Dicarba-*closo*-dodecaboranes $C_2B_{10}H_{12}$ and Their Derivatives

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I. Introduction

The synthesis and properties of dicarba-*closo*-dodecaboranes were first reported at the end of 1963 in both the United States and the USSR.[1-4] Their chemistry is one of the most complete in the field of boranes and heteroboranes.

One of the most striking features of the carboranes is the capability of the 2 carbon atoms and 10 boron atoms to adopt the icosahedral geometry in which the carbon and boron atoms are hexacoordinate. This feature of the icosahedral structure gives rise to the unusual properties of such molecules and their carbon and boron derivatives.

The stability of the carborane cage is demonstrated under the many reaction conditions used to prepare a wide range of *C*- and *B*-carborane derivatives. It is interesting to study such derivatives, especially the properties of the unique B-substituted carboranes compared with either the C-substituted, or tricoordinated boron compounds. For this reason, this review will emphasize the preparation and reactivity of compounds in which the carborane cage system remains intact, thus influencing the properties of the products.

The field of icosahedral carboranes has developed extensively since the first publications almost 30 years ago. The results of early investigations are cited in R. Grimes' monograph which completely covered the literature up to 1969.[5a] The literature and list of carboranes prepared up to 1984 are presented in the *Gmelin Handbook*.[5b] The latest theoretical studies on carborane structures, which utilize either a localized bonding approach or a molecular orbital treatment of the skeletal bonding in *closo*-carboranes, are presented in several monographs and papers.[6] These theoretical concepts are usually applied to boranes, *closo*-carboranes, and other carboranes. These concepts are discussed in a separate review and are only cited here. Carboranes with carbon–metal and boron–metal bonds were reviewed in 1982[7] and boron-substituted carboranes in 1980[8a] and 1988[8b]. Developments in carborane chemistry were reviewed yearly in *Journal of Organometallic Chemistry* until 1979. Accordingly, only the most important results of the synthesis, properties, and derivatives prior to 1980 are briefly presented in this review. The last five years will be covered in more depth.

Vibrational spectra of icosahedral carborane molecules and the application of boron compounds are reviewed in separate articles in this issue and will be mentioned very briefly. The chemistry of the 1,2- and 1,7-$C_2B_9H_{12}$ ions prepared by degradation of the car-

V. I. Bregadze graduated from the Chemistry Department of the M. V. Lomonosov Moscow State University in 1960. He carried out his Ph.D. work in the field of carborane chemistry under guidance of L. I. Zakharkin and O. Yu. Okhlobystin at the Institute of Organo-Element Compounds in Moscow. He received Ph.D. degree in 1967. In 1969-1970 he spent six months as a research chemist in the Virginia Polytechnic Institute and State University (Blacksburg, Virginia) in the laboratory headed by Raymond Dessy. He is currently Head of the Laboratory of Organoaluminum and -boron Compounds of the A. N. Nesmeynov Institute of Organo-Element Compounds of the USSR Academy of Sciences. His research interest is concerned with the carborane chemistry and organic derivatives of non-transition metals. He studied a new type of carboranes containing a boron–non-transition metal σ-bond which is unstable in usual organo-element compounds. Carboranes with such a B–M bond were shown to take part in the reactions typical of organometallic compounds. He developed several methods for the synthesis of organometallic compounds used to prepare semiconductors. He is the author of approximately 200 papers. He is an Executive Secretary of the new Russian Journal *Metalloorganicheskaya Khimia* (*Organometallic Chemistry in the USSR*, in English translation).

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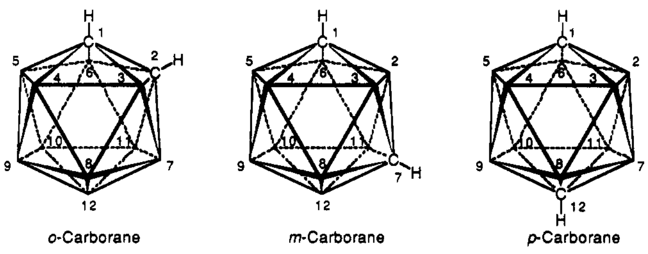


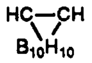
o-Carborane *m*-Carborane *p*-Carborane

Unmarked vertices =BH

Figure 1. 1,2-, 1,7-, and 1,12-dicarba-*closo*-dodecaborane(12).

borane cage is beyond the scope of this review.

According to IUPAC nomenclature the names of these isomers are 1,2-, 1,7- and 1,12-dicarba-*closo*-dodecaboranes(12). Usually the symbol



$$\underset{B_{10}H_{10}}{HC\text{—}CH}$$

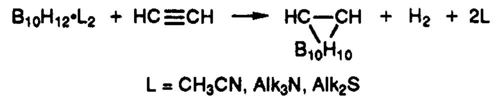
is used to represent the ortho isomer, whereas $HCB_{10}H_{10}CH$ and $H\overline{CB_{10}H_{10}C}H$ denote the *m*- and *p*-carborane isomers, respectively. In this review *o*-$C_2B_{10}H_{12}$, *m*-$C_2B_{10}H_{12}$, and *p*-$C_2B_{10}H_{12}$ will be designated *o*-, *m*-, and *p*-carborane, respectively. These three isomers and the numbering of the carbon and boron atoms of the cage are shown in Figure 1.

II. Synthesis and Properties of 1,2-, 1,7-, and 1,12-Dicarba-closo-dodecaboranes (o-, m-, and p-Carboranes)

The dicarba-*closo*-dodecaboranes have been the most extensively investigated of all known carboranes during the last 30 years.

The first *o*-carboranes were obtained by the reaction of acetylene with complexes prepared from decaborane and Lewis bases such as acetonitrile, alkylamines, and alkyl sulfides (eqs 1 and 2).[1-4]

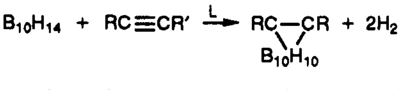
$$B_{10}H_{14} + 2L \longrightarrow B_{10}H_{12}{\cdot}L_2 + H_2 \qquad (1)$$



$$B_{10}H_{12}{\cdot}L_2 + HC{\equiv}CH \longrightarrow \underset{B_{10}H_{10}}{HC\text{—}CH} + H_2 + 2L \qquad (2)$$

$L = CH_3CN, Alk_3N, Alk_2S$

The reaction of decaborane with acetylenes in the presence of Lewis bases is now a general method for carborane synthesis (eq 3). The structure of 1,2-carborane and its derivatives has been established by X-ray diffraction[9-14] and ^{11}B NMR studies.[15] Electron diffraction data have been reviewed.[16,17] The 10 boron and 2 carbon atoms of 1,2-carboranes form an almost regular icosahedron, with the following interatomic distances: C–C = 1.62–1.70; B–C = 1.70–1.75; B–B 1.70–1.79 Å. The B–C distance in carborane is longer than the B–C bond length in trimethylborane (1.578 Å).[18] C–H and B–H bonds as well as the bonds of substituted carbon and boron atoms have normal-length σ bonds; the C–H length is 1.1 Å, and the C–Me length is 1.53 Å.



$$B_{10}H_{14} + RC{\equiv}CR' \xrightarrow{L} \underset{B_{10}H_{10}}{RC\text{—}CR} + 2H_2 \qquad (3)$$

Unlike the starting boron hydride, carborane is stable in the presence of oxidizing agents, alcohols, and strong acids and exhibits phenomenal thermal stability in temperatures up to 400 °C. Under inert atmosphere, it rearranges to *m*-carborane between 400 and 500 °C. This latter compound isomerizes to *p*-carborane between 600 and 700 °C.[5]

One of the most important features of a carborane system is its ability to enter into substitution reactions at both the carbon and boron atoms without degradation of the carborane cage. On the one hand, the strong electron-withdrawing character of the *o*-carborane unit facilitates the metalation of the carborane C–H group (eq 4).[5]

$$HCB_{10}H_{10}CH + RLi \rightarrow HCB_{10}H_{10}CLi + RH \qquad (4)$$

On the other hand, direct electrophilic halogenation,[5] alkylation,[5,19] sulfhydrylation,[20] and metalation[21,22] take place at the boron atom. The introduction of substituents onto the carbon and boron atoms of the carborane cage influences the reactivity of the unsubstituted atoms. These reactions are typical of aromatic compounds, and for this reason the carborane molecule has been characterized as a "pseudoaromatic" system.

According to ^{11}B NMR data and other physical methods, substitution at one atom of the carborane cage influences the overall charge distribution. Electrophilic substitution usually occurs first at the 9,12 and then at the 8,10 positions of the *o*-carborane cage. The carbon atoms and the adjacent boron atoms do not appear susceptible to electrophilic substitution. Although these experimental results are in general agreement with theoretical calculations of the charge distribution,[13,23] they do not always correlate quantitatively.

A carborane charge distribution calculation was performed for the first time by Hoffmann and Lipscomb.[24] The NEMO method was then used to compute the charge distribution on carboranes in numerous theoretical studies.[13,25-28] On the basis of the experimental pK_a values of carboranecarboxylic acids,[29] hydroxycarboranes,[30] mercaptocarboranes,[31] and basicity of aminocarboranes,[32,33] sequences for the electron density increase on the atoms of the carborane units were established. Electron density increases in the order 1 (2) < 3 (6) < 4 (5,7,11) < 8 (10) < 9 (12) for *o*-carborane, 1 (7) < 2 (3) < 5 (12) < 4 (6,8,11) < 9 (10) for *m*-carborane, and 1 (12) < 2 (3–11) for *p*-carborane (positions listed in parentheses are chemically equivalent to those in front of the parentheses).

Recently Zakharkin and Ol'shevskaya[34] reported the experimental evaluation of the charge distribution on the skeletal atoms of *o*-, *m*-, and *p*-carboranes using carboranecarboxylic acids. The authors compared their results with those of Plešek and Heřmánek,[31] obtained on HS-derivatives and from theoretical charge distribution calculations. These data are summarized in Table I.

The pK_a values of carboranecarboxylic acids are compared with those of mercaptocarboranes in Table II.

The charge distribution in icosahedral carboranes has been investigated using UV photoelectron spectroscopic studies of *p*-carboranes, 1- and 3-phenyl-*o*-carborane, as well as several thio-*o*(*m*)-carboranes.[35] The electron density in *o*-carborane was shown to decrease in the order 9 > 8 > 4 > 3 > 1. The electron density at the B(9) position in *m*-carborane is approximately equal to that in the B(8) position in *o*-carborane, and the B(2) position in *p*-carborane is equivalent to the B(4) posi-

TABLE I. Charge Density Distribution[a]

position	1	2	3	4[b]	5	6	7	8	9
1-*o*	0.172	0.156	0.29	0.239	0.29	0.22	0.38		0.49
1-*m*	0.132	0.080	0.15	0.183		0.04		0.24	0.03
1-*p*	0.115	0.059	0.15	0.160		0.02			0.04
2-*m*	0.034		0.10	0.048		0.09		0.13	0.04
3-*o*	0.017		0.08	0.027	0.26	0.07	0.22		0.03
4-*o*	−0.003		−0.03	−0.004	−0.02	0.02	−0.02		0.00
2-*p*	−0.023	−0.012	−0.03	−0.004		0.00			−0.01
5-*m*	−0.026		−0.03	−0.036		0.01		−0.06	0.00
4-*m*	−0.030	0.002	−0.03	−0.041		0.02		−0.03	−0.01
8-*o*	−0.070	−0.071	−0.16	−0.097	−0.28	−0.16	−0.20		−0.05
9-*m*	−0.080	−0.076	−0.16	−0.111		−0.19		−0.25	−0.05
9-*o*	−0.115	−0.100	−0.16	−0.160	−0.24	−0.17	−0.27		−0.05

[a] Determined from pK_a values of carborancarboxylic acids (column 1)[34] and mercaptocarboranes (column 2)[31] in comparison with charge distribution obtained by means EHMO (column 3)[24] and NEMO (columns 5–9)[13,25–28] methods. Charge density values (ϵ) were determined using $pK_a = pK_a^0 - \rho\epsilon$ equation proposed by Plesek and Heřmánek.[31] [b] Calculated charge density values for the case[24] ϵ(9-*o*) = −0.16.

TABLE II. pK_a Values of Carboranecarboxylic Acids and MercaptoCarboranes in 50% C_2H_5OH

position of X in $C_2B_{10}H_{11}X$	X = COOH	X = SH
1-*o*	2.61	3.30
1-*m*	3.34	5.30
1-*p*	3.64	5.85
2-*m*	5.11	
3-*o*	5.38	
4-*o*	5.80	
2-*p*	6.16	7.75
5-*m*	6.22	
4-*m*	6.28	7.38
8-*o*	7.01	9.32
9-*m*	7.19	9.45
9-*o*	7.83	10.08

TABLE III. σ-Constants of *o*-, *m*-, and *p*-Carboranyl Groups

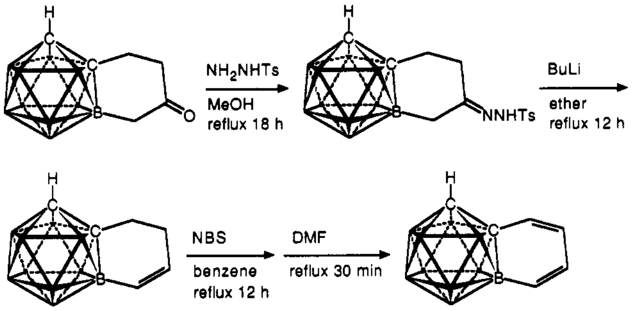
position of substitution	inductive and resonance constants		Hammett constants		ref(s)
	σ_I	σ_R^0	σ_p	σ_m	
1-*o*	0.375	0.003	0.46	0.47	36
1-*o*	0.380	0.0	0.43	0.49	37, 38
1-*m*	0.21	−0.05			37
1-*m*	0.194	−0.039	0.33	0.25	36, 38
1-*p*	0.14	−0.002			39
2-*m*	0.12	0.05	0.15	0.14	40
3-*o*	0.11	0.07	0.19	0.19	37, 38
3-*o*	0.01	0.06			41
2-*p*	0.02	0.02			42
4-*o*	−0.04	0.02	−0.05	−0.03	43, 44
4-*m*	−0.04	0.02	0.02	−0.02	45, 46
9-*m*	−0.12	−0.02			42
9-*o*	−0.16	−0.03			42
9-*o*	−0.23	−0.02			43, 44

tion in *o*-carborane. The irregular electron density distribution on the carborane vertices causes a difference in the electronic effects of the carboranyl group depending on the position of the substituent in the carborane cage.

