ready availability of **74** has recently led to a relatively extensive exploration of its exoskeletal substitution chemistry. Antipin et al.[238] determined the structure of the 9,10,11-Me_3 derivative of **74** by X-ray diffraction. Zakharkin et al.[239] prepared a series of 9-benzyl-substituted derivatives of **74**, and its 7,8-Me_2 analogue, by treatment of the $[7,8\text{-}R_2\text{-}7,8\text{-}C_2B_9H_9]^{2-}$ dianions with benzyl halogenides $R'C_6H_4CH_2X$ (R′ = H, *o*-Me, *m*-Me, *p*-Me, *p*-Br; X = Cl, Br) in liquid ammonia. Repeated benzylation gave 9,11-dibenzylated isomers and iodination in THF gave the 9- and 9,11-I_2 derivatives. An X-ray diffraction study of the 7-Ph derivative of **74** was reported by Yanovski[240a] and that of 7-(*closo*-1′,2′-$C_2B_{10}H_{11}$)·**74** [$Rh(PPh_3)_3^+$ salt] by Knobler et al.[240b] The TLC properties of other C-substituted anions of the **74** type on silica plates were reported by Serino and Hawthorne.[241] Of interest are the fluorinated derivatives of **74** that arise from stereoselective degradation of the corresponding fluoroderivatives of *o*-carborane.[242]

One of the most versatile reagents based on **74** is the 7,8-dimercapto derivative, 7,8-$(HS)_2$-7,8-$C_2B_9H_9$ (**76**), which was prepared by Teixidor et al.[243,244] from the corresponding 1,2-$(HS)_2$ derivative of *o*-carborane and structurally characterized by an X-ray diffraction analysis.[244] The two mercapto groups have proved to be reactive and versatile reaction centers, particularly toward alkylating and oxidizing reagents. Thus, oxidation with KI_3 gave a disulfide product 7,7′:8,8′-$(S_2)_2$-[7,8-$C_2B_9H_{10}$][7′,8′-$C_2B_9H_{10}$] (schematic structure **77**), whose molecular structure is in agreement with the low-energy anti disposition of the two {C_2B_9} subclusters.[244]

Reflux of **76** with ethanol in the presence of dichloromethane[245] afforded a product with an expanded 10-membered intercage ring, 7,7′:8,8′-$(SCH_2S)_2$-[7,8-$C_2B_9H_{10}$][7′,8′-$C_2B_9H_{10}$] (simplified structure **78**). The same authors[246,247] have also built up exomacropolycyclic rings on the **74** moiety from a general reaction involving 1,2-$(HS)_2$-1,2-$C_2B_{10}H_{10}$ as a starting material at high dilution of the reagents:



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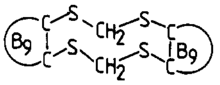
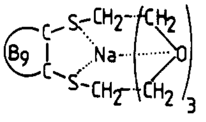


78

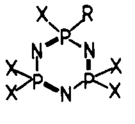
$$(HS)_2C_2B_{10}H_{10} + 3EtOH + 3OH^- + ClCH_2(CH_2OCH_2)_nCH_2Cl \rightarrow 2Cl^- + B(OEt)_3 + [\overline{CH_2(CH_2OCH_2)_nCH_2S_2C}{}_2B_9H_{10}]^- + 3H_2O + H_2 \qquad (31)$$

Moderate yields of the desired compounds were obtained in the form of sodium salts. As shown by the X-ray diffraction study of the derivative with $n = 3$, the sodium ion is encapsulated in the exocyclic ring in a crown ether manner via bonding to the O and S centers, as in **79** [Na–S 294.2 (2) and Na–O (mean) 239.0 pm]. The synthesis as in eq 31 was extended[247] by using other alkylene dihalide-like reagents, such as $(Cl(CH_2)_2)_2NTs$ (Ts = tosyl), $Br(CH_2)_nBr$ (n = 3,4), to give the corresponding exocyclic products.

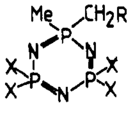
Allcock et al.[248] have prepared 7-substituted cyclotriphosphazene derivatives of **74**, **80**, and **81** (X =



79



80



81

$C_5H_{10}N$ and R = [7,8-$C_2B_9H_{11}$]) by the degradation of the *o*-carborane analogues. Miszusawa et al.[249] prepared 7-R-substituted derivatives of 74 (R = *p*-$NH_2C_6H_4$ and *p*-$SCNC_6H_4$) and converted the last *p*-isothiocyanatophenyl compound into [7-*p*-$SCNC_6H_4$-9-I-7,8-$C_2B_9H_{10}$]$^-$. The structure of this derivative was determined by an X-ray diffraction study [selected exocluster distances were B(9)–I 221.4 (8) and C(7)–C(Ph) 150.1 pm]. The aim of the study was to develop a new multifunctional compound for boron neutron capture therapy (BNCT) with high affinity to antibody proteins. Numerous other derivatives of 74 substituted by amino acid and peptide functionalities have been recently reviewed by Hawthorne[250] and will not be discussed here.

