SOME RECENT ADVANCES IN THE CHEMISTRY OF DICARBA-*CLOS O*-DODECA-BORANES(12), $B_{10}H_{10}C_2RR'$

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ABSTRACT
Experimental data on the mutual rearrangements of isomeric dicarba-*closo*-dodecaboranes(12) and their *B*-halogen derivatives are reviewed. Reactions involving electron transfer to dicarba-*closo*-dodecaboranes(12), and the properties of the resulting dodecahydrodicarba-*nido*-dodecaborates(2−) as intermediates of the rearrangements of 1.7- and 1,12-dicarba-*closo*-dodecaboranes(12) are discussed. Attention is also paid to the introduction of an NH_2 group into 1,2-dicarba-*closo*-dodecaborane(12) via the formation of dodecahydro-1,2-dicarba-*nido*-dodecaborate(2−) and to the reactions of 3-amino-1,2-dicarba-*closo*-dodecaborane(12).

INTRODUCTION
In 1963 Russian and American chemists were the first to report on dicarba-*closo*-dodecaboranes(12) and to stimulate interest in carborane chemistry which was generally directed towards the following:
(a) Investigation of the properties of dicarba-*closo*-dodecaboranes(12);
(b) Synthesis and study of novel dicarba-*closo*-boranes and heterocarboranes;
(c) Preparation and study of metalcarboranes—cyclopentadienyl analogues of transition metal derivatives.
This paper is concerned with experimental work on the mutual rearrangements of dicarba-*closo*-dodecaboranes and also with the related topic of the properties of dodecahydrodicarba-*nido*-dodecaborates(2−) and 3-amino-1.2-dicarba-*closo*-dodecaboranes. Part of this work has been carried out at the Institute of Organo-Element Compounds in Moscow.

MUTUAL REARRANGEMENTS OF ISOMERIC DICARBA-*CLOSO*-DODECABORANES(12)†

Thermal rearrangements of isomeric carboranes
One of the specific features of isomeric carboranes is their ability to undergo mutual rearrangements. In 1963 on the basis of theoretical calculations

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† For convenience the following nomenclature is used in this paper: carborane = dicarba-*closo*-dodecaborane(12); *o*-carborane, *m*-carborane and *p*-carborane = 1,2-, 1,7- and 1.12-dicarba-*closo*-dodecaboranes (12), respectively.

Hoffman and Lipscomb predicted[1] that among isomeric carboranes, m-carborane is more stable thermodynamically than the o-isomer, that the stability of p-carborane is comparable with that of m-carborane, and that o-carborane should rearrange to the m-isomer and the latter to p-carborane. These predictions have been confirmed by subsequent experiments. Grafstein and Dvorak first discovered an irreversible isomerization of o-carborane to the m-isomer at $450°-500°C^2$.

$$\underset{B_{10}H_{10}}{\overset{HC-CH}{\diagdown O \diagup}} \xrightarrow{500°C} m\text{-}B_{10}H_{10}C_2H_2$$
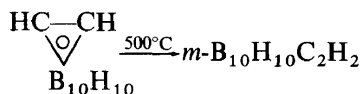
In a similar manner, rearrangement of 1-methyl-o-carborane to 1-methyl-m-carborane has been observed. Numerous examples were reported for C- and B-substituted o-carboranes which also irreversibly rearranged to the respective m-carboranes[3-7]. In studies of the kinetics of isomerization of o- to m-carborane, Salinger and Frey[8] have shown that the bulky substituents at the 1- and 2-positions of the o-carborane nucleus essentially enhance the rate of this reaction. Kinetic data on the rearrangements of o-carborane and 1.2-bis(diphenylmethylsilyl)-o-carborane are presented in *Table 1*[8].

Table 1. Kinetic data on the rearrangement of o-$B_{10}H_{10}C_2H_2$ and 1.2-$[(C_6H_5)_2CH_3Si]_2$-o-$B_{10}H_{10}C_2$

	o-$B_{10}H_{10}C_2H_2$		1.2-$[(C_6H_5)_2CH_3Si]_2$-o-$B_{10}H_{10}C_2$		
Temp..°C	425	455	475	263	280	300
$K \times 10^4 cm^{-1}$	0.22	1.54	4.7	0.03	0.22	1.28
	$\Delta H^* = 62$ kcal $\Delta S^* = 7$ eu $\Big\}$ at 455°C		$\Delta H^* = 45$ kcal $\Delta S^* = -1$ eu $\Big\}$ at 280°C		

We have determined the enthalpies of formation of o- and m-carboranes in the gaseous phase[9]:

o carborane $\Delta H_f^° {}_{298\cdot15}(g) = -26.4$ kcal/mole

m-carborane $\Delta H_f^° {}_{298\cdot15}(g) = -42.5$ kcal/mole

The observed difference between these values (equal to 16 kcal/mole) provides experimental evidence that o-carborane is thermodynamically less stable than m-carborane. In 1964, Papetti and Heying showed[10] that m-carborane rearranged to p-carborane at 617°C.
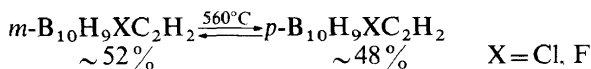
In agreement with Hoffman and Lipscomb's predictions, we established[11] that rearrangement of m- to p-carborane at $650°-700°C$ in the gaseous phase is a reversible equilibrium process:

$$m\text{-}B_{10}H_{10}C_2H_2 \overset{650-700°C}{\rightleftharpoons} p\text{-}B_{10}H_{10}C_2H_2$$
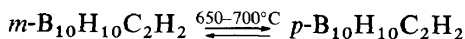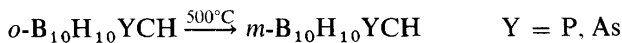
The equilibrium mixture contained 47 per cent of p-carborane and 53 per cent of m-carborane at this temperature which indicates the close thermodynamic stabilities of these isomers.