The *C*- and *B*-carboranyl σ-constants were recently determined using the usual physical organic methods.[36–48] These are presented in the order of decreasing electron-withdrawing effect in Table III. Hammett constants were determined using carboranylbenzoic acids in 75% ethanol. Inductive and resonance constants were determined by the Taft method using ^{19}F NMR chemical shifts of (fluorophenyl)carboranes in the equation: $\delta_m^F = -7.10\sigma_I + 0.6$ and $\delta_p^F - \delta_m^F = -29.5\sigma_R^0$. General trends using different methods were established: *C*-carboranyl groups have a strong electron-acceptor effect which decreases in the order *o*- > *m*- > *p*-carborane. The electronic effects of the *B*-carboranyl group changes according to the following sequence: the more remote the boron atom is from the carbon atoms in the carborane cage, the stronger are the electron-donating effects of the *B*-carboranyl groups. Thus, 3-*o*- and 2-*m*-carboranyl groups are still electron acceptors, whereas 4-*o*-, 4-*m*-, and 2-*p*-carboranyls are actually electroneutral. 9-*m*-carboranyl and in particular 9-*o*-carboranyl groups clearly show electron-donating properties.

The relationship between inductive and resonance effects and the problem of potential carborane aromaticity are still under discussion. Wu and Jones'[49] ^1H NMR studies of bridged benzo-*o*-carborane led them to conclude that ring–cage conjugation could play an important role, whereas another study[36] suggested that the icosahedral cage effect is purely inductive and has no resonance component. The synthesis of bridged benzo-*o*-carborane is presented in Scheme I.

SCHEME I



Unmarked vertices of icosahedra = BH
Unmarked vertices of rings = CH_2 or CH

Thermal and chemical stability, rearrangement, and degradation of the icosahedral cage are other important aspects of carborane chemistry. The results of a wide range of their investigations are summarized elsewhere.[5,50–53]

One of the most important reactions in carborane chemistry was reported by Wiesboeck and Hawthorne in 1964.[54] They showed that *o*-carborane can be degraded using alcoholic alkali removing one boron atom and forming the 1,2-dicarbaundecaborate(1−) ion (eq 5).[54]

$$o\text{-}C_2H_2B_{10}H_{10} + CH_3O^- + 2CH_3OH \xrightarrow{40\ ^\circ C} C_2B_9H_{12}^- + H_2 + B(OCH_3)_3 \quad (5)$$

Starting from this anion, Hawthorne et al. obtained a number of "sandwich" derivatives which are analogues of the transition metal cyclopentadienide derivatives. The first member of this series was obtained by the interaction of ferrous chloride with the dicarbollide ion, $C_2B_9H_{11}^{2-}$, which was in turn prepared by the reduction of the $C_2B_9H_{12}^-$ ion (eq 6).[55] The extensive area of

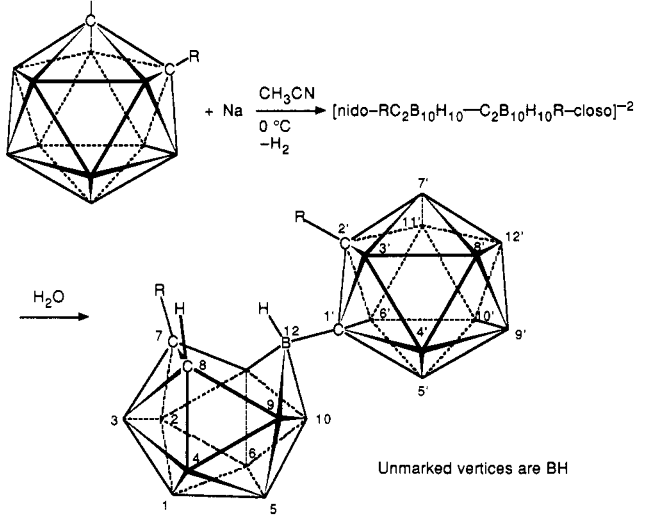
$$C_2B_9H_{12}^- \xrightarrow{\text{Na or NaH}} C_2B_9H_{11}^{2-} \xrightarrow{\text{FeCl}_2} (C_2B_9H_{11})_2Fe^{2-} \xrightarrow{O_2} (C_2B_9H_{11})_2Fe^- \quad (6)$$

heterocarboranes has developed from these results but a more detailed discussion is beyond the scope of this review.

Both *o*- and *m*-carboranes are known to add two electrons without hydrogen evolution under the action of alkali metals in THF or liquid ammonia to quantitatively form the $C_2B_{10}H_{12}^{2-}$ dianion.[56-58]

Recently, Zakharkin et al.[59] have found that when 1-phenyl- or 1-methyl-*o*-carborane in acetonitrile are treated with sodium the reaction proceeds unexpectedly with hydrogen evolution to give the condensation products of two carborane molecules instead of the $C_2B_{10}H_{11}R^{2-}$ dianion. The dimers are dianions with one *closo*- and one *nido*-carborane nuclei, which on protonation produce the 7-phenyl- or 7-methyl-12-(2′-phenyl-1′,2′-dicarba-*closo*-dodecaborane-1′-yl)-7,8-dicarba-*nido*-dodecaborate anions (Scheme II). They were characterized as the methylpyridinium salts. The same dimer is formed as a result of a new type of carborane cage degradation under the action of DMF or DMSO on 1-phenyl-2-lithio-*o*-carborane (eq 7).[60]

SCHEME II



$$2\ Ph\text{-}o\text{-}CB_{10}H_{10}CLi \xrightarrow[\text{Et}_2\text{O–C}_6\text{H}_6]{\text{DMF or DMSO}} [nido\text{-}Ph\text{-}C_2B_{10}H_{10}\text{-}C_2B_{10}H_{10}\text{-}Ph\text{-}closo]^{2-}Li_2^+ \xrightarrow{H_2O} [nido\text{-}Ph\text{-}C_2B_{10}H_{11}\text{-}C_2B_{10}H_{10}\text{-}Ph\text{-}closo]^-Li^+ \quad (7)$$

X-ray diffraction studies have unambiguously established the structure of the monoanion. It is of great interest to compare these results with the results of two-electron reduction of compounds which already contain two carborane cages connected by a C–C bond.

Hawthorne et al.[61] obtained an unusual product with a double bond between the two carbon atoms connecting the carborane nuclei when *C,C*′-bis(*o*-carborane) was treated with 2 equiv of sodium metal in THF or sodium naphthalide solution. The disodium salt of the biscarborane dianion was converted to its triphenylmethylphosphonium salt, whose molecular structure was determined (Figure 2).

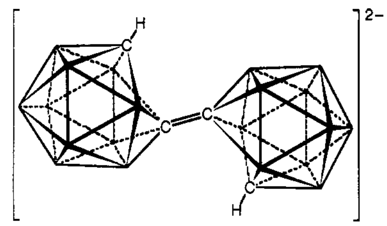
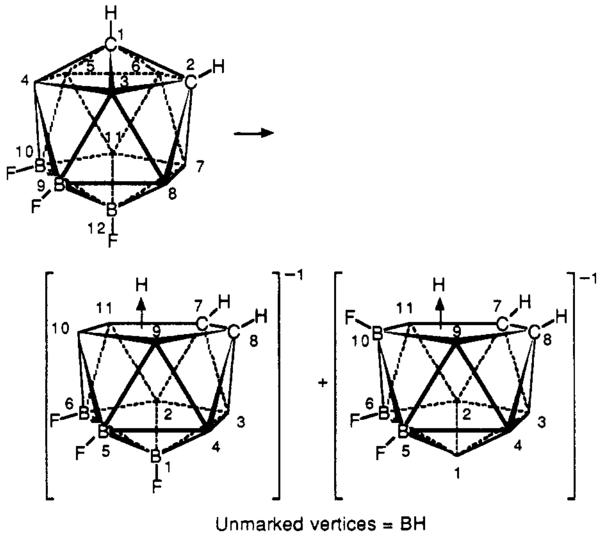


Figure 2. The structure of $(C_2B_{10}H_{11}{=}C_2B_{10}H_{11})^{2-}$.

The C12–C12′ distance is 1.377 (4) Å, which reveals the existence of substantial double bond character. The biscarborane anion represents the first example of a species that exhibits multiple bond character between the carbon atoms of two adjacent carborane cages. The reduction leads to the rupture of the polyhedral C–C bonding interaction (the C7–C12 distance is 2.414 (4) Å). The C12–B9 and C12–B10 interatomic distances (1.628 (4) and 1.643 (4) Å) are shorter, but the C12–B8 and C12–B11 distances (1.838 (4) and 1.925 (4) Å) are longer than average C–B distances in carboranes. These results seem to be similar to the rupture of B12–C7 and B12–C8 bonding interaction in the dianion obtained by Zakharkin et al. (Scheme II).

The action of alcoholic alkali on 9-fluoro-, 9,12-difluoro-, 8,9,12-trifluoro-, and 8,9,10,12-tetrafluoro-*o*-carboranes leads to their degradation under mild conditions to give 6-fluoro-, 1,6-difluoro-, 1,5,6-trifluoro-, 5,6,10-trifluoro-, and 1,5,6,10-tetrafluoro-7,8-dicarba-*nido*-undecaborate(−1) ions, respectively.[62] For the first time, it was shown that degradation of 8,9,12-trifluoro-*o*-carborane proceeds regioselectively. Two isomers of fluorine substituents in different cage positions were identified using ^{19}F and ^{11}B NMR (Scheme III).

SCHEME III



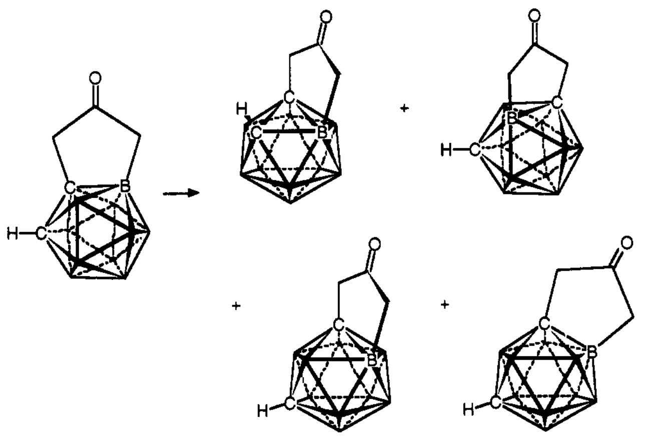
One more example of carborane cage transformation reactions is the insertion of the $[Co(PEt_3)_2]$ fragment into the *o*-carborane icosahedron.[63] Interaction of 1-Me-1,2-$C_2B_{10}H_{11}$ with 2 equiv of $[Co(PEt_3)_4]$ in toluene at room temperature for 3 h leads to an unusual 13-vertex *closo*-carbacobaltaborane.

The electrolysis of *o*-carborane at a nickel anode in the presence of bipyridyl leads directly to the formation of $C_2B_9H_{11}Ni\cdot bipy$ (bipy = bipyridyl) complex.[64]

An important aspect of carborane chemistry is the mechanism of the thermal isomerization of *o*-carborane to *m*- and *p*-carboranes. Recently, the following rearrangement processes have been reviewed:[65–67] the diamond–square–diamond (DSD) mechanism, the rearrangement based on a cuboctahedral intermediate, a rotation of the bicapped pentagonal prism, a triangular face rotation, and the rearrangement based on a 12-vertex nido intermediate.

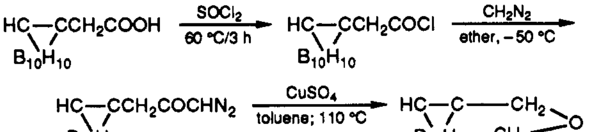
Wu and Jones[65] suggested a new and original model of bridged *o*-carborane for studying the thermal isomerization process (Scheme IV). They introduced a three-carbon bridge between a carbon and a boron at the 4-position of the cage. The ability of such a small bridge to span only adjacent atoms limits the possible rearrangement products.

SCHEME IV



Unmarked icosahedral vertices = BH

The synthesis of the bridged *o*-carborane was accomplished starting from *o*-carboranylacetic acid according to eq 8, and its molecular structure was described.[68]



$$\underset{B_{10}H_{10}}{HC\!-\!CCH_2COOH} \xrightarrow[60\ ^\circ C/3\ h]{SOCl_2} \underset{B_{10}H_{10}}{HC\!-\!CCH_2COCl} \xrightarrow[ether,\ -50\ ^\circ C]{CH_2N_2}$$

$$\underset{B_{10}H_{10}}{HC\!-\!CCH_2COCHN_2} \xrightarrow[toluene;\ 110\ ^\circ C]{CuSO_4} \begin{matrix} HC\!-\!C\!-\!CH_2 \\ B_{10}H_9\!-\!CH_2 \end{matrix}\!\!>\!O \qquad (8)$$

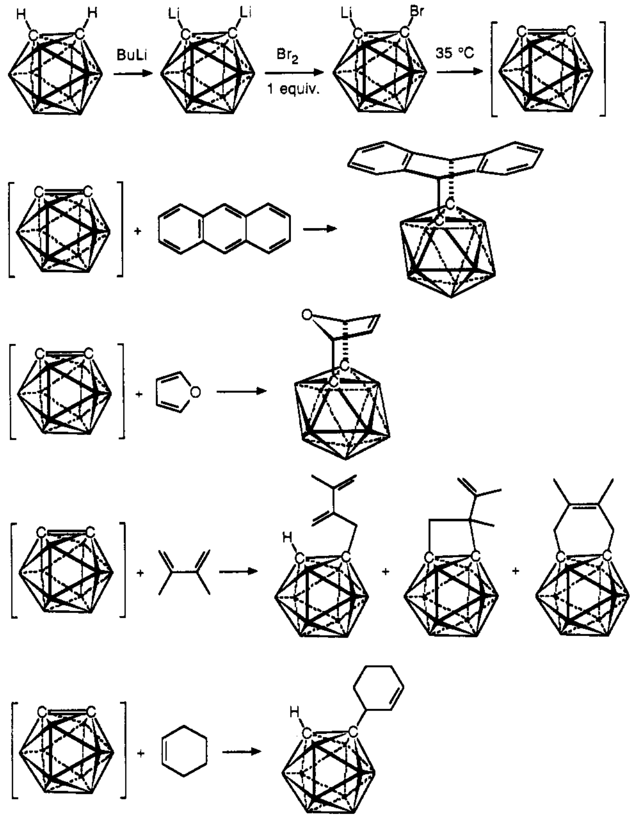
On the basis of the experimental results, triangle rotation was concluded to be the major contributor to the rearrangement mechanism. This process was named the extended triangle rotation (ETR) mechanism, which focuses on the preservation of triangular faces throughout the rearrangement, and was suggested to rationalize both data from the literature and the results from the pyrolysis of the bridged *o*-carborane.