Zakharkin et al.[251] report an interesting silylation of [7,8-$C_2B_9H_{11}$]$^{2-}$ with $PhMe_2SiCl$ in THF and isolated either exo or endo 10-$PhMe_2Si$ derivatives of 74, depending on reaction conditions. The last compound has no extra hydrogen in the open part of the cluster. Plešek et al.[252] have prepared the [1-H_3B-*closo*-1,2-$C_2B_{10}H_{11}$]$^-$ anion by heating 74 with excess Et_3NBH_3 at 200 °C. The anion can be hydrolyzed by hydrochloric acid to give quantitatively 1,2-$C_2B_{10}H_{12}$.

Selected substituted derivatives of 74 are in Table 17, and selected mean interatomic distances for the structurally determined compounds in Table 18.

An interesting variation of the earlier reviewed[5] cage rearrangements among substituted derivatives of 74 and 75 (see ref 253 for example) was investigated[254,255] by Zakharkin et al.:

$$[8\text{-R-}7,9\text{-R}'_2\text{-}7,9\text{-}C_2B_9H_9]^- \underset{-\,H^+}{\overset{+\,H^+}{\rightleftharpoons}} 11\text{-R-}2,7\text{-R}'_2\text{-}2,7\text{-}C_2B_9H_{10} \xrightarrow[(2)\ +H^+]{(1)\ -2H^+} [9\text{-R-}7,8\text{-R}'_2\text{-}7,8\text{-}C_2B_9H_{10}]^- \quad (32)$$
$$R = Me \text{ or } PhCH_2;\ R' = Me \text{ or } H$$

All of the compounds in eq 32, interconvertible by protonation and deprotonation, were characterized by NMR. An X-ray diffraction study of the 11-$PhCH_2$-2,7-Me_2-2,7-$C_2B_9H_{10}$ derivative[255] [cage structure 71, selected cage distances: C(2)–C(7) 165.0 (6), C(2)–B(3,6) (mean) 167.3, C(7)–B(8,11) (mean) 164.4, and mean B–B(bridging sites) 184.9 pm] has confirmed unambiguously the 71 constitution. The "protonation rearrangement" outlined in eq 32 is applicable only for the substituted derivatives of 75, while the parent compound 75 is known to undergo dehydrogenative rearrangement to *closo*-2,3-$C_2B_9H_{11}$ (70) under comparable conditions.[256] Leites et al.[257] detailed the preparation of the 11-Me derivative of 71 and reported vibrational spectra of this compound. Bushby and Hawthorne[258] isolated the isomeric [2,9-$C_2B_9H_{12}$]$^-$ anion (deprotonated structure 72)[259] upon degradation of 1,10-$C_2B_{10}H_{12}$ with potassium hydroxide in the presence of 18-crown ether.

Another well-known category of the eleven-vertex *nido*-dicarbaborane family are species of the type $LC_2B_9H_{11}$ (L = Lewis base).[5,260] The presence of L and the two cage carbons dictates many isomeric structural variations with one extra hydrogen in the open part of the general structure XX. Grushin et al.[261] have reported the synthesis of 5-Me_2SO-7,8-$C_2B_9H_{11}$ (for X-ray structure see Figure 12) from the reaction between *closo*-$PhIC_2B_{10}H_{11}$ and dimethyl sulfoxide. Leites et al. have assigned the vibrational characteristics of the extra hydrogen atom in the structure of the former compound.[262] The X-ray diffraction study of the asym-

TABLE 17. Derivatives of [*nido*-7,8-$C_2B_9H_{12}$]$^-$ (Cage Structure 74)

substituent(s)	measured data	ref(s)
H	^1H,[a] ^{11}B,[a] XR, Ram, UV, DTA	231–236, 239
7-Ph	XR	240a
7-(1′,2′-$C_2B_{10}H_{11}$)	XR	240b
9,10,11-Me_3	XR	238
9-$RC_6H_4CH_2$[b]	^1H, ^{11}B	239
7,8-Me_2-9-$RC_6H_4CH_2$[b]	^1H, ^{11}B	239
9-I and 9,11-I_2	^1H, ^{11}B	239
9,11-$(PhCH_2)_2$	^1H, ^{11}B	239
7:7′,8:8′-$(S_2)_2$	^1H, ^{11}B, XR	244
7:7′,8:8′-$(SCH_2S)_2$	^1H, ^{11}B, ^{13}C	245
7,8-$SCH_2(CH_2OCH_2)_nCH_2S$[c]	^1H, ^{11}B, ^{13}C, XR	246, 247
7-*p*-$NH_2C_6H_4$	^1H, ^{11}B, IR	249
7-*p*-$SCNC_6H_4$	^1H, ^{11}B, IR	249
7-*p*-($SCNC_6H_4$)-9-I	^1H, ^{11}B, IR, XR	249
7,8-Me_2-9-I	^1H, ^{11}B, IR	239
10(exo and endo)-Me_2PhSi	^1H, ^{11}B, mp	251
6-F	^1H, ^{11}B, ^{19}F	242
1,6-F_2	^1H, ^{11}B, ^{19}F	242
1,5,6-F_3	^1H, ^{11}B, ^{19}F	242
1,5,6,10-F_4	^1H, ^{11}B, ^{19}F	242