In the study by Hart and Lipscomb[12] the thermodynamic stabilities of B-chloro- and B-fluoro- p- and m-carboranes were also practically the

same and these compounds underwent a mutual reversible rearrangement.

$$m\text{-}B_{10}H_9XC_2H_2 \underset{}{\overset{560°C}{\rightleftharpoons}} p\text{-}B_{10}H_9XC_2H_2$$
$$\sim 52\% \qquad\qquad\qquad \sim 48\% \qquad X = Cl, F$$

It is interesting to note that in spite of the fact that the isomers of phospha- and arsacarba-*closo*-dodecaboranes(11) differ from carboranes by the presence of P or As atoms instead of a CH group, they behave in a similar manner to carboranes during thermal rearrangements: the *o*-isomers rearrange irreversibly to the *m*-species[13]:

$$o\text{-}B_{10}H_{10}YCH \xrightarrow{500°C} m\text{-}B_{10}H_{10}YCH \qquad Y = P, As$$

Rearrangement of the *m*- to the *p*-isomers is a reversible equilibrium process[14]:

$$m\text{-}B_{10}H_{10}YCH \underset{}{\overset{600-650°C}{\rightleftharpoons}} p\text{-}B_{10}H_{10}YCH \qquad Y = P, As$$
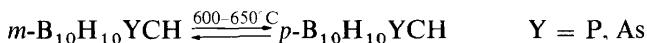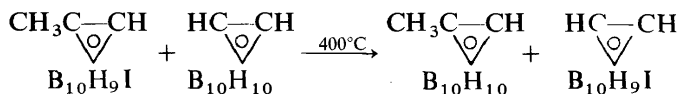
The equilibrium mixture contains equal quantities of both isomers. Thus it is evident that, in a similar manner to carboranes, the *o*-isomers of phospha- and arsacarba-*closo*-dodecaboranes(11) are less stable thermodynamically with respect to the *m*-isomers whose stabilities almost match those of the *p*-isomers. The use of labelled atoms at various positions in carboranes provides a powerful tool for the study of the rearrangement of these compounds.

In our view, studies of the isomerization of *B*-halocarboranes have made an essential contribution to the elucidation of the mechanism of carborane rearrangement. We first reported that isomerization of 9-halogen-*o*-carboranes at 380°–415°C led to a mixture of isomeric *B*-halogen-*m*-carboranes[15]. Prolonged heating of 9-halogen-*m*-carboranes at 490°C resulted in the isomeric *B*-halogen-*m*-carboranes via halogen rearrangement[16]. Then, with these data as a starting point, Lipscomb and his associates[17] investigated a rearrangement of 9-bromo-*o*-carborane at 395°–425°C in more detail, and showed that at this temperature the bromine rearrangement produces a mixture of 3-, 4-, 8- and 9-bromo-*o*-carboranes; simultaneously rearrangement of *o*-carborane to 2-, 4-, 5- and 9-bromo-*m*-carboranes was taking place. As a continuation of this work we compared the rearrangements of 9-chloro-, 9-bromo- and 9-iodo-*o*-carboranes at 420°C[15] and found that 9-chloro- and 9-iodo-*o*-carboranes in a similar manner to 9-bromo-*o*-carborane gave a mixture of 3-, 4-, 8- and 9-chloro-(iodo)-*o*-carboranes and a mixture of 2-, 4-, 5- and 9-chloro-(iodo)-*m*-carboranes. It has been found that the rate of rearrangement of halogen in *B*-halogen *o*-carborane depends to some extent upon its nature, and decreases in the series I > Br ⩾ Cl. Hart and Lipscomb[12] have established that fluorine rearrangement is slower than that of bromine. Thus at 420°C, 3-fluoro-*o*-carborane gave only 4-fluoro-*o*-carborane and 2- and 4-fluoro-*m*-carboranes. Interesting data have been obtained by Lipscomb and Hart[12] concerning the mechanism of rearrangement of 9-, 2-, 4- and 5-chloro-*m*-carboranes, 2- and 4-fluoro-*m*-carboranes, chloro-*p*- and fluoro-*p*-carboranes at 560–570°C. We have also obtained interesting results on the rearrangement of 9-chloro-, 9-bromo- and 9-iodo-*m*-carboranes at 480°–490°C[15].

Irrespective of the nature of chloro-*m*-carborane isomers, the reaction

at $560°-570°C^{12}$ led to the same equilibrium mixture of chloro-p- (48 per cent), 2-chloro- (9 per cent), 4-chloro- (19 per cent), 5-chloro- (16 per cent) and 9-chloro-(8 per cent)-m-carboranes. A similar mixture was produced from chloro-p-carborane. We have established that halogen rearrangement in B-halogen-o-carboranes is considerably faster than that in the m-isomers. In the case of 9-halogen-m-carboranes, the rearrangement rate depends essentially upon the nature of the halogen and increases in the order Cl < Br < I.

At present four mechanisms have been proposed for the rearrangement: (a) rearrangement through mutual rotation of two pentagonal pyramids forming an icosahedron[2]; (b) rearrangement of icosahedra through the intermediate cuboctahedral structures[1]; (c) rearrangement through cuboctahedra[12] with rotation by 120 degrees of the triangles; (d) rearrangement through rotation by 120 degrees of the triangular face in the icosahedron[18]. However, it is quite obvious that none of the mechanisms suggested