The thermal isomerization of the bridged *o*-carborane, as well as the previously described isomerization of halogenated carboranes, takes place in substituted carboranes, and its mechanism may differ from the isomerization mechanism of unsubstituted carboranes. However, the triangular-face rotation mechanism was supported by the calculations made by Gimarc et al.[66]

A different conclusion was reached by Edvenson and Gaines[67] on the basis of a study of thermal isomerization of an unsubstituted carborane, namely, regiospecifically ^{10}B-labeled icosahedral carborane. They proposed a mechanism which involved the opening of the closo-icosahedral structure to a nido structure.

The most fascinating result of the past year in the field of carborane chemistry is the series of transformations of the *o*-carborane molecule via intermediate formation of the 1,2-didehydro-*o*-carborane, a carborane version of dehydrobenzene. Jones and co-workers[69,70] discovered a way to the dehydro-*o*-carborane by treatment of 1,2-dithio-*o*-carborane with 1 equiv of bromine (Scheme V). 1-Bromo-2-lithio-*o*-carborane is stable below 0 °C. Its heating in the presence of dienes leads to the formation of carborane derivatives typical of dehydrobenzene reactions with dienes. Products of the reaction of 1,2-didehydro-*o*-carborane with furans, anthracene, cycloxene, norbornadiene, hexadiene, 2,3-dimethyl-1,3-butadiene, and other dienes were obtained and studied.

SCHEME V



Unmarked icosahedral vertices = BH

Transformations of the 1,2-didehydro-*o*-carborane present new evidence for the aromatic character of a carborane molecule.

III. Carbon-Substituted Carboranes

Early investigations of carboranes showed that it is in fact possible to prepare a variety of organic compounds with carboranyl substituents. Two synthetic methods leading to carbon substituted carboranes were used in the early years: the reaction of substituted acetylenes with decaborane and substitution on carboranyllithium. The properties of carboranyl derivatives resemble organic compounds with electron-accepting groups. The influence of such bulky electron-deficient substituents on the properties of organic and organometallic compounds has been extensively studied. The synthesis and properties of numerous carboranyl-substituted organic compounds are summarized in monographs.[5] The last comprehensive review covering carborane chemistry up until 1979 was written by Matteson.[71]

During the past decade investigations in the field of C-substituted carboranes were directed at creating new models to be used in theoretical investigations (see the elegant studies of Wu and Jones[49] in section 2) and at improving the synthetic methods for known compounds. These methods were used in the preparation of organic and organometallic carboranyl compounds used in the production of polymeric materials as well as in biological and medical investigations. These compounds proved particularly useful in the boron neutron capture therapy for cancer (BNCT).

A. Organic Compounds with a *C*-Carboranyl Group

Phase transfer catalysis conditions appear to be more convenient in the preparation of some carborane derivatives.

Kabachii, Valetskii et al. have developed a new method for the synthesis of 1,7-dichloro-*m*-carborane by chlorination of *m*-carborane with CCl_4 using phase transfer catalysis (eq 9).[72]

$$m\text{-}HCB_{10}H_{10}CH \xrightarrow[-2NaCl;\ 2H_2O]{[R_4N]^+Cl^-;\ NaOH} [R_4N]^+C^-B_{10}H_{10}C^{-+}[NR_4] \xrightarrow{CCl_4} ClCB_{10}H_{10}CCl + 2[R_4N]^+C^-Cl_3 \quad (9)$$

$$R_4N = Et_3NBz$$

Zakharkin et al. have obtained 1-alkyl- and 1,2-dialkyl-*o*-carboranes by alkylating *o*-carborane, and 1-methyl- or 1-phenyl-*o*-carborane with alkyl halides in solid alkali–THF (or DMSO) systems using dibenzo-18-crown-6-ether (eq 10).[73] Allyl ethers of 1-(hydroxymethyl)-*o*- and *m*-carboranes, and diallyl ethers of 1,2-bis(hydroxymethyl)-*o*- and 1,7-bis(hydroxymethyl)-*m*-carboranes were prepared by reacting allyl bromide with 1-(hydroxymethyl)-*o*- and *m*-carboranes and 1,2-bis(hydroxymethyl)-*o*- and 1,7-bis(hydroxymethyl)-*m*-carboranes respectively, in the CH_2Cl_2 aqueous alkali two-phase system using tetrabutylammonium bromide.[74]

$$o\text{-}C_2H_2B_{10}H_{10} + RX + KOH \xrightarrow[\text{dibenzo-18-crown-6-ether}]{THF} o\text{-}RCCHB_{10}H_{10} + KX + H_2O \quad (10)$$

$$X = Cl, Br, I$$

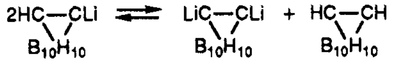
$$R = CH_3, C_6H_{13}, C_6H_5CH_2, \alpha\text{-}C_{10}H_7$$

Earlier, ethynylcarboranes were obtained by interacting diacetylene with decaborane. Recently a new method has been developed for the synthesis of 1-ethynyl-*o*-, *m*-, and *p*-carboranes via carboranylcopper compounds (eq 10a).[75] The authors also studied the stereochemical aspects of Br_2, HCl, and HI addition to 1-ethynylcarboranes.[76a]

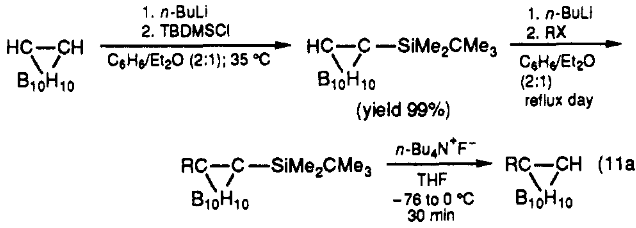
$$HCB_{10}H_{10}CH \xrightarrow{BuLi} HCB_{10}H_{10}CLi \xrightarrow{CuCl} HCB_{10}H_{10}CCu \xrightarrow{BrC\equiv CR} HCB_{10}H_{10}CC\equiv CR \quad (10a)$$

$$R = Ph, Me_3Si$$

The synthesis of a mono-C-substituted *o*-carborane is a difficult problem due to the disproportionation of monolithio-*o*-carborane which leads to the undesired di-C-substituted product (eq 11).[5]

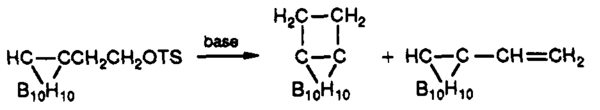

(11)

Hawthorne et al.[76b] proposed to protect one carbon atom of *o*-carborane by a new protecting group: *tert*-butyldimethylsilyl (TBDMS). The protecting effect is based on the ability of TBDMS to react only with monolithio component of the equilibrium mixtures and on the further facile removal of TBDMS in the deprotection step (eq 11a).


(11a)

Chari et al.[77] have shown that the addition reaction of *o*(*m*)-carboranylcarbene to olefins is largely stereospecific. Methyl(*o*-carboranyl)carbene behaves like tolylcarbene in intramolecular reactions.

The synthesis of 1,2-ethano-*o*-carborane using this method proved impractical since it involved several steps. However, two new more efficient syntheses were later described.[78] The elimination of *p*-toluenesulfonic acid from the corresponding tosylate gives varying amounts of 1,2-ethano-*o*-carborane, depending upon the solvent (eq 12). This observation led to the first synthetic method:


(12)

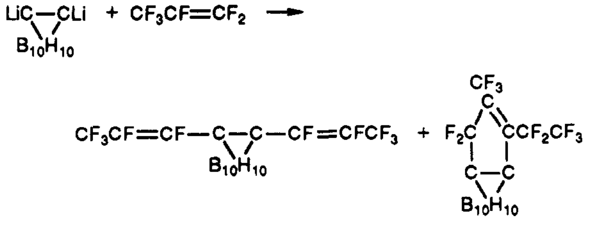
In benzene/*n*-BuLi with an optimal solvent/base combination the yield was 40% with the ratio of 1,2-ethano-*o*-carborane to 1-vinyl-*o*-carborane as high as 99/1. The second, even better route is the decomposition of 1-(1-*o*-carboranyl)-2-bromoethane over *n*-butyllithium in the gas phase at 140 °C.

Contrary to 1-(chloromethyl)-*o*-carborane, 1-(fluoromethyl)-*o*-carborane has been shown to alkylate aromatic hydrocarbons in the presence of $AlCl_3$ (eq 13).[79]

$$CHC(CH_2F)B_{10}H_{10} + ArH \xrightarrow{AlCl_3} CHC(CH_2Ar)B_{10}H_{10} + CHC(CH_2Cl)B_{10}H_{10} \quad (13)$$

$$ArH = C_6H_6, PhMe, p\text{-}Me_2C_6H_4$$

The interaction of 1,2-dilithio-*o*-carborane with perfluoropropene results in an unusual cyclization reaction along with 1,2-bis(pentafluoropropenyl)-*o*-carborane formation (eq 14).[80]


(14)

The synthesis and reactivity of (trifluorocyclobutenyl)-*o*-carborane has been described.[81] Zhakharkin and Zhigareva[82] proposed a new method of preparation of 1-amino-*o*(*m*)-carborane (eq 15).

$$\mathrm{CHB_{10}H_{10}C{-}N{=}N{-}Ph} \xrightarrow{\mathrm{H_2/Ni}} \mathrm{CHB_{10}H_{10}C{-}NH_2 + PhNH_2} \quad (15)$$

o-Carborane and its *C*-alkyl (*C*-aryl) derivatives were reduced electrochemically on transition metals in aprotic solvents and in the presence of tetraalkylammonium salts via a one-electron mechanism with the cleavage of the C–H bond to form the corresponding *o*-carboranyl anion. The electrolysis in the presence of CO_2 leads to *o*-carboranecarboxylic acid (eq 16).[83]

$$\mathrm{1,2\text{-}C_2RB_{10}H_{11}} \xrightarrow[\mathrm{Fe;\ -2.2\ V}]{+e^-} \mathrm{[1,2\text{-}C_2RB_{10}H_{10}]^-} \xrightarrow{+\mathrm{CO_2}} \mathrm{[1,2\text{-}RCB_{10}H_{10}CCOO^-]} \xrightarrow{\mathrm{HCl}} \mathrm{1,2\text{-}RCB_{10}H_{10}CCOOH} \quad (16)$$

$$R = \mathrm{H}(45\%\ \text{yield}),\ \mathrm{CH_3}\ (60\%)$$

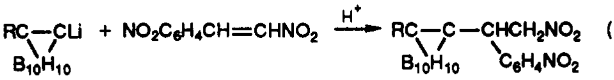
The synthesis and reactivity of peroxides with the *C*-carboranyl group has also been described.[84] The *C*-carboranyl group was shown to increase the stability of a phosphaalkene (eq 17).[85]

$$m\text{-}\mathrm{HCB_{10}H_{10}C{-}C(O)Cl + (Me_3Si)_3P} \xrightarrow[\mathrm{Me_3SiCl}]{} m\text{-}\mathrm{HCB_{10}H_{10}C{-}C(O){-}P(SiMe_3)_2} \rightarrow m\text{-}\mathrm{HCB_{10}H_{10}C{-}C(OSiMe_3){=}PSiMe_3} \quad (17)$$

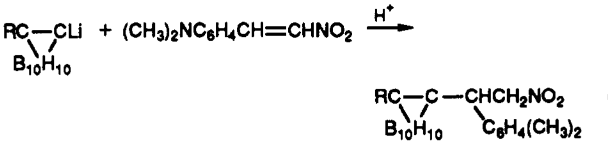
The syntheses of isoxazoles and izoxazolines[86] containing the carboranyl group and isocyanatocarboranes[87] (eq 18) have also been reported.

$$o(m)\text{-}\mathrm{RCB_{10}H_{10}C(CH_2)_{\mathit{n}}COCl + Me_3SiN_3} \xrightarrow{100\text{–}110\ ^\circ\mathrm{C}} o(m)\text{-}\mathrm{RCB_{10}H_{10}C(CH_2)_{\mathit{n}}CON_3} \xrightarrow[-\mathrm{N_2}]{} o(m)\text{-}\mathrm{RCB_{10}H_{10}C(CH_2)_{\mathit{n}}NCO} \quad (18)$$

Reactions of lithio-*o*-carboranes with α,β-nitroolefins and their functional derivatives have also been studied (eqs 19 and 20).[88] The regiospecificity of the reactions and their possible application to the synthesis of dinitroalkanes, nitro esters, α-halonitroalkenes, esters of hydroxamic acids, and secondary nitro acids containing the carboranyl group have been shown.



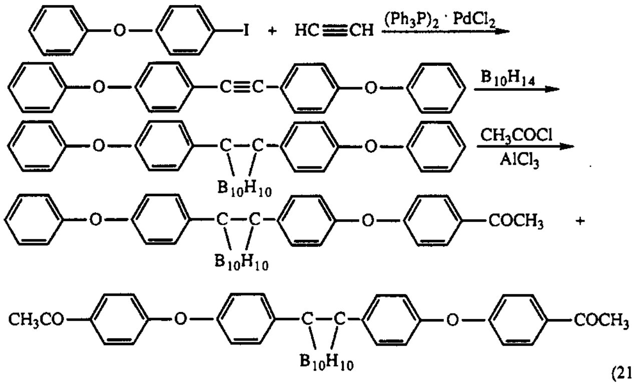
$$\mathrm{RC{-}CLi\ (B_{10}H_{10}) + NO_2C_6H_4CH{=}CHNO_2} \xrightarrow{\mathrm{H^+}} \mathrm{RC{-}C(B_{10}H_{10}){-}CH(C_6H_4NO_2)CH_2NO_2} \quad (19)$$



$$\mathrm{RC{-}CLi\ (B_{10}H_{10}) + (CH_3)_2NC_6H_4CH{=}CHNO_2} \xrightarrow{\mathrm{H^+}} \mathrm{RC{-}C(B_{10}H_{10}){-}CH(C_6H_4(CH_3)_2)CH_2NO_2} \quad (20)$$

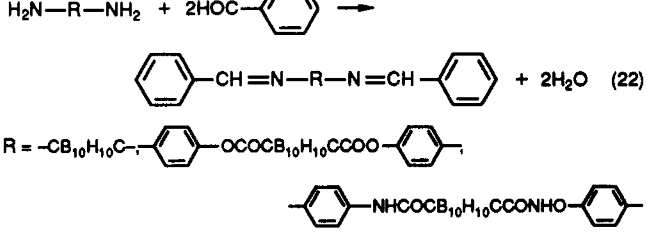
For more than 25 years the chemistry of carborane-containing polymers has been extensively studied. Introduction of carborane cages into the polymer chain not only increases polymer thermal stability and solubility in organic solvents, but also gives rise to other important properties. The carborane unit has been successfully incorporated into many classes of polymers such as polyarylenes, polyesters, polyamides, polyformals, polycarboranylenes, and polysiloxanes. Advances in this field have been described in a review[89] in 1984 and a monograph[90] in 1988. Recently the concept of stabilization of aromatic polymers as exemplified by arylene carboranes was reported.[91]

The polycyclocondensation of *C,C′*-bis[4-(4′-acetylphenoxy)phenyl]-*o*-carborane has been studied.[91] The synthesis of a diacetylarylene containing *o*-carborane is shown in eq 21.