[a] 2-D measurements. [b] R = H, *o*-Me, *m*-Me, *p*-Me, and *p*-Br. [c] *n* = 1–3.

TABLE 18. Mean Cage Distances (pm) for Selected Derivatives of [*nido*-7,8-$C_2B_9H_{12}$]$^-$ (Structure 74)

	substituent/s						
	H[a]	R[b]	R^1[c]	R^2[d]	R^3[e]	R^4[f]	R^5[g]
C(7)–C(8)	154.2	158.4	158.1	159.4	159.6	152.3	163.0
C–B(interbelt)	171.7	172.0	170.1	172.5	173.1	174.7	174.0
C–B(open face)	161.0	164.0	165.5	162.3	161.2	161.2	168.0
B(1)–B	177.9	174.2	178.7	177.0	176.6	178.4	178.0
B–B(lower belt)	177.1	175.4	176.8	177.2	177.2	178.9	179.0
B–B(interbelt)	177.5	175.3	177.8	178.1	178.5	177.4	180.0
B–B(open face)	183.3	181.0	180.4	182.5	180.3	179.4	174.0

[a] Data from ref 231. [b] R = 7-Ph, data from ref 240a. [c] R^1 = 7,8-$(HS)_2$, data from ref 243. [d] R^2 = 7:7′,8:8′-$(S_2)_2$, data from ref 244. [e] R^3 = 7,8-$SCH_2(CH_2OCH_2)_3CH_2S$, data from ref 246. [f] R^4 = 7-(*p*-$SCNC_6H_4$)-9-I, data from ref 249. [g] R^5 = 7-(1′,2′-$C_2B_{10}H_{11}$), data from ref 240b.

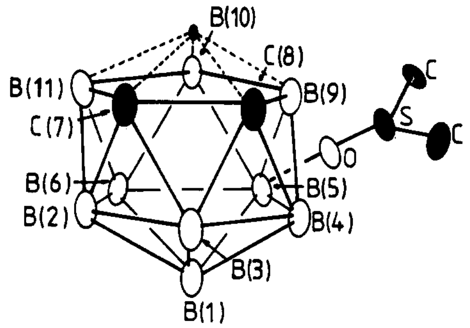


Figure 12. Representation of the structure of 5-Me_2SO-*nido*-7,8-$C_2B_9H_{11}$. Selected exocluster bond lengths were[261] B(5)–S 188.0 (4), mean C(Me)–S 175.4, and S–O 145.4 (2). The extra hydrogen is supposed to cap the open pentagonal face. For mean cage distances see Table 20.

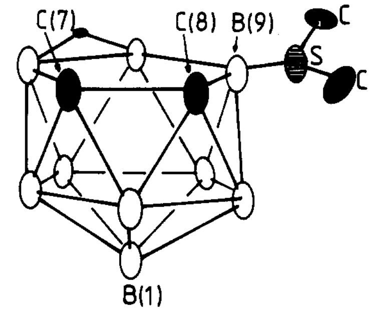


Figure 13. Schematic drawing of the molecular structure of 9-Me_2S-*nido*-7,8-$C_2B_9H_{11}$. Selected exocage bond distances were[263] B(9)–S 188.4 (3) and mean C(Me)–S 178.2 pm. For characteristic cage distances see Table 20.

TABLE 19. Eleven-Vertex Carboranes of the L-*nido*-7,8-$C_2B_9H_{11}$ Type

L	cage structure	measured data	ref(s)
5-Me_2SO	74	IR, Ram, XR, mp	261, 262
9-Me_2S	74	XR, ^1H, $^{11}B^a$	98, 263
9-Ph_2PH	74	^1H, ^{11}B, ^{31}P, ^{13}C	266
9-Ph_2PMe	74	^1H, ^{11}B, ^{31}P, ^{13}C	266
9-Ph_3P	74	^1H, ^{11}B, ^{31}P, XR	266, 267
10(*endo*)-Ph_2PH	83	^1H, ^{11}B, ^{31}P, ^{13}C	266
10(*exo*)-Ph_2PH	82	^1H, ^{11}B, ^{31}P, ^{13}C	266
10(*exo*)-Ph_2PMe	82	^1H, ^{11}B, ^{31}P, ^{13}C	266
10(*exo*)-Ph_3P	82	^1H, ^{11}B	266