(21)

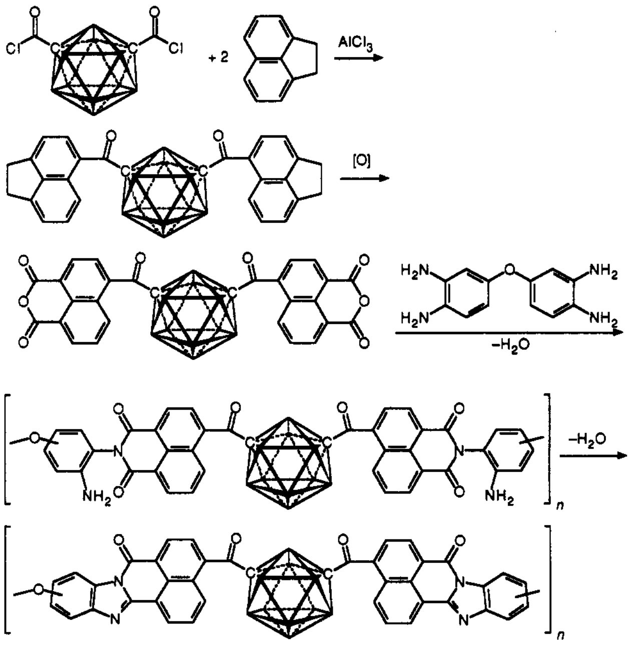
New soluble polymeric Schiff bases, containing *m*-carborane have been prepared by the polycondensation of *m*-carboranylenediamine, 1,7-bis[(4-aminophenyl)carboxy]-*m*-carborane and 1,7-bis[(4-aminophenyl)amino]carbonyl]-*m*-carborane using different dialdehydes in various solvents (eq 22).[93,94]



(22)

The carborane unit has been introduced into poly(naphthoylenebenzimidazole), thus increasing the solubility of the polymer.[95] The synthesis was carried out according to Scheme VI.

SCHEME VI



Unmarked icosahedral vertices = BH

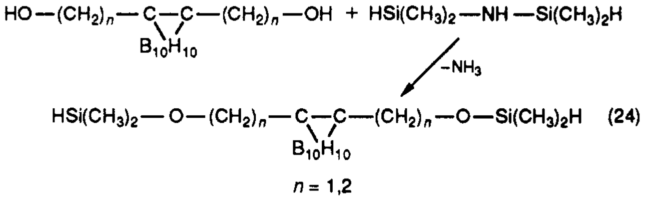
The interaction of carboranes with aromatic compounds at high temperatures (>200 °C) was shown to result in the formation of arylenecarboranes where the carborane cage is linked to an aryl group via a boron atom.[96] On the basis of this investigation, a new type of polymer was obtained.

The best known of the carborane polymers, the carborane–siloxane polymers, known under the trade name Dexsil, were obtained in the mid 1960s. Numerous investigations were reported during that time in the fields of carborane–siloxane polymers and organosilicon derivatives.

The reaction of lithiocarboranes with compounds containing the Si–Cl bond was usually used in the preparation of silicon derivatives of carboranes. But the Si–C(carborane) bond is easily ruptured by both nucleophilic and electrophilic reagents. Therefore, the synthesis of more stable compounds using the Si–C-H_2–$CB_{10}H_{10}C$– fragment was carried out (eq 23).[97]

$$CH_3CB_{10}H_{10}CLi + ClCH_2Si(CH_3)_2\text{-}O\text{-}Si(CH_3) \xrightarrow[\text{boiling}]{\text{ether/benzene}} CH_3CB_{10}H_{10}C\text{-}CH_2Si(CH_3)_2\text{-}O\text{-}Si(CH_3)_3 + (CH_3)_3SiOLi + CH_3CB_{10}H_{10}CSi(CH_3)_2CH_2Cl \quad (23)$$

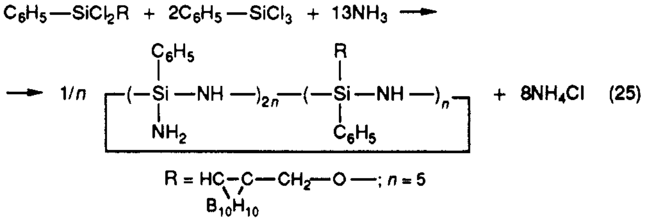
Bis(hydridosilyl) derivatives of *o*-carborane alcohols were obtained by the silylation of carborane alcohols (eq 24) and used in cross-linking reactions of polymer precursors of the polyphenylene type.[98]



$$HO{-}(CH_2)_n{-}\underset{B_{10}H_{10}}{C{-}C}{-}(CH_2)_n{-}OH + HSi(CH_3)_2{-}NH{-}Si(CH_3)_2H \xrightarrow{-NH_3} HSi(CH_3)_2{-}O{-}(CH_2)_n{-}\underset{B_{10}H_{10}}{C{-}C}{-}(CH_2)_n{-}O{-}Si(CH_3)_2H \quad (24)$$

$n = 1,2$

Cross-linking reactions of polyphenylene type polymers containing acetyl terminal groups with *o*-carboranylmethoxy-containing organosilazanes were also carried out. A carborane-containing oligoorganosilazane was prepared by the coammonolysis of (*o*-carboranylmethoxy)dichlorophenylsilane and trichlorophenylsilane (eq 25).[99]



$$C_6H_5{-}SiCl_2R + 2C_6H_5{-}SiCl_3 + 13NH_3 \rightarrow 1/n\left[(-\underset{NH_2}{\overset{C_6H_5}{Si}}-NH-)_{2n}-(-\underset{C_6H_5}{\overset{R}{Si}}-NH-)_n\right] + 8NH_4Cl \quad (25)$$

$R = H\underset{B_{10}H_{10}}{C{-}C}{-}CH_2{-}O{-}$; $n = 5$

The first attempts at introducing the carborane unit into molecules used for the purpose of boron neutron capture therapy (BNCT) were carried out soon after its discovery. However, it has been only during the past few years that its development has intensified. A full coverage of BNCT is beyond the scope of this review, and we confine ourselves to citing some recent papers in the field.

Using conventional carborane synthetic methods (via the acetylene–decaborane reaction or via lithiocarborane) carborane-containing steroids, nucleosides, porphyrins, and proteins for BNCT were prepared and studied.[100–105] The latest results in this field were presented at the VII International Symposium on Boron Chemistry (IMEBORON).[106]

B. Organophosphorus Derivatives of Carboranes

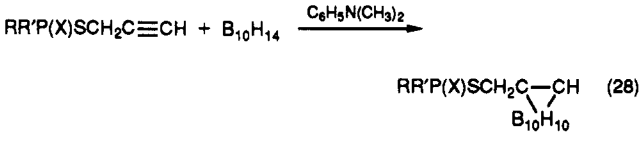
The first carborane organophosphorus derivatives were obtained by the reaction of lithiocarboranes with phosphorus compounds containing a P–Cl bond.[107–109] This is the principal synthesis of carborane trivalent phosphorus derivatives. Their oxidation as well as Arbuzov and Perkin type reactions result in the preparation of P(V) compounds (eqs 26 and 27).[110,111]

$$HCB_{10}H_{10}CP(OC_2H_5)_2 + C_2H_5I \rightarrow HCB_{10}H_{10}CP(O)(OC_2H_5)C_2H_5 \quad (26)$$

$$RCB_{10}H_{10}CP(OC_2H_5)_2 + CCl_3CHO \xrightarrow[-C_2H_5Cl]{} RCB_{10}H_{10}CP(OCHCCl_2)(O)OC_2H_5 \quad (27)$$

The anticholinesterase activity and other types of biological activity of the carborane derivatives of the esters of phosphorus acids proved interesting. The lability of the P–C(carborane) bond does not permit the achievement of a high anticholinesterase activity.[112]

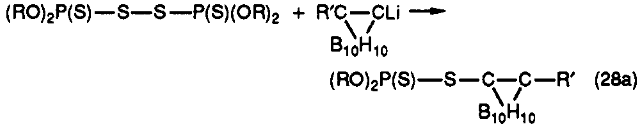
It was necessary, therefore, to make the pentavalent phosphorus acid esters with the carboranyl group in the ester moiety of the molecule.[113] These compounds were synthesized by the interaction of decaborane with acetylene-containing organophosphorus compounds (eq 28).



$$RR'P(X)SCH_2C{\equiv}CH + B_{10}H_{14} \xrightarrow{C_6H_5N(CH_3)_2} RR'P(X)SCH_2\underset{B_{10}H_{10}}{C{-}CH} \quad (28)$$

R = CH_3, C_6H_5, OC_2H_5; R′ = C_6H_5, OC_2H_5; X = O, S

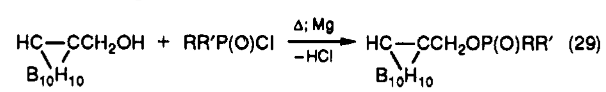
Organophosphorus esters with the carborane unit in the ester moiety were also obtained by the action of lithiocarborane on bis(dialkoxyphosphoryl) disulfide (eq 28a).[114]



$$(RO)_2P(S){-}S{-}S{-}P(S)(OR)_2 + R'\underset{B_{10}H_{10}}{C{-}CLi} \rightarrow (RO)_2P(S){-}S{-}\underset{B_{10}H_{10}}{C{-}C}{-}R' \quad (28a)$$

R = CH_3, C_2H_5; R′ = H-*o*, H-*m*, C_6H_5, CH_3

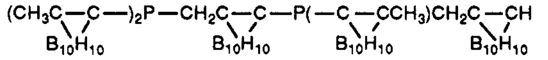
o-Carboranylmethanol was found to undergo catalytic phosphorylation when treated by $POCl_3$ or chlorophosphates in the presence of magnesium upon heating for 0.5–3 h (eq 29).[115]



$$H\underset{B_{10}H_{10}}{C{-}C}CH_2OH + RR'P(O)Cl \xrightarrow[-HCl]{\Delta;\,Mg} H\underset{B_{10}H_{10}}{C{-}C}CH_2OP(O)RR' \quad (29)$$

R = R′ = Cl; R = Cl, R′ = CF_3CH_2O; R = R′ = CF_3CH_2O; R = R′ = PhO

Interaction of bis(2-methyl-*o*-carboran-1-yl)chlorophosphine with (2-methyl-*o*-carboran-1-yl)lithium resulted in the unexpected formation of compounds containing two phosphorus atoms and five methylcarborane units; two of them being linked by phosphorus atoms via a methylene group.[116]



$$(CH_3\underset{B_{10}H_{10}}{C{-}C}{-})_2P{-}CH_2\underset{B_{10}H_{10}}{C{-}C}{-}P({-}\underset{B_{10}H_{10}}{C{-}C}CH_3)CH_2\underset{B_{10}H_{10}}{C{-}CH}$$

This compound was characterized by X-ray diffraction.

C. Organometallic Derivatives of Carboranes

Carborane compounds with M–C and M–B σ-bonds are known for most transition and non-transition metals, as well as some lanthanides. It is possible, therefore, to have some understanding about the influence of the carboranyl group on the properties and reactivity of organometallic compounds.

The first organometallic derivatives of carboranes were obtained from the reaction of lithiocarborane with compounds with metal–halogen bond (eq 30).[108,109] The

$$R_nMX + R'CB_{10}H_{10}CLi \rightarrow R_nM{-}CB_{10}H_{10}CR' + LiX \quad (30)$$

synthesis and properties of these compounds were summarized both in monographs[5,7] and a review.[117]

Carboranyl derivatives of non-transition metals have been shown to possess unusual properties compared to classical organometallic compounds. Thus, mercury *o*-carboranyl derivatives with a Hg–C(carborane) bond have a high thermal stability (up to 300 °C). Even after refluxing in acetone solution with electrophiles such as HCl, Br_2, and $HgCl_2$ they remain unchanged. The action of nucleophilic reagents, however, results in cleavage of the Hg–C(carborane) bond even at room temperature. Bis(carboranyl)thallium halides containing the Tl–C bond[118] exhibit similar behavior.

Bis(1-*o*-carboranyl) mercury was also obtained by the action of mercuric salts in alkali solution on *o*-carborane (eq 31).[119]

$$2\,o\text{-}RCB_{10}H_{10}CH + HgBr_4^{2-} + 2OH^- \xrightarrow{DMF} (o\text{-}RCB_{10}H_{10}C)_2Hg + 4Br^- + 2H_2O \quad (31)$$

The interaction of Al, Ga, In, and Tl trialkyls with carboranes in the presence of TMEDA, HMPA, or DME leads either to metalation of the carborane cage at a carbon atom or degradation of the carborane cage.[120]

Thus, the interaction of trimethylgallium with *o*- and 1-phenyl-*o*-carborane in benzene in the presence of TMEDA results in the formation of undecaborate(−1) containing gallium. According to ^{11}B NMR data, in this anion the Me_2Ga fragment occupies the place of the extra hydrogen over the open face of the carborane cluster.[121]

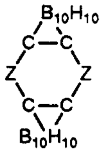
The metalation of decachloro-*o*-carborane, which has more acidic C–H bonds than the unsubstituted carborane, proceeds in the absence of TMEDA without degradation of the carborane cage (eq 32).[120]

$$HCB_{10}Cl_{10}CH + Me_3M \xrightarrow{L} HCB_{10}Cl_{10}CMMe_2{\cdot}L_n + CH_4 \quad (32)$$

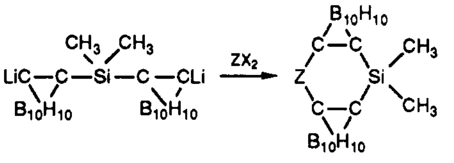
$$M = Al,\ L = HMPA,\ n = 3$$
$$M = In,\ L = DME,\ n = 1$$

The interaction of *o*-carborane with $(i\text{-}Bu)_2AlH$ gives a mixture of carborane derivatives with a C–Al bond as well as products of carborane cage degradation.[121]

Zakharkin and Shemyakin presented a series of papers in the 1970s on the synthesis of cyclic carborane containing compounds of the general formula:



The six-membered ring consists of four carbon atoms of two *o*-carborane cages and two groups of "Z" (where $Z = Si(CH_3)_2$, $Ge(CH_3)_2$, $Sn(CH_3)_2$, PC_6H_5, or $AsCH_3$). The synthesis of such cyclic carborane compounds was based on the following method (eq 33):[122]



(33)

$Z = Ge(CH_3)_2$, $Sn(CH_3)_2$, PC_6H_5, or $AsCH_3$

The introduction of one or two methylene groups into the ring was also achieved. The molecular structure determination of some of these compounds was possible.

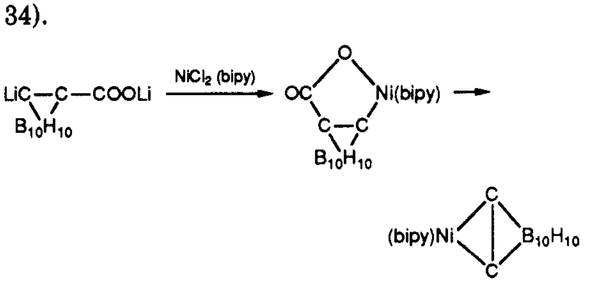
In addition, five-membered heterocycles containing two carbon atoms of the *o*-carborane unit, two methylene groups, and Ni, Pd, Pt, Ti, Zr, Si, Ge, or Sn atoms, as well as six-membered heterocycles containing four carbon atoms of two *o*-carborane units, a silicon atom, and Ni, Co, Pd, Cu, or S atoms, have been synthesized.[123,124] The structure of the latter has been determined.[125]

Transition metals were found capable of forming σ-bonds with the carbon atoms of the carborane cage. So far derivatives with M–C(carborane) bonds are known for the following transition metals: Cu, Au, Ti, Zr, Mn, Re, Fe, Co, Rh, Ir, Ni, Pd, and Pt.

Some transition metal carboranyl derivatives are unstable. Stabilization can be achieved by introducing metals into the carborane-containing ring (previously mentioned in this section) or by complex formation with electron-donating molecules such as bipyridyl. The synthesis and properties of these compounds were reviewed in 1982 by Bresadola.[7] Since 1982 there have been no extensive developments in this area.

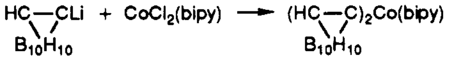
Bresadola and co-workers investigated the catalytic activity of carboranyl–iridium compounds.[126–130] The complex $Ir(\sigma\text{-}C_2B_{10}H_9)(CO)(PhCN)(PPh_3)$ was found to be an effective catalyst for the homogeneous hydrogenation of terminal olefins and acetylenes at room temperature and normal pressure. This complex adds hydrogen to give a *cis*-dihydroirridium adduct which appears to be the true catalyst.

Ol'dekop et al.[131] developed a decarboxylation procedure for the preparation of complexes with the Ni–C(carborane) σ-bond stabilized by a bipyridyl ligand (eq 34).



(34)

Compounds with a Co–C(carborane) σ-bond were obtained by the interaction of lithiocarboranes with bipyridyl complexes of $CoCl_2$ (eqs 35 and 36).[132]



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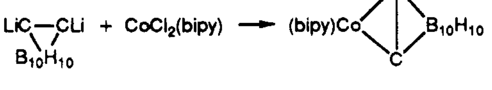
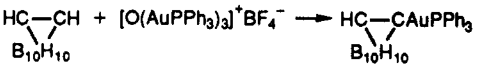


(36)

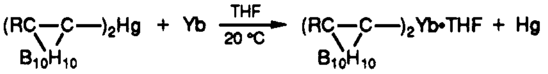
A new synthesis of the organogold derivative of carborane using the direct auration of *o*-carborane with $[O(AuPPh_3)_3]^+BF_4^-$ was achieved in THF in the presence of catalytic amounts of NaH (eq 37).[133] The



$$HC(B_{10}H_{10})CH + [O(AuPPh_3)_3]^+BF_4^- \rightarrow HC(B_{10}H_{10})CAuPPh_3 \quad (37)$$

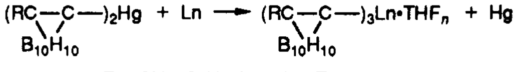
substitution of a hydrogen atom at just one carbon atom of *o*-carborane takes place. X-ray diffraction studies of the molecule were carried out revealing an Au–P bond 2.271 (2) Å long and Au–C bond equal to 2.039 (8) Å.

Carboranyl derivatives of lanthanides were obtained by two routes. The first one involved interaction of *C*-mercurocarboranes with metallic lanthanides to give divalent Yb and trivalent La and Tm compounds (eqs 38 and 39).[134]



$$(RC(B_{10}H_{10})C—)_2Hg + Yb \xrightarrow[20\ °C]{THF} (RC(B_{10}H_{10})C—)_2Yb•THF + Hg \quad (38)$$

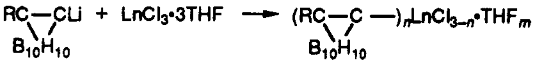
R = CH_3, C_6H_5



$$(RC(B_{10}H_{10})C—)_2Hg + Ln \rightarrow (RC(B_{10}H_{10})C—)_3Ln•THF_n + Hg \quad (39)$$

R = CH_3, C_6H_5; Ln = La, Tm; *n* = 1–3

The second route involves the reaction of lithiocarborane with lanthanide chlorides (eq 40).[135,136]



$$RC(B_{10}H_{10})CLi + LnCl_3•3THF \rightarrow (RC(B_{10}H_{10})C—)_nLnCl_{3-n}•THF_m \quad (40)$$

Ln = La, Tm, Yb; *n* = 1–3; *m* = 1–5

Mono-, di-, or tri-substituted derivatives or ate-complexes are formed depending on the reaction conditions.

IV. Boron-Substituted Carboranes

The chemistry of boron-substituted carboranes is not as developed as that of the carbon analogues due to the difficulty of introducing functional groups at the boron atom of the carborane cage. B-Halogenated carboranes, the first boron-substituted species, appear to be inert to substitution reactions. However, it is of interest to compare the properties of functional groups on the hexacoordinated carborane boron atom with those of organoboron compounds.

The chemistry of boron-substituted carboranes developed rapidly after the discovery of the reaction that would introduce an amino group at the boron atom of the carborane nucleus. *B*-Carboranyl compounds can be viewed as analogues of organic compounds because the *B*-carboranyl group acts as either an alkyl or aryl group in most transformations.[8] We will, therefore, consider the properties of *B*-carboranyl compounds compared with the corresponding organic compounds such as hydrocarbons, acids, hydroxy, and amino compounds, their sulfur and halogen derivatives, as well as their organometallic analogues.

The latest review[8] devoted to this field was published in 1988, therefore, only the main advances before 1987 will be cited together with a summary for the last four years.

A. Boron-Carboranyl Analogues of Organic Compounds

The first compound with a C–B(carborane) bond was obtained by the reaction of acetylene with a mixture of 1- and 2-ethyldecaboranes in acetonitrile to give a mixture of 8- and 9-ethyl-*o*-carboranes (eq 41).[1]

$$\text{1- and 2-}C_2H_5B_{10}H_{13} + HC{\equiv}CH \xrightarrow[-H_2]{CH_3CN} \text{8- and 9-}C_2H_5B_{10}H_9C_2H_2 \quad (41)$$

The second route to alkylcarboranes involves the electrophilic alkylation of carboranes with alkyl halides[19] or vinyltrichlorosilane[137] in the presence of $AlCl_3$ (eqs 42 and 43).

$$C_2H_2B_{10}H_{10} + RX \xrightarrow{AlCl_3} C_2H_2B_{10}H_{10-n}R_n \quad (42)$$

$$C_2H_2B_{10}H_{10} + CH_2{=}CHSiCl_3 \xrightarrow{AlCl_3} C_2H_2B_{10}H_{10-n}(CH_2CH_2SiCl_3)_n \quad (43)$$

$$n = 1\text{–}3$$

The mechanism of this alkylation is similar to that of the Friedel–Crafts' reaction.[137] Recently, 1-isopropyl-*o*-carborane was alkylated with 4-chlorobutyric acid (eq 44).[138] *o*(*m*)-Carboranes were not alkylated

$$i\text{-}C_3H_7\text{-}o\text{-}C_2HB_{10}H_{10} + Cl(CH_2)_3COOH \xrightarrow[85\text{–}90\ °C]{AlCl_3/CS_2} i\text{-}C_3H_7\text{-}o\text{-}C_2HB_{10}H_9(CH_2)_3COOH\text{-9 and -12} \quad (44)$$

under these conditions.

Electrophilic alkylation of *o*(*m*)-carborane with perfluorotoluene in the presence of SbF_5 occurs accordingly to eq 45.[139]

$$C_2H_2B_{10}H_{10} + C_6F_5CF_3 \xrightarrow{SO_2/SbF_5} [C_6F_5CH_2F] + [C_2H_2B_{10}H_9F] \rightarrow C_2H_2B_{10}(CH_2C_6F_5)H_8F + C_2H_2B_{10}H_8F_2 \quad (45)$$

B-Arylcarboranes as well as some oligomeric products with B–C bonds were formed by the reaction of carborane with free B-centered carboranyl radicals[140] generated by thermolysis of *tert*-butyl peroxide.

High-temperature condensation of carborane with 1,2-dichloroethylene was shown to result in the formation of *B*-(β-chlorovinyl)carborane and oligomeric products (eq 46).[141]

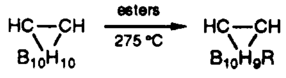
$$C_2H_2B_{10}H_{10} + CHCl{=}CHCl \rightarrow C_2H_2B_{10}H_9{—}CH{=}CHCl + Cl{—}[CH{=}CH{—}CH{=}CH{—}C_2B_{10}H_8{—}]_x{—}H \quad (46)$$

Irradiation of ethyl diazoacetate in a C_6F_6 solution of *o*-carborane leads to four products containing a C–B(carborane) bond (eq 47).[142a]

$$C_2H_2B_{10}H_{10} + N_2CHCOOEt \rightarrow C_2H_2B_{10}H_9CH_2COOEt \quad (47)$$

Carbenes (CH_2, CCl_2, CF_2) were reported to attack *o*-carborane at the boron atoms in the positions 4, 9, 3, and 8,[142b] but this conclusion appears to be incorrect.

Simple pyrolysis of *o*-carborane in the presence of dialkyl acetylenedicarboxylates and trialkyl methanetricarboxylates in sealed tubes at 200–275 °C produces 9-alkyl-*o*-carboranes in reasonable yield (eq 47a).[143a]



$$HC(B_{10}H_{10})CH \xrightarrow[275\ °C]{esters} HC(B_{10}H_9R)CH \quad (47a)$$

esters = ROOC—C≡C—COOR and $(ROOC)_3CH$;
R = CH_3, C_2H_5, C_3H_7, *s*-C_4H_9

o-Carborane was suggested to be acting as a mild catalyst in this Friedel–Crafts-like alkylation reaction.

o-Carborane reacts with the cluster $[(\mu\text{—H})_3(CO)_9Os_3(\mu_3\text{—C})]_3(O_3B_3O_3)$ in the presence of BF_3 to form the boron-substituted complex with B(9)–C bond which is stable on air (eq 47b).[143b] *m*-Carborane does not react under the same conditions.

$$1,2\text{-}C_2B_{10}H_{12} + [(\mu\text{—H})_3(CO)_9Os_3(\mu_3\text{—C})]_3(O_3B_3O_3) \xrightarrow{BF_3} (\mu\text{—H})_3(CO)_9Os_3(\mu_3\text{—C})(C_2B_{10}H_{11}) \quad (47b)$$

An organic group was introduced at the boron atom of the carborane cage through reaction of iodocarboranes with organomagnesium compounds in the presence of Ni and Pd complexes (eq 48).[144,145]

$$C_2H_2B_{10}H_9I + RMgX \rightarrow C_2H_2B_{10}H_9R \quad (48)$$

The first carborane functional derivative with a B–C bond, 3-carboxy-*o*-carborane, was synthesized in 1968 by the oxidation of 3-vinyl-*o*-carborane with chromic anhydride (eq 49).[146] 3-Carboxy-*o*-carborane has properties typical of common organic acids.

$$C_2H_2B_{10}H_9CH{=}CH_2 \xrightarrow{CrO_3} C_2H_2B_{10}H_9COOH \quad (49)$$

Contrary to the *C*-carboranyl derivatives, *B*-carboranylethylenes readily add HCl in the presence of $AlCl_3$. In this respect *B*-carboranyl compounds resemble organic compounds to a greater extent than their *C*-carboranyl analogues.

The first *B*-aminocarborane was obtained by Zakharkin and Kalinin in 1967. They showed that the dicarbadodecaborate(14) anion, formed by the addition of two electrons to the carborane nucleus, reacts with liquid ammonia at low temperature to give a B-aminated dianion which was then converted to 3-amino-*o*-carborane by oxidation with $KMnO_4$ or $CuCl_2$ (eq 50).[147] The 3-amino-*o*-carboranes show reactions typical of aliphatic and aromatic primary amines. They are readily arylated and acylated with formic acid or acetic anhydride.

$$C_2H_2B_{10}H_{10} \xrightarrow[NH_3\,(liq)]{2Na} (C_2H_2B_{10}H_{10})^{2-} \xrightarrow[-H_2]{NH_3\,(liq)} (C_2H_2B_{10}H_9NH_2)^{2-} \xrightarrow[NH_3]{KMnO_4\text{ or }CuCl_2} C_2H_2B_{10}H_9NH_2 \quad (50)$$

Like aliphatic and aromatic formamides, formyl derivatives of *o*-carboranes react with phosphorus oxychloride in pyridine to give *o*-carboran-3-ylisonitriles (eq 51).[148] The latter are used as ligands in transition metal complexes (Mo, W, Mn, Re, Fe, Ru, Rh, Ni, Pd, Pt).[149]

$$C_2H_2B_{10}H_9NHCHO \xrightarrow[C_5H_5N]{POCl_3} C_2H_2B_{10}H_9NC \quad (51)$$

B-Hydroxycarboranes were obtained by the oxidation of carboranes with HNO_3, $KMnO_4$, or CrO_3. Unlike borinic acids, *B*-hydroxy-*o*-carboranes are similar in their properties to the organic hydroxy derivatives. They react readily with boric acid, $(CH_3)_3SiCl$ and PCl_3 to form the corresponding esters.[150a]

Plešek and Heřmánek[150b] obtained the first carborane with a B–S bond by the action of elemental sulfur on carborane in the presence of $AlCl_3$ (eq 52).