[a] 2-D measurements.

metrically substituted 9-Me_2S-7,8-$C_2B_9H_{11}$ derivative was reported by Cowie et al.[263] (see Figure 13). The data point to a localized B(10)–H–B(11) hydrogen bridge, which is also in agreement with the recently reported 2-D NMR measurements.[98] The author's group has recently reported the preparation of the last compound from the degradation of **10** with aqueous $FeCl_3$ in the presence of dimethyl sulfide.[98]

A symmetrical variation of these structures is that of 10-$Me_2S(CH_2)_2O(CH_2)_2O$-7,8-$C_2B_9H_{11}$,[264] which was prepared from the reaction between **73** and dimethyl sulfide in boiling dioxane. The extra hydrogen atom was found to be bound to the B(9, 10, and 11) atoms in an asymmetric fashion (see schematic structure **82**).[265]

The reaction between Ph_2PCl and **74** in THF[266] gave 9-Ph_2PH-7,8-$C_2B_9H_{11}$ via transfer of the extra hydrogen to the P center. In contrast to the monoanion **74**, the same reaction with the $[7,8\text{-}C_2B_9H_{11}]^{2-}$ dianion produced exo (**82**) and endo (**83**) isomers of 10-Ph_2PH-7,8-$C_2B_9H_{11}$ that differ substantially in the location of the H(10) hydrogen. The endo isomer can be converted into the exo species by heating in THF. Methylation of the Ph_2PH ligand in the 9- and 10(exo)-substituted species by MeI/NaOEt gave the isomeric 9- and 10-(*exo*)-Ph_2PMe-7,8-$C_2B_9H_{11}$ compounds (see the related structure in Figure 13 and schematic structure **82**). The structures of 9-PPh_2Me-7,8-$C_2B_9H_{11}$[266] and of the structurally similar 9-PPh_3-7,8-$C_2B_9H_{11}$[267] derivative were determined by X-ray diffraction studies.

Selected compounds of the L-7,8-$C_2B_9H_{11}$ type are listed in Table 19 and salient bond distances are in Table 20.

TABLE 20. Mean Cage Bond Distances for Selected Compounds of the L-*nido*-7,8-$C_2B_9H_{11}$ Type

	ligand				
	L^{1a}	L^{2b}	L^{3c}	L^{4d}	L^{5e}
C(7)–C(8)	153.8	152.8	153.6	154.9	154.7
C–B(interbelt)	169.6	172.0	178.0	178.0	171.3
C–B(open face)	160.8	159.7	160.8	160.9	159.8
B(1)–B	177.1	177.0	176.3	176.3	176.7
B–B(lower belt)	175.5	176.5	175.6	176.0	176.4
B–B(interbelt)	177.6	177.1	177.6	176.6	176.5
B–B(open face)	182.2	181.1	184.3	179.9	182.8

[a] L^1 = 5-Me_2SO, data from ref 261 (see Figure 12). [b] L^2 = 9-Me_2S, data from ref 263 (see Figure 13). [c] L^3 = 10-$Me_2S(CH_2)_2O(CH_2)_2O$, data from ref 264. [d] L^4 = 9-Ph_2PMe, data from ref 266. [e] L^5 = 10(*exo*)-PH_2PMe, data from ref 266.

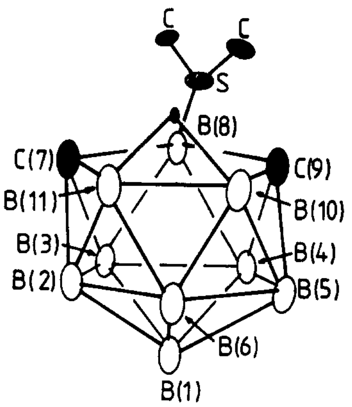
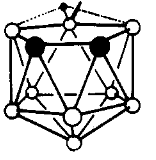


Figure 14. Schematic drawing of the structure of 8-Me_2S-*nido*-7,9-$C_2B_9H_{11}$. Selected distances are[268] S–B(8) 188.6 (4), mean C(Me)–S 179.0, mean C–B(open face) 164.2, mean C–B(interbelt) 167.5, B(10)–B(11) 184.1 (6), and other B–B(mean) 177.5 pm.

Šubrtová et al.[268] have reported the X-ray diffraction analysis of the previously reported cage[260] isomer, 8-Me_2S-*nido*-7,9-$C_2B_9H_{11}$ (see Figure 14).