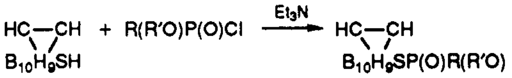
$$C_2H_2B_{10}H_{10} + S_8 \xrightarrow{AlCl_3} C_2H_2B_{10}H_9SH \quad (52)$$

Another method for the introduction of sulfur to the carborane icosahedron consists of the action of sulfur chlorides in the presence of $AlCl_3$. The same routes were used for the preparation of selenium and tellurium derivatives (eq 53).[150a] The latter were used for the preparation of *O,O*-dialkyl *Se*-(*o*-carboran-9-yl) selenophosphates (eq 54).[151a] Several types of 9-thio- and 9-selenocarborane derivatives of the phosphorus esters were obtained in a search for biologically active compounds.

$$C_2H_2B_{10}H_{10} + Se_2Cl_2 \xrightarrow{AlCl_3} (9\text{-}C_2H_2B_{10}H_9)_2Se_2 \quad (53)$$

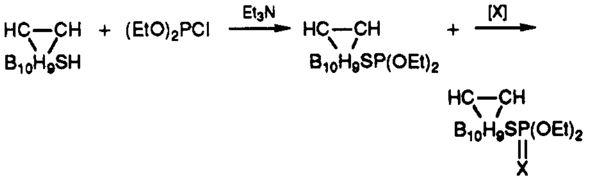
$$(9\text{-}C_2H_2B_{10}H_9)_2Se_2 + (RO)_3P \rightarrow (RO)_2P(O)SeB_{10}H_9C_2H_2 \quad (54)$$

The reaction of 9-mercaptocarboranes with the chlorides of phosphorus acids was carried out (eq 54a).[151b]



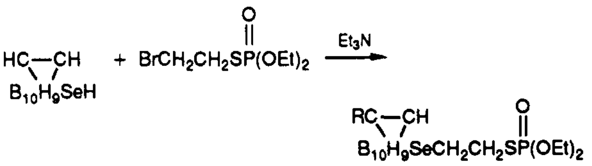
$$HC\text{—}CH(B_{10}H_9SH) + R(R'O)P(O)Cl \xrightarrow{Et_3N} HC\text{—}CH(B_{10}H_9SP(O)R(R'O)) \quad (54a)$$

O,O-Diethyl *S*-(*o*-carboran-9-yl) thiophosphite was prepared from diethyl chlorophosphite and *o*-carborane-9-thiol in ether in the presence of Et_3N at −30 °C. It reacts with oxygen, sulfur, and selenium to give the corresponding derivatives of pentavalent phosphorus (eq 54b).[151c] The interaction of *o*(*m*)-carborane-9-selenol[152a] with *S*-*β*-bromoethylthiophosphonate in the presence of Et_3N leads to *O,O*-diethyl *S*-*β*-(carboran-9-ylseleno)ethyl thiophosphates (eq 55).[152b] These compounds hold interest as potentially physiologically active compounds.



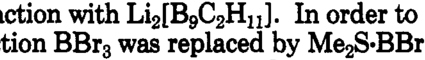
$$HC\text{—}CH(B_{10}H_9SH) + (EtO)_2PCl \xrightarrow{Et_3N} HC\text{—}CH(B_{10}H_9SP(OEt)_2) + \xrightarrow{[X]} HC\text{—}CH(B_{10}H_9SP({=}X)(OEt)_2) \quad (54b)$$

X = O, S, Se



$$HC\text{—}CH(B_{10}H_9SeH) + BrCH_2CH_2SP({=}O)(OEt)_2 \xrightarrow{Et_3N} RC\text{—}CH(B_{10}H_9SeCH_2CH_2SP({=}O)(OEt)_2) \quad (55)$$

Li and Jones proposed a modification of the synthesis of 3-bromo-*o*-carborane.[153a] They found that in the method of Roscoe, Kongpricha, and Papetti[153b] complications are introduced by the necessity of separating an unreported side product identified as 3-ethoxy-*o*-carborane (eq 55a). The source of this side reaction is the formation of $EtOBBr_2$ from Et_2O and BBr_3 and its interaction with $Li_2[B_9C_2H_{11}]$. In order to avoid this side reaction BBr_3 was replaced by $Me_2S{\cdot}BBr_3$ complex which serves to convert $Li_2[B_9C_2H_{11}]$ into 3-bromo-*o*-carborane without complicating side products (eq 55b).



$$Li_2[B_9C_2H_{11}] \xrightarrow[Et_2O]{BBr_3} HC\text{—}CH(3\text{–}BrB_{10}H_9) + HC\text{—}CH(3\text{–}EtOB_{10}H_9) \quad (55a)$$

$$Li_2[B_9C_2H_{11}] + Me_2S{\cdot}BBr_3 \longrightarrow HC\text{—}CH(3\text{–}BrB_{10}H_9) \quad (55b)$$

(yield 65.4%)

Andrews, Zayas, and Jones[153c] found that the synthesis of 9-iodo-*o*-carborane by treatment of *o*-carborane with I_2 and $AlCl_3$ in CCl_4 described previously[153d] leads to a mixture of halogenated carboranes containing only 28% of 9-iodo-*o*-carborane. The use of CH_2Cl_2 instead of CCl_4 was investigated, and this procedure gave 9-iodo-*o*-carborane in 93% yield and high purity. After this publication Zakharkin et al.[153e] studied in detail the electrophilic monohalogenation of *o*- and *m*-carboranes by iodine and bromine in the presence of $AlCl_3$ in polychloromethanes. The yield of 9-iodo-*o*-carborane was shown to depend on the solvent, on the quality and quantity of $AlCl_3$, and on the time of the reaction.

Selective fluorination of *o*- and *m*-carboranes with SbF_5 resulting in the preparation of 9-fluoro-, 9,12-difluoro-, 8,9,12-trifluoro-, and 8,9,10,12-tetrafluoro-*o*-carboranes and of 9-fluoro- and 9,10-difluoro-*m*-carboranes[154] has been reported.

The use of these compounds in synthesis was, however, limited due to the low reactivity of the halogen linked to the boron. When carboranes containing the boron–onium halogen bond were prepared (eq 56)[155] their potential utility improved. The high reactivity

$$9\text{-}o(m)\text{-}C_2H_2B_{10}H_9I \xrightarrow[CCl_4]{Cl_2} 9\text{-}o(m)\text{-}C_2H_2B_{10}H_9ICl_2 \xrightarrow[CH_3CN]{CF_3COOAg} 9\text{-}o(m)\text{-}C_2H_2B_{10}H_9I(OCOCF_3)_2 \xrightarrow[BF_4^-]{1.\ PhH;\ H^+} 9\text{-}o(m)\text{-}C_2H_2B_{10}H_9I^+PhBF_4^- \quad (56)$$

of such onium compounds toward nucleophilic reagents makes them useful in the synthesis of otherwise poorly accessible boron-substituted carboranes. Their synthesis and reactions have been reviewed.[8b]

One new synthetic use of carboranylhalonium salts is in the synthesis of the previously unknown bis(9-*m*-carboranyl)ether by alkaline hydrolysis of phenyl(9-*m*-carboranyl)bromonium tetrafluoroborate.[156] X-ray structural analysis as well as the vibrational spectrum of this ether have been published.[157]

Recently the influence of the nature of the onium halogen atom on the reactivity and the reaction pathways of phenyl(*m*-carboran-9-yl)halonium compounds have been discussed. Authors suggested three pathways, i.e. nucleophilic substitution, one-electron reduction, and degradation of the carborane icosahedron.[158]

B. Carboranes with Boron–Non-Transition Element Bonds

Carboranes with boron–non-transition metal bonds became widely available when the direct mercuration and thallation of carboranes were discovered (eqs 57 and 58).[21,22]

$$C_2R_2B_{10}H_{10} + (CF_3CO_2)_2Hg \rightarrow CF_3CO_2HgB_{10}H_9C_2R_2 \quad (57)$$

$$C_2R_2B_{10}H_{10} + (CF_3CO_2)_3Tl \rightarrow (CF_3CO_2)_2TlB_{10}H_9C_2R_2 \quad (58)$$

The reaction of boron-mercurated carboranes with the salts of non-transition metals allowed the preparation of the carborane derivatives in which the boron atom is linked with an atom of an element of main groups III–V (eq 59).

$$(C_2R_2B_{10}H_9)_2Hg + EX_n \rightarrow C_2R_2B_{10}H_9X_{n-1} \quad (59)$$

$$E = Ga, In, Tl, Sn, P, As, Sb$$

Organometallic compounds and boron–carboranyl derivatives of non-transition metals react similarly with a wide variety of reagents. Comprehensive reviews for these covering the years up until 1987 are available.[8,159]

Recent interest in this field concerns the formation and reactivity of boron-centered and metal-centered radicals (eqs 60 and 61).[160,161]

$$(C_2H_2B_{10}H_9)_2Hg \xrightarrow{UV} C_2H_2B_{10}H_9^\bullet + {}^\bullet HgC_2H_2B_{10}H_9 \quad (60)$$

$$C_2H_2B_{10}H_9MX_2 \xrightarrow{UV} C_2H_2B_{10}H_9^\bullet + {}^\bullet MX_2 \quad (61)$$

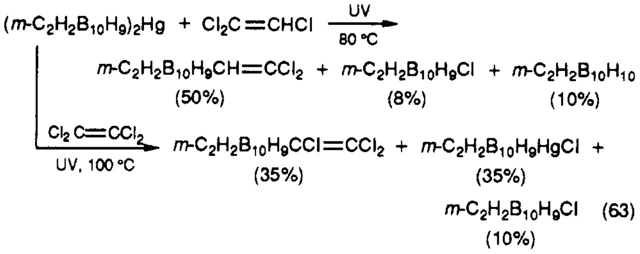
$$M = Ga, In, Tl$$

The photodecomposition of bis(*m*-carboran-9-yl)mercury and (*m*-carboran-9-yl)thallium bis(trifluoroacetate) in arene medium gives aryl-*m*-carborane (>50% yield) with 90% substitution in the 9 position of the carborane nucleus (eq 62).[162]

$$(m\text{-}C_2H_2B_{10}H_9)_2Hg \xrightarrow[ArH]{UV} m\text{-}C_2H_2B_{10}H_9Ar + (m\text{-}C_2H_2B_{10}H_9)_2 + m\text{-}C_2H_2B_{10}H_{10} \quad (62)$$

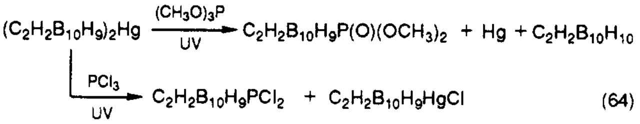
$$Ar = C_6H_5, C_6F_5, 1,4\text{-}Me_2C_6H_3$$

The reactions of bis(*m*-carboran-9-yl)mercury with trichloroethylene and tetrachloroethylene are believed to proceed via the formation of B-centered and Hg-centered radicals (eq 63).[163]



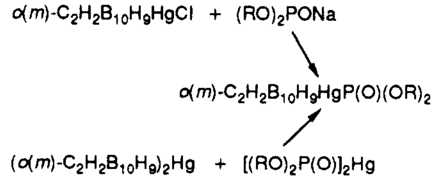
(63)

Photolysis of bis(carboranyl)mercury in trimethyl phosphite[164] or PCl_3[165a] results in the formation of the corresponding carboranyl compounds with a B–P bond (eq 64).



(64)

Carboranylmercuric compounds with boron–mercury–phosphorus bonds were synthesized by two methods (eq 64a).[165b] Electrochemical properties of these compounds were studied on a platinum electrode in acetonitrile.[165c] The mechanism of the electrochemical redox process of the *o*-carborane derivatives was shown to differ from that of the corresponding *m*-carborane derivatives. In the first case the rupture of the boron–mercury bond occurred on a platinum cathode, in the second case the rupture of the phosphorus–mercury bond took place.



(64a)

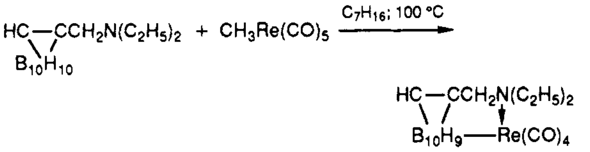
The decomposition of the P–Hg bond by UV light in $C_2H_2B_{10}H_9HgP(O)(OR)_2$ was shown by spin trapping in an ESR experiment.[165d]

C. Carboranes with Boron–Transition Metal Bonds

Carboranes with boron–transition metal bonds were obtained for the first time only in 1970 by Zakharkin and Orlova[166] (see eq 65).

$$C_2H_2B_{10}H_9COCl + NaFe(CO)_2C_5H_5\text{-}\pi \xrightarrow[\text{THF}]{-70\ °C} C_2H_2B_{10}H_9COFe(CO)_2C_5H_5\text{-}\pi \xrightarrow[\text{-CO}]{170\ °C} C_2H_2B_{10}H_9Fe(CO)_2C_5H_5\text{-}\pi \quad (65)$$

Up to 1981 there were few developments until Kalinin, Usatov, and Zakharkin discovered the intramolecular oxidative addition of carborane B–H bonds to transition metal atoms.[167] An example of such carborane cyclometalation reactions is represented in eq 66.



(66)

The results obtained in this field are summarized in the review found in refs 8b and 168.

V. Conclusion

An interesting peculiarity of carboranes is their ability to take part in electrophilic substitution reactions typical of aromatic compounds. The course of these reactions and the influence of the substituent on the electron charge distribution are similar in many respects to the corresponding organic reactions. It seems suitable, therefore, to call such carborane three-dimensional systems "superaromatic" or "pseudoaromatic".

Rapid development in the field of B-substituted carboranes reveals their peculiar resemblance to the chemical properties of organic alkyl and aryl compounds. B-Metalated carborane behavior is in agreement with this point of view. In addition, compounds with a B–M bond undergo reactions typical of organometallic compounds.

Although carborane chemistry has been the source of much exciting chemistry there are still many important aspects awaiting future investigation.