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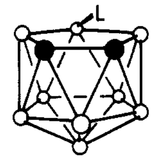


83

V. Tri- and Tetracarbaboranes

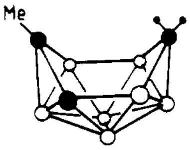
Tricarbaboranes can be notionally derived by replacing three {BH^-} units by {CH} groups in the corresponding $[B_nH_n]^{4-}$ and $[B_nH_n]^{6-}$ borane prototypes. This formal procedure leads, after protonation, to the neutral species *nido*-$C_3B_{n-3}H_{n+1}$ and *arachno*-$C_3B_{n-3}H_{n+3}$.

The only new tricarbaborane reported over the reviewed period is the methyl derivative of *nido*-$C_3B_7H_{11}$, viz. 6-Me-5,6,9-$C_3B_7H_{10}$ (**84**). This compound was prepared by Sneddon et al.[269] from an interesting one-carbon insertion reaction between acetonitrile and the [*arachno*-4,6-$C_2B_7H_{12}$]$^-$ anion as in eq 33, followed by the protonation of the resulting anion:

$$[C_2B_7H_{12}]^- + MeCN \rightarrow [CH_3C_3B_7H_9]^- + NH_3 \qquad (33)$$

Compound **84** is so far the only representative of the ten-vertex family of tricarbaboranes. In this context it should be noted that the compound, originally formulated as 5,6,10-Me_3-5,6,10-*nido*-$C_3B_7H_8$ by the author's group,[270] was later proved to be an isomeric tetracarbaborane compound, 6,11-Me_2-*arachno*-5,6,10,11-$C_4B_7H_{11}$ (see structure **91**).

Much more chemistry has been generated over the past 10 years in the area of tetracarbaboranes, more specifically compounds of the general formulas *nido*-$C_4B_{n-4}H_n$ and *arachno*-$C_4B_{n-4}H_{n+2}$. The smallest representative of this class of carboranes is the long-known[2,5] six-vertex *nido*-2,3,4,5-$C_4B_2H_6$ compound (**85**).



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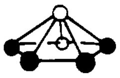

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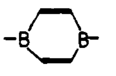


86

The recent chemistry of **85** derives from numerous polyalkyl-substituted derivatives, of which the preparation is in part discussed in ref 271. Depending on the nature of substituents, these compounds can also exist in the classical nonpolyhedral form **86** (1,6-diboracyclohexadiene) and **87** (bicyclohexane).

Wrackmeyer[271] reported ^{11}B and ^{13}C NMR data for a long series of peralkylated derivatives of **85**, $R_6C_4B_2$ (where R is a combination of Me, Et, and ^iPr substituents on carbon and boron) and gathered all available NMR information from these measurements. Van der Kerk et al.[272] have isolated peralkylated derivatives of **85**, of the general formula 1,6-Me_2-2,3,4,5-R_4-C_4B_2 (R = Me and Et), from the so-called methylborylene-generating system, 2-C_8K/$MeBBr_2$, in the presence of alkynes R_2C_2 (room temperature, 6 days). The *nido*-tetracarbaboranes were isolated only for R = Me, other alkynes giving the corresponding derivatives of structure **86**. Other authors,[273] however, failed to reproduce the preparation of these last diboracyclohexadienes, obtaining instead the corresponding peralkylated compounds of type **85** in the presence of 3-hexyne and 5-decyne (R = Et or Bu). Herberich et al.[274] have reported the first amino derivative of **85**, 1-Me-6-$^iPr_2N$-2,3,4,5-$C_4B_2H_4$, which is available from the reaction of $Li_2[(^iPr_2N)BC_4H_4]^{2-}$ with $MeBBr_2$.

No representative of the seven-vertex class of tetracarbaboranes has so far been reported, but two groups[275,276] have found efficient routes for the synthesis of the *C*-peralkyl derivatives of the eight-vertex *nido*-tetracarbaborane 4,5,7,8-$C_4B_4H_8$ (**88**). The first method, by Fehlner,[275] consists of the photolysis of the *nido*-[1,1,1-$(CO)_3$-FeB_4H_4] ferraborane (20 °C, 360 nm) in the presence of alkynes to give the $R_4C_4B_4$ compounds (R = Me and Ph). Although a different structure was suggested,[275] the constitution **88** proposed by Mirabelli and Sneddon[276] is in better agreement with the NMR data and the carborane stability rules.[26a,c] The above reaction generates also a number of other products inclusive of higher polycarbaborane species, such as $Me_6C_6B_4H_4$ and $Me_8C_8B_4H_4$, as identified by mass spectroscopy.