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VI. References

(1) Heying, T. L.; Ager, J. W., Jr.; Clark, S. L.; Mangold, D. J.; Goldstein, H. L.; Hillman, M.; Polak, R. J.; Szymanski, J. W. *Inorg. Chem.* **1963**, *2*, 1089.
(2) Fein, M. M.; Bobinski, J.; Mayes, N.; Schwartz, N.; Cohen, M. S. *Inorg. Chem.* **1963**, *2*, 1111.
(3) Zakharkin, L. I.; Stanko, V. I.; Brattsev, V. A.; Chapovsky, Yu. A.; Struchkov, Yu. T. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1963**, 2069.
(4) Zakharkin, L. I.; Stanko, V. I.; Brattsev, V. A.; Chapovsky, Yu. A.; Okhlobystin, O. Yu. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1963**, 2238.
(5) (a) Grimes, R. N. *Carboranes*; Academic Press: New York, 1970. (b) *Gmelin Handbook of Inorganic Chemistry*, 8th ed.; Springer Verlag: Berlin, 1988; 3rd Supplement, Vol. 4.
(6) (a) Olah, G. A.; Surya Prakash, G. K.; Williams, R. E.; Field, L. D.; Wade, K. *Hypercarbon Chemistry*; Wiley: New York, 1987. (b) Olah, G. A.; Wade, K.; Williams, R. E. *Electron Deficient Boron and Carbon Clusters*; Wiley: New York, 1991. (c) Wales, D. J.; Stone, A. J. *Inorg. Chem.* **1987**, *26*, 3845. (d) Wales, D. J.; Mingos, D. M. P. *Inorg. Chem.* **1989**, *28*, 2748. (e) Wales, D. J.; Mingos, D. M. P.; Zhenyang, L. *Inorg. Chem.* **1989**, *28*, 2754. (f) Dewar, M. J. S.; McKee, M. L. *Inorg. Chem.* **1980**, *19*, 2662. (g) Ott, J. J.; Gimarc, B. M. *J. Am. Chem. Soc.* **1986**, *108*, 4303; *J. Comput. Chem.* **1986**, *7*, 673.
(7) Bresadola, S. In *Metal Interactions with Boron Clusters*; Grimes, R. N., Ed.; Plenum Press: New York, 1982; p 173.
(8) (a) Kalinin, V. N. *Usp. Khim.* (*Russ. Chem. Rev.*) **1980**, *49*, 2188. (b) Grushin, V. V.; Bregadze, V. I.; Kalinin, V. N. *J. Organomet. Chem. Lib.* 20, **1988**, *20*, 1.
(9) Potenza, J. A.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1964**, *86*, 1874.
(10) Potenza, J. A.; Lipscomb, W. N. *Inorg. Chem.* **1964**, *3*, 1673.
(11) Voet, D.; Lipscomb, W. N. *Inorg. Chem.* **1964**, *3*, 1679.
(12) Stanko, V. I.; Struchkov, Yu. T. *Zh. Obshch. Khim.* **1965**, *35*, 930.
(13) Potenza, J. A.; Lipscomb, W. N. *Inorg. Chem.* **1966**, *5*, 1471.
(14) Potenza, J. A.; Lipscomb, W. N. *Inorg. Chem.* **1966**, *5*, 1478.
(15) Eaton, G. R.; Lipscomb, W. N. *NMR Studies of Boron Hydrides and Related Compounds*; W. A. Benjamin, Inc.: New York, 1969.
(16) Mastryukov, V. S.; Dorofeeva, O. V.; Vilkov, L. V. *Uspekhi Khimii* **1980**, *49*, 2377.
(17) Mastryukov, V. S. In *Stereochemical Applications of Gas-Phase Electron Diffraction*; Hargittai, I., Hargittai, M., Eds.; VCH: New York, 1988; Part B.
(18) Bartell, L. S.; Carroll, B. L. *J. Chem. Phys.* **1965**, *42*, 3076.
(19) Zakharkin, L. I.; Pisareva, I. V.; Bikkineev, R. Kh. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1977**, 641.
(20) Plešek, J.; Heřmánek, S. *Chem. Ind.* **1977**, 360.
(21) Bregadze, V. I.; Kampel, V. Ts.; Godovikov, N. N. *J. Organomet. Chem.* **1976**, *112*, 249.
(22) Bregadze, V. I.; Usiatinsky, A. Ya.; Godovikov, N. N. *J. Organomet. Chem.* **1985**, *292*, 75.
(23) Potenza, J. A.; Lipscomb, W. N.; Vickers, G. D.; Schroeder, H. A. *J. Am. Chem. Soc.* **1966**, *88*, 628.
(24) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 2179.
(25) Koetzle, T. F.; Lipscomb, W. N. *Inorg. Chem.* **1970**, *9*, 2743.
(26) Newton, M. D.; Boer, F. P.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1966**, *88*, 2353.
(27) Beall, H.; Lipscomb, W. N. *Inorg. Chem.* **1967**, *6*, 874.
(28) Dixon, D. A.; Kleier, D. A.; Helgren, T. A.; Hall, J. H.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1977**, *99*, 6226.
(29) Zakharkin, L. I.; Kalinin, V. N.; Kobel'kova, N. I. *Synth. React. Inorg. Met.-Org. Chem.* **1976**, *6*, 91.
(30) Stanko, V. I.; Brattsev, V. A.; Klimova, A. I. *Zh. Obshch. Khim.* **1974**, *44*, 2482.
(31) Plešek, J.; Heřmánek, S. *Collect. Czech. Chem. Commun.* **1979**, *44*, 24.
(32) Zakharkin, L. I.; Kalinin, V. N.; Gedymin, V. V. *J. Organomet. Chem.* **1969**, *16*, 371.
(33) Zakharkin, L. I.; Kalinin, V. N.; Gedymin, V. V. *Zh. Obshch. Khim.* **1973**, *43*, 1974.
(34) Zakharkin, L. I.; Ol'shevskaya, V. A. *Zh. Obshch. Khim.* **1987**, *57*, 368.
(35) Vondrak, T.; Plešek, J.; Heřmánek, S.; Stibr, B. *Polyhedron* **1989**, *8*, 805.
(36) Hawthorne, M. F.; Berry, T. E.; Wegner, P. A. *J. Am. Chem. Soc.* **1965**, *87*, 4746.
(37) Zakharkin, L. I.; Kalinin, V. N.; Snyakin, A. P.; Kvasov, B. A. *J. Organomet. Chem.* **1969**, *18*, 19.
(38) Zakharkin, L. I.; Kalinin, V. N.; Shepilov, I. P. *Dokl. Akad. Nauk SSSR*, **1967**, *174*, 606.
(39) Zakharkin, L. I.; Kalinin, V. N.; Rys, E. G. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1974**, 2632.
(40) Zakharkin, L. I.; Kalinin, V. N. *Zh. Obshch. Khim.* **1973**, *43*, 853.
(41) Adler, R. G.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1970**, *92*, 6174.
(42) Zakharkin, L. I.; Kovredov, A. I.; Ol'shevskaya, V. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1981**, 2159.
(43) Kalinin, V. N.; Kobel'kova, N. I.; Astakhin, A. V.; Zakharkin, L. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1977**, 2376.
(44) Kalinin, V. N.; Kobel'kova, N. I.; Astakhin, A. V.; Gusev, A. I.; Zakharkin, L. I. *J. Organomet. Chem.* **1978**, *149*, 9.
(45) Kalinin, V. N.; Kobel'kova, N. I.; Zakharkin, L. I. *Zh. Obshch. Khim.* **1978**, *48*, 938.
(46) Kalinin, V. N.; Kobel'kova, N. I.; Zakharkin, L. I. *J. Organomet. Chem.* **1979**, *172*, 391.
(47) Zakharkin, L. I.; Kalinin, V. N.; Gedymin, V. V. *Tetrahedron* **1971**, *23*, 1317.
(48) Kalinin, V. N.; Kobel'kova, N. I.; Zakharkin, L. I. *Zh. Obshch. Khim.* **1980**, *50*, 919.
(49) Wu, S.; Jones, M., Jr. *Inorg. Chem.* **1988**, *27*, 2005.

(50) (a) Muetterties, E. L.; Knoth, W. H. *Polyhedral Boranes*; Marcel Dekker: New York, 1968. (b) Muetterties, E. L., Ed. *Boron Hydride Chemistry*; Academic Press: New York, 1975.
(51) Williams, R. E. *Progress in Boron Chemistry*; Pergamon Press: Oxford, 1970; Vol. 2.
(52) Stanko, V. I.; Brattsev, V. A.; Knyasev, S. P. *Usp. Khim.* **1975**, *44*, 1377.
(53) Stanko, V. I.; Brattsev, V. A.; Knyasev, S. P. *Usp. Khim.* **1979**, *48*, 241.
(54) Wiesboeck, R. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1964**, *86*, 1642.
(55) Hawthorne, M. F.; Young, D. C.; Wegner, P. A. *J. Am. Chem. Soc.* **1965**, *87*, 1818.
(56) Zakharkin, L. I.; Podvisotskaya, L. S. *Zh. Obshch. Khim.* **1967**, *37*, 506.
(57) Zakharkin, L. I.; Kalinin, V. N.; Podvisotskaya, L. S. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1967**, 2310.
(58) Stanko, V. I.; Goltyapin, Yu. V.; Brattsev, V. A. *Zh. Obshch. Khim.* **1969**, *39*, 1175.
(59) Zakharkin, L. I.; Ol'shevskaya, V. A.; Antonovich, V. A.; Lebedev, A. V.; Bukhtiarov, A. V. *Metalloorg. Khim.* **1990**, *3*, 20 [English translation in *Organomet. Chem. USSR* **1990**, *3*, 8].
(60) Zakharkin, L. I.; Zhigareva, G. G.; Polyakov, A. V.; Yanovskii, A. I.; Struchkov, Yu. T. *Izv. Akad. SSSR, Ser. Khim.* **1987**, 872.
(61) Getman, T. D.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1990**, *112*, 4593.
(62) Lebedev, V. N.; Galakhov, M. V.; Bakhmutov, V. I.; Zakharkin, L. I. *Metalloorg. Khim.* **1989**, *2*, 940.
(63) Barker, G. K.; Garcia, V. P.; Green, M.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1983**, 137.
(64) Erdman, A. A.; Baranova, T. V.; Zubreichuk, Z. P.; Mayer, N. A.; Ol'dekop, Yu. A. *Metalloorg. Khim.* **1990**, *3*, 199.
(65) Wu, S.; Jones, M., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 5373.
(66) Gimarc, B. M.; Warren, D. S.; Ott, J. J.; Brown, C. *Inorg. Chem.* **1991**, *30*, 1598.
(67) Edvenson, G. M.; Gaines, D. F. *Inorg. Chem.* **1990**, *29*, 1210.
(68) (a) Wu, S.; Jones, M., Jr. *Inorg. Chem.* **1986**, *25*, 4802. (b) Wu, S.; Van Engen, D.; Jones, M., Jr. *Acta Crystallogr.* **1990**, *C46*, 656.
(69) (a) Gingrich, H. L.; Ghosh, T.; Hyang, Q.; Jones, M., Jr. *J. Am. Chem. Soc.* **1990**, *112*, 4082. (b) Ghosh, T.; Gingrich, H. L.; Kam, C. K.; Mobraaten, E. C.; Jones, M., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 1313.
(70) Huang, Q.; Gingrich, H.; Jones, M., Jr. *Inorg. Chem.* **1991**, *30*, 3254.
(71) Matteson, D. S. *J. Organomet. Chem.* **1981**, *207*, 13.
(72) Kabachii, Yu. A.; Valetskii, P. M.; Vinogradova, S. V.; Korshak, V. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1985**, 1932.
(73) Zakharkin, L. I.; Ol'shevskaya, V. A.; Kobak, V. V.; Boiko, N. B. *Metalloorg. Khim.* **1988**, *1*, 364.
(74) Zakharkin, L. I.; Kovredov, A. I.; Shaugumbekova, Zh. S.; Petrovskii, P. V. *Metalloorg. Khim.* **1989**, *2*, 690.
(75) Zakharkin, L. I.; Kovredov, A. I.; Ol'shevskaya, V. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1986**, 1388.
(76) (a) Zakharkin, L. I.; Ol'shevskaya, V. A.; Kovredov, A. I. *Zh. Obshch. Khim.* **1982**, *52*, 1911. (b) Gomez, F. A.; Johnson, S. E.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1991**, *113*, 5915.
(77) Chari, S. L.; Chiang, S. H.; Jones, M., Jr. *J. Am. Chem. Soc.* **1982**, *104*, 3138.
(78) L'Esperance, R. P.; Li, Z.; Engen, D. V.; Jones, M., Jr. *Inorg. Chem.* **1989**, *28*, 1823.
(79) Lebedev, V. N.; Balagurova, E. V., Zakharkin, L. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1987**, 1134.
(80) Zakharkin, L. I.; Lebedev, V. N. *Zh. Obshch. Khim.* **1986**, *56*, 2163.
(81) Zakharkin, L. I.; Lebedev, V. N.; Shustova, T. V.; Balagurova, E. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1986**, 2813.
(82) Zakharkin, L. I.; Zhigareva, G. G. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1989**, 193.
(83) Lebedev, A. V.; Bukhtiarov, A. B.; Golyshin, V. N.; Kudryavtsev, Yu. G.; Lovchinovsky, I. Yu.; Rozhkov, I. N. *Metalloorg. Khim.* **1991**, *4*, 426.
(84) Churkina, L. A.; Zvereva, T. D.; Shingel, I. A.; Malashonok, L. I.; Ol'dekop, Yu. A. *Zh. Obshch. Khim.* **1986**, *56*, 848.
(85) Markovskii, L. I.; Romanenko, V. D.; Ruban, A. V.; Sarina, T. V.; Ol'shevskaya, V. A.; Zakharkin, L. I. *Zh. Obshch. Khim.* **1990**, *60*, 694.
(86) Kalinin, V. N.; Astakhin, A. V.; Kazantsev, A. V.; Zakharkin, L. I. *Zh. Obshch. Khim.* **1982**, *52*, 1932.
(87) Kalinin, V. N.; Astakhin, A. V.; Kazantsev, A. V.; Zakharkin, L. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1984**, 1644.
(88) Kazantsev, A. V.; Aksartov, M. M.; Aksartova, L. M. *Metalloorg. Khim.* **1990**, *3*, 1345.
(89) Bekasova, N. I. *Usp. Khim.* **1984**, *53*, 107.
(90) Bekasova, N. I.; Komarova, L. G. In *Advances in Synthesis of Organoelement Polymers*; Korshak, V. V., Ed.; Nauka: Moscow, 1988; p 56.
(91) Kabachii, Yu. A.; Valetskii, P. M. *Int. J. Polym. Mater.* **1990**, 13.
(92) Korshak, V. V.; Teplyakov, M. M.; Khotina, I. A.; Kovalev, A. I. *Acta Polym.* **1988**, *39*, 440.
(93) Korshak, V. V.; Bekasova, N. I.; Komarova, L. G.; Vagin, V. V.; Solomatina, A. I. *Vysokomol. Soed.* **1989**, *A31*, 54.
(94) Korshak, V. V.; Bekasova, N. I.; Komarova, L. G.; Komarova, N. G.; Vagin, V. V. *Acta Polym.* **1989**, *40*, 439.
(95) Korshak, V. V.; Rusanov, A. L.; Prigozhina, M. P.; Bulycheva, E. G.; Edlinskii, Z.; Bekasova, N. I. *Plast. Massy* **1990**, *5* (in Russian).
(96) Kabachii, Yu. A.; Valetskii, P. M.; Vinogradova, S. V.; Korshak, V. V. *Dokl. Akad. Nauk SSSR* **1986**, *291*, 888.
(97) Izmailov, B. A.; Kalinin, V. N.; Myakushev, V. D.; Zhdanov, A. A.; Zakharkin, L. I. *Dokl. Akad. Nauk SSSR* **1985**, *280*, 114.
(98) Teplyakov, M. M.; Khotina, I. A.; Dmitrenko, A. V.; Kovalev, A. I.; Kalinin, V. N.; Korshak, V. V.; Izmailov, B. A. *Macromol. Chem.* **1990**, *191*, 801.
(99) Teplyakov, M. M.; Khotina, I. A.; Dmitrenko, A. V.; Korshak, V. V.; Izmailov, B. A.; Myakushev, V. D. *Macromol. Chem.* **1990**, *191*, 809.
(100) Maurer, J. L.; Berchier, F.; Serio, A. J.; Knobler, C. B.; Hawthorne, M. F. *J. Org. Chem.* **1990**, *55*, 838.
(101) Anisuzzaman, A. K. M.; Alam, F.; Soloway, A. H. *Polyhedron* **1990**, *9*, 891.
(102) Miura, M.; Gabel, D.; Oenbrink, G.; Fairchild, R. G. *Tetrahedron Lett.* **1990**, *31*, 2247.
(103) (a) Kahl, S. B. *Tetrahedron Lett.* **1990**, *31*, 1517. (b) Kahl, S. B.; Koo, M. S. *J. Chem. Soc., Chem. Commun.* **1990**, 1769.
(104) Nemoto, H.; Rong, F. G.; Yamamoto, Y. *J. Org. Chem.* **1990**, *55*, 6065.
(105) Reynolds, R. C.; Trask, T. W.; Sedwick, W. D. *J. Org. Chem.* **1991**, *56*, 2391.
(106) (a) Hawthorne, M. F. *Pure Appl. Chem.* **1991**, *63*, 327. (b) Hatanaka, H.; Sweet, W. H.; Sano, K.; Ellis, F. *Pure Appl. Chem.* **1991**, *63*, 373. (c) Soloway, A. H.; Anisuzzman, A. K. M.; Alam, F.; Barth, R. F.; Lin, L. *Pure Appl. Chem.* **1991**, *63*, 441. (d) Yamamoto, Y. *Pure Appl. Chem.* **1991**, *63*, 423.
(107) Alexander, R. P.; Schroeder, H. A. *Inorg. Chem.* **1963**, *2*, 1107.
(108) Zakharkin, L. I.; Bregadze, V. I.; Okhlobystin, O. Yu. *J. Organomet. Chem.* **1965**, *4*, 211.
(109) Zakharkin, L. I.; Bregadze, V. I.; Okhlobystin, O. Yu. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1964**, 1539.
(110) Degtyarev, A. N.; Godovikov, N. N.; Bregadze, V. I.; Kabachnik, M. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1973**, 2369.
(111) Godovikov, N. N.; Degtyarev, A. N.; Bregadze, V. I.; Kabachnik, M. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1975**, 2797.
(112) Zakharova, L. M.; Degtyarev, A. N.; Agabekyan, R. S.; Bregadze, V. I.; Godovikov, N. N.; Kabachnik, M. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1978**, 2178.
(113) (a) Kabachnik, M. I.; Godovikov, N. N.; Rys, E. G. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1980**, 1455. (b) Rys, E. G.; Godovikov, N. N.; Kabachnik, M. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1983**, 2640.
(114) Balema, V. P.; Rys, E. G.; Godovikov, N. N.; Kabachnik, M. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1989**, 194.
(115) Kabachnik, M. I.; Zakharov, L. S.; Gefter, E. L.; Molchanova, G. N.; Petrovskii, P. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1990**, 1933.
(116) Furmanova, N. G.; Yanovsky, A. I.; Struchkov, Yu. T.; Bregadze, V. I.; Godovikov, N. N.; Degtyarev, A. N.; Kabachnik, M. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1979**, 2346.
(117) Bregadze, V. I.; Okhlobystin, O. Yu. *J. Organomet. Chem. Rev. A*, **1969**, *4*, 345.
(118) Bregadze, V. I.; Usiatinsky, A. Ya.; Godovikov, N. N. *Dokl. Akad. Nauk SSSR* **1978**, *241*, 364.
(119) Zakharkin, L. I.; Krainova, N. Yu. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1984**, 1184.
(120) Bregadze, V. I.; Usiatinsky, A. Ya.; Kampel, V. Ts.; Golubinskaya, L. M.; Godovikov, N. N. *Izv. Akad. Nauk SSSR* **1985**, 1212.
(121) Bregadze, V. I.; Usiatinsky, A. Ya.; Antonovich, V. A.; Godovikov, N. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1988**, 670.
(122) Zakharkin, L. I.; Shemyakin, N. F. *Zh. Obshch. Khim.* **1974**, *44*, 1085.
(123) Zakharkin, L. I.; Shemyakin, N. F. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1981**, 1856.
(124) Zakharkin, L. I.; Shemyakin, N. F. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1984**, 2807.
(125) Zakharkin, L. I.; Shemyakin, N. F.; Polyakov, A. V.; Yanovsky, A. I.; Struchkov, Yu. T. *Zh. Obshch. Khim.* **1987**, *57*, 611.
(126) Morandini, F.; Longato, B.; Bresadola, S. *J. Organomet. Chem.* **1982**, *239*, 377.
(127) Longato, B.; Bresadola, S. *Inorg. Chem.* **1982**, *21*, 168.
(128) Basato, M.; Longato, B.; Morandini, F.; Bresadola, S. *Inorg. Chem.* **1984**, *23*, 3972.
(129) Longato, B.; Morandini, F.; Bresadola, S. *Inorg. Chim. Acta* **1980**, *39*, 27.