An efficient route to the *C*-peralkyl derivatives of **88** is the reaction between 2,3-Et_2-2,3-*nido*-$C_2B_4H_6$ (cage structure **38** above) and 2-butyne in the presence of $NiCl_2$ and sodium hydride in THF.[276] The authors suggest a reasonable mechanism, consisting of a metal-promoted fusion of the alkyne with the $\{C_2B_4\}$ cage via an intermediate $[(Me_2C_2)Ni(2,3\text{-}Et_2\text{-}2,3\text{-}C_2B_4H_4)]$ complex, which is decomposed to 4,5-Me_2-7,8-Et_2-4,5,7,8-$C_4B_4H_4$ at room temperature:

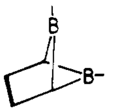
TABLE 21. Eleven-Vertex *nido*-$C_4B_7H_{11}$ and *arachno*-$C_4B_7H_{13}$ Tetracarbaboranes

isomer substituent	cage structure	measured data	ref(s)
nido			
1,2,8,10	**97**	^1H, ^{11}B, ^{13}C, IR, MS, R_v	146
2,7,8,11	**95**	^1H, ^{11}B,[a] MS	279
7,8,9,10	**96**	^1H, ^{11}B,[a] MS	279
arachno			
5,6,10,11-Me_4[b]	**91**	^1H, ^{11}B,[a] IR, MS, XR	280
iso-5,6,10,11-Me_4	**93**	^1H, ^{11}B,[a] IR, MS, XR	280
5,6,9,11[c]	**94**	^1H, ^{11}B,[a] MS	270
6,11-Me_2-5,6,10,11	**91**	^1H, ^{11}B,[a] MS	270

[a] 2-D measurements. [b] Inclusive of the 9-Br derivative. [c] Inclusive of the 9,11-Me_2 derivative.

$$[(Me_2C_2)Ni(Et_2C_2B_4H_4)] \rightarrow Ni^0 + Me_2Et_2C_4B_4H_4 \qquad (34)$$

As far as the author is aware, no representatives of the nine-vertex family of tetracarbaboranes have been reported to date. Of the ten-vertex species of this class, two nido compounds of the proposed cage structures **89** and **90** have been prepared. The structural arrangement as in **89** was assigned by Koester et al.[277] to the perethylated compound $Et_4C_4B_6Et_6$ that was prepared from an interesting cage-fusion reaction between Et_5-*closo*-1,5-C_2B_3 (cage structure **32** above) and potassium metal, followed by oxidation with iodine. A similar reaction of the 1,5-Me_2-1,5-$C_2B_3Et_3$ derivative of **32** was found to proceed via the $Me_4C_4B_6Et_6$ hexaboraadamantane, which on heating to 160 °C was transformed to the isomeric *nido*-tetracarbaborane 1,3,4,6-$Me_4C_4B_6Et_6$.[278] Both peralkylated carboranes thus prepared are fluxional in solution and were suggested to adopt the unprecendented cage structure **89** with three carbon atoms at high-connectivity positions. Williams has also proposed other structural alternatives for the peralkylated derivatives of **89**.[11c] In agreement with Williams' stability rules[26a,c] is the parent *nido*-carborane 5,6,8,9-$C_4B_6H_{10}$ (**90**), which was isolated in low yield (3%) as a side product from the reaction between 4,5-$C_2B_7H_{13}$ (**59**) and acetylene.[279]



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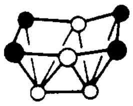
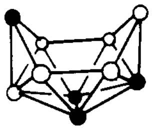
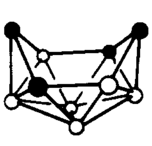


88



89

Relatively more explored has been the area of the eleven-vertex tetracarbaboranes (for individual compounds see Table 21). Finster and Grimes[280] reported the first species of this series, 5,6,10,11-Me_4-*arachno*-5,6,10,11-$C_4B_7H_9$, which is a tetramethyl derivative of cage structure **91**. The compound was prepared from the degradation of the twelve-vertex $Me_4C_4B_8H_8$ carborane (cage structure **98** below) by ethanol in air (40–60%). Direct bromination of Me_4-**91** with $AlCl_3$/Br_2 in CS_2 led to its 9-Br derivative (numbering as in XXI), of which the structure was determined by X-ray diffraction [selected cage bond distances in the open part were C(6)–C(11) 154.6 (6), C(5)–C(6) 161.1 (5), C(5)–C(10) 151.6 (4), C(6)–B(7) 184.6 (6), B(9)–C(10) 169.8 (5), B(9)–C(11) 161.6 (6), B(8)–B(9) 193.7 (6), and B(7)–B(8) 181.1 (6) pm (numbering as in XXI)].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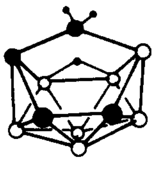
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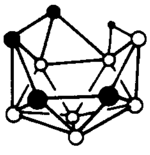
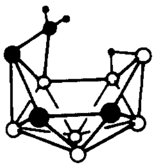