(130) Basato, M.; Morandini, F.; Longato, B.; Bresadola, S. *Inorg. Chem.* **1984**, *23*, 649.

(131) Ol'dekop, Yu. A.; Mayer, N. A.; Erdman, A. A.; Prokopovich, V. P. *Dokl. Akad. Nauk SSSR* **1981**, *257*, 647.

(132) Ol'dekop, Yu. A.; Mayer, N. A.; Erdman, A. A.; Prokopovich, V. P. *Zh. Obshch. Khim.* **1982**, *52*, 2256.

(133) Baukova, T. V.; Kuz'mina, L. G.; Dvortsova, N. V.; Porai-Koshits, M. A.; Kravtsov, D. N.; Perevalova, E. G. *Metallogr. Khim.* **1989**, *2*, 1098.

(134) Suleimanov, G. Z.; Bregadze, V. I.; Koval'chuk, N. A.; Beletskaya, I. P. *J. Organomet. Chem.* **1982**, *235*, C17.

(135) Bregadze, V. I.; Koval'chuk, N. A.; Godovikov, N. N.; Suleimanov, G. Z.; Beletskaya, I. P. *J. Organomet. Chem.* **1983**, *241*, C13.

(136) Suleimanov, G. Z.; Bregadze, V. I.; Koval'chuk, N. A.; Godovikov, N. N.; Beletskaya, I. P. *Dokl. Akad. Nauk SSSR* **1983**, *270*, 343.

(137) Mironov, V. F.; Grigos, V. I.; Pechurina, S. Ya.; Zhigach, A. F. *Zh. Obshch. Khim.* **1972**, *42*, 2583.

(138) Zakharkin, L. I.; Ol'shevskaya, V. A.; Anikina, E. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1987**, 869.

(139) Lebedev, V. N.; Troitskaya, M. V.; Zakharkin, L. I. *Metalloorg. Khim.* **1991**, *4*, 954.

(140) Kabachii, Yu. A.; Sidorenko, V. I.; Kuzaev, A. I.; Babushkina, T. A.; Valetskii, P. M.; Vinogradova, S. V.; Korshak, V. V. *Dokl. Akad. Nauk SSSR* **1985**, *281*, 633.

(141) Seregina, M. V.; Kabachii, Yu. A.; Valetskii, P. M.; Tumanskii, B. L.; Kampel, V. Ts. *Vysokomol. Soed.* **1991**, *B33*, 105.

(142) (a) Zheng, G.; Jones, M., Jr. *J. Am. Chem. Soc.* **1983**, *105*, 6487. (b) Sung, D. D.; Lee, J. D.; Choi, S. K. *Bull. Korean Chem. Soc.* **1987**, *8*, 63; *Chem. Abstr.* **1987**, *108*, 167545s.

(143) (a) Albagi, D.; Zheng, G.; Jones, M., Jr. *Inorg. Chem.* **1986**, *25*, 129. (b) Wermer, J. R.; Jan, D. Y.; Getman, T. D.; Moher, E.; Shore, S. G. *Inorg. Chem.* **1988**, *27*, 4274.

(144) Zakharkin, L. I.; Kovredov, A. I.; Ol'shevskaya, V. A.; Shaugumbekova, Zh. S. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1980**, 1691.

(145) Kovredov, A. I.; Shaugumbekova, Zh. S.; Petrovskii, P. V.; Zakharkin, L. I. *Zh. Obshch. Khim.* **1989**, *59*, 607.

(146) Zakharkin, L. I.; Kalinin, V. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1968**, 1423.

(147) Zakharkin, L. I.; Kalinin, V. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1967**, 2585.

(148) Zakharkin, L. I.; Kalinin, V. N.; Gedymin, V. V. *Synth. Inorg. Met.-Org. Chem.* **1971**, *1*, 45.

(149) Zakharkin, L. I.; Ol'shevskaya, V. A.; Sulaimankulova, D. D. *Metalloorg. Khim.*, in press.

(150) (a) Zakharkin, L. I.; Pisareva, I. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1981, 2794. (b) Plešek, J.; Heřmánek, S. *Collect. Czech. Chem. Commun.* **1981**, *46*, 687.

(151) (a) Rys, E. G.; Balema, V. P.; Godovikov, N. N.; Kabachnik, M. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1988**, 2187. (b) Rys, E. G.; Godovikov, N. N.; Kabachnik, M. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1986**, 719. (c) Balema, V. P.; Rys, E. G.; Godovikov, N. N.; Kabachnik, M. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1990**, 2857.

(152) (a) Rys, E. G.; Balema, V. P.; Godovikov, N. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1987**, 2398. (b) Rys, E. G.; Balema, V. P.; Godovikov, N. N.; Kabachnik, M. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1990**, 1653.

(153) (a) Li, J.; Jones, M., Jr. *Inorg. Chem.* **1990**, *29*, 4162. (b) Roscoe, J. S.; Kongpricha, S.; Papetti, S. *Inorg. Chem.* **1970**, *9*, 1561. (c) Andrews, J. S.; Zayas, J.; Jones, M., Jr. *Inorg. Chem.* **1985**, *24*, 3715. (d) Zakharkin, L. I.; Kalinin, V. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1966**, 575. (e) Zakharkin, L. I.; Ol'Shevskaya, V. A.; Poroshin, T. Yu.; Balgurova, E. V. *Zh. Obshch. Khim.* **1987**, *57*, 2012.

(154) Lebedev, V. N.; Balagurova, E. V.; Polyakov, A. V.; Yanovsky, A. I.; Struchkov, Yu. T.; Zakharkin, L. I. *J. Organomet. Chem.* **1990**, *385*, 307.

(155) Grushin, V. V.; Tolstaya, T. P.; Lisichkina, I. N. *Dokl. Akad. Nauk SSSR* **1981**, *261*, 99.

(156) Demkina, I. I.; Grushin, V. V.; Tolstaya, T. P.; Vasyukova, N. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1989**, 1849.

(157) Grushin, V. V.; Polyakov, A. V.; Yanovsky, A. I.; Struchkov, Yu. T.; Bukalov, S. S.; Leites, L. A. *Metalloorg. Khim.* **1991**, *4*, 828.

(158) Grushin, V. V.; Demkina, I. I.; Tolstaya, T. P. *Inorg. Chem.* **1991**, *30*, 1760.

(159) (a) Bregadze, V. I. In *Boron Chemistry*; World Scientific: Singapore, 1987; p 244. (b) Bregadze, V. I. *Proc. Indian Natl. Sci. Acad.* **1989**, *55*, A, 414.

(160) Tumansky, B. L.; Kampel, V. Ts.; Solodovnikov, S. P.; Bregadze, V. I.; Godovikov, N. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1985**, 2644.

(161) Tumansky, B. L.; Usiatinsky, A. Ya.; Prokof'ev, A. I.; Bubnov, N. N.; Solodonikov, S. P.; Kampel, V. Ts.; Bregadze, V. I.; Godovikov, N. N.; Kabachnik, M. I. *Metalloorg. Khim.* **1988**, *1*, 47.

(162) Usiatinsky, A. Ya.; Kampel, V. Ts.; Bregadze, V. I.; Sherbina, T. M.; Antonovich, V. A.; Godovikov, N. N. *Metalloorg. Khim.* **1988**, *1*, 1420.

(163) Yashkina, L. V.; Velichko, F. K.; Kampel, V. Ts.; Dostovalova, V. I.; Antonovich, V. A.; Bregadze, V. I. *Metalloorg. Khim.* **1991**, *4*, 39.

(164) Bregadze, V. I.; Kampel, V. Ts.; Matrosov, E. I.; Antonovich, V. A.; Yanovsky, A. I.; Struchkov, Yu. T.; Godovikov, N. N.; Kabachnik, M. I. *Dok. Acad. Nauk SSSR* **1985**, *285*, 1127.

(165) (a) Kampel, V. Ts.; Bregadze, V. I.; Ermanson, L. V.; Antonovich, V. A.; Matrosov, E. I.; Godovikov, N. N.; Kabachnik, M. I. *Metalloorg. Khim.*, in press. (b) Kampel, V. Ts.; Ermanson, L. V.; Bregadze, V. I.; Antonovich, V. A.; Matrosov, E. I.; Godovikov, N. N. *Metalloorg. Khim.*, in press. (c) Rakhimov, R. D.; Butin, K. P.; Ermanson, L. V.; Kampel, V. Ts.; Godovikov, N. N.; Bregadze, V. I. *Metalloorg. Khim.* **1991**, *4*, 823. (d) Tumansky, B. L.; Kampel, V. Ts.; Ermanson, L. V.; Bubnov, N. N.; Solodovnikov, S. P.; Prokof'ev, A. I.; Godovikov, N. N. *Metalloorg. Khim.* **1991**, *4*, 941.

(166) Zakharkin, L. I.; Orlova, L. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1970**, 2417.

(167) Kalinin, V. N.; Usatov, A. V.; Zakharkin, L. I. *Zh. Obshch. Khim.* **1981**, *51*, 2151.

(168) Kalinin, V. N.; Usatov, A. V.; Zakharkin, L. I. *Proc. Indian Natl. Sci. Acad.* **1989**, *55*, A, 293.