92

Deprotonation of Me_4-**91** with NaH in THF led to an interesting rearrangement of the C(11) apex to generate an isomeric anion *iso*-$[5,6,10,11\text{-}Me_4\text{-}5,6,10,11\text{-}C_4B_7H_8]^-$ (**92**), which gave the neutral carborane **93** on protonation.[280] Isomeric with carboranes **91**–**93** is the parent carborane *arachno*-$5,6,9,11\text{-}C_4B_7H_{13}$ (**94**), which was isolated by the author's group as the main product from the reaction of dicarbaborane **59** with acetylene (hexane, 120 °C, yield 15%).[270] This reaction is accompanied by the formation of *nido*-$2,7,8,11\text{-}C_4B_7H_{11}$ (**95**) and compound **90** already mentioned above.[279] A similar reaction with 2-butyne yielded the 9,11-Me_2 derivative of **94** (30%) and the 6,11-Me_2 analogue of **93** (15%). Heating of an anion generated by the deprotonation of **94** (NaH/Et_2O)[279] resulted in the formation of another isomeric eleven-vertex *nido*-tetracarbaborane, the symmetrically structured $7,8,9,10\text{-}C_4B_7H_{11}$ compound (**96**). Isomeric with compounds **95** and **96** is the parent *nido*-$1,2,8,10\text{-}C_4B_7H_{11}$ (**97**),[146] which is one of the products from the gas-phase thermolysis of **31** in a hot–cold reactor (400 °C, 5%).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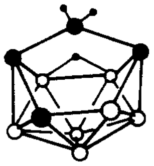
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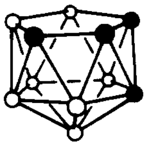
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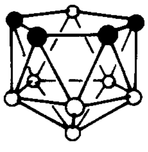
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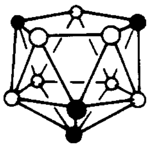

97

The most systematically explored area of tetracarbaborane chemistry is undoubtedly that of the C-substituted derivatives of the twelve-vertex *nido*-2,3,7,8-$C_4B_8H_{12}$ carborane (**98**) (numbering as in XXII), which has not yet been isolated in the parent form. The relevant chemistry has already been reviewed by Grimes,[10,14] and therefore only new and general features will be briefly mentioned.

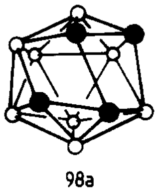
The compounds $R_4C_4B_8H_8$ (R = Me, Et, ^{n}Pr, ^{n}Bu, $^iC_5H_{11}$, and $^nC_6H_{13}$)[164,281,282] are known to be fluxional in solution between structures **98a** and **98b**. Structure **98a** with the two quadrilateral open faces is that found in the solid phase for R = Me,[281] while structure **98b** with the open hexagonal face was found in the solid phase for R = Et.[282] From variable-temperature NMR measurements, the ΔH and ΔS parameters for the **98a** → **98b** conversion, which involves a cleavage of a framework C–C bond, were determined to be small (for R = Me, Et, and ^{n}Pr).[282] Compounds with bulkier substituents, such as R = $PhCH_2$,[172,283] indenylmethyl, fluorenylmethyl,[163] and also oligomeric derivatives,[165] are nonfluxional in solution and adopt the more open configuration **98b**.

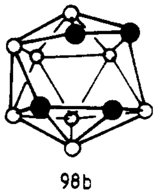
TABLE 22. Selected Tetracarbaboranes of the *nido*-$R_4C_4B_8H_8$ Type (Structures 98a and 98b)

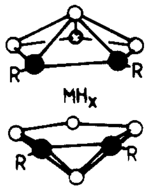
R	measured data	ref(s)
Me^a	^{1}H, ^{11}B, IR, MS, XR	281, 282, 284
Et	^{1}H, ^{11}B, IR, MS, XR	282, 284
$^nC_3H_7$	^{1}H, ^{11}B, IR, MS	282
^{n}Bu	^{1}H, ^{11}B, IR, MS	164
$^iC_5H_{11}$	^{1}H, ^{11}B, IR, MS	164
$^nC_6H_{13}$	^{1}H, ^{11}B, IR, MS	164
$PhCH_2$	^{1}H, ^{11}B, IR, MS, XR	283
$R^{1\,b}$	^{1}H, ^{11}B, IR, MS	163
$R^{2\,c}$	^{1}H, ^{11}B, IR, MS	163

^{a} Inclusive of the 4-ferrocenyl derivative. ^{b} R^1 = indenylmethyl. ^{c} R^2 = fluorenylmethyl.

As discovered by Grimes et al. more than a decade ago,[10,14] all carboranes of the type **98** have been prepared from the transition metal-promoted face-to-face fusion of the two $\{nido\text{-}2,3\text{-}R_2\text{-}2,3\text{-}C_2B_4H_4^{2-}\}$ ligands of the closo complexes $[(R_2C_2B_4H_4)MH_x]$ (MH_x = FeH_2 or CoH) (**99**), which are then quantitatively converted to the $R_4C_4B_8H_8$ carboranes on air oxidation in THF. The fusion mechanism has been extensively probed, revealing the existence of a paramagnetic diiron intermediate complex[14,16] that contains both low-spin and high-spin Fe(II).[284,285] The fusion process was found to be intramolecular, with respect to the carborane ligands[284] and has been extended to the trisubstituted carboranes of the type 2,3,4-R_3-*nido*-2,3-$C_2B_4H_5$ to obtain hexasubstituted $R_6C_4B_8H_6$ compounds.[172] Most representative compounds of the **98** type, generated from the fusion process are listed in Table 22.


98a


98b



99

Some of the homosubstituted carboranes **98** (R = Me, Et, and $PhCH_2$) were structurally characterized by X-ray diffraction, and another crystallographically characterized compound is the *B*-ferrocenyl-substituted derivative of $Me_4C_4B_8H_8$, viz. 4-$[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)]$-2,3,7,8-$Me_4C_4B_8H_7$.[286] Open-face bond distances in selected compounds of types **98a** and **98b** are given in Table 23.

A new, open area of transition metal-promoted fusion reactions is the attempt to prepare fused products via mixed-ligand complexes of the $[(2,3\text{-}R_2\text{-}2,3\text{-}C_2B_4H_4)FeL]$ type, where L is a different cage-borane ligand.[287] For instance, simultaneous treatment of the $[2,3\text{-}Me_2\text{-}2,3\text{-}C_2B_4H_4]^-$ and $[B_5H_8]^-$ anions with $FeCl_2$ in THF gave, after the usual workup, low yields of supraicosahedral tetracarbaboranes identified as $Me_4C_4B_xH_x$ (x = 9–11) in addition to the usual compound of the Me_4-**98** type.

Another variation of a fusion reaction leading to mixed-substituted derivatives of the $R_2R'_2C_4B_8H_8$ type is the recently reported[288] series of reactions between the complexes $[(R_2C_2B_4H_4)Fe(\eta^6\text{-}C_8H_{10})]$ and the salts

TABLE 23. Selected Cage Bond Distances (in pm with ESD's in Parentheses) for *nido*-$R_4C_4B_8H_8$ Tetracarbaboranes

	R			
	Me[a]	Me[b]	Et[c]	$PhCH_2$[d]
C(2)–C(3)	143 (1)	149.3 (6)	136.2 (6)	140.7 (1)
C(2)–B(1)	166 (1)	172.0 (6)	173.2 (8)	174.8 (2)
C(2)–B(6)	170 (1)	165.3 (8)	162.7 (6)	165.0 (2)
C(2)–B(11)	173 (1)	164.1 (7)	218.1 (6)	217.5 (3)
C(3)–C(7)	153 (1)	151.5 (8)	288.6 (2)[e]	285.8 (1)[e]
C(3)–B(1)	170 (1)	166.6 (7)	166.9 (6)	168.1 (3)
C(3)–B(4)	215 (1)	225.6 (8)	160.3 (8)	158.1 (2)
C(3)–B(8)	150 (1)	149.0 (6)	140.8 (7)	141.8 (1)
C(7)–B(11)	215 (1)	219.7 (7)	157.4 (6)	156.5 (2)
C(7)–B(12)	162 (1)	167.3 (7)	165.6 (7)	167.9 (3)
C(8)–B(4)	169 (1)	168.4 (6)	214.5 (7)	213.1 (2)
C(8)–B(9)	170 (1)	167.7 (7)	167.2 (7)	164.7 (2)
C(8)–B(12)	171 (1)	169.5 (7)	176.3 (6)	174.7 (2)

[a] Data from ref 280 (structure **98a**). [b] 4-Ferrocenyl derivative (structure **98a**), data from ref 286. [c] Data from ref 282 (structure **98b**). [d] Data from ref 283 (structure **98b**). [e] Nonbonding distances.

$Na^+[2,3\text{-}R'_2\text{-}2,3\text{-}C_2B_4H_5]^-$ (R = Et, ^{n}Bu, $PhCH_2$; R′ = Me, Et, ^{n}Bu, $PhCH_2$) at 150 °C in the absence of solvent. Multinuclear NMR studies of the carboranes thus prepared indicated an equilibrium between the **98a** and **98b** forms in solution.

Hosmane et al.[289] have reported an interesting high-yield (82%) and stereospecific fusion reaction (without involvement of a transition-metal complex) between two molecules of 2,3-$(Me_3Si)_2$-*nido*-2,3-$C_2B_4H_6$, induced by heating at 210 °C:

$$2(Me_3Si)_2C_2B_4H_6 \rightarrow (Me_3Si)_2C_4B_8H_{10} + 2Me_3SiH \qquad (35)$$

The reaction is believed to involve the $Me_3Si^{\bullet}$ radical and the isolated product is of structure **98a** and is nonfluxional in solution.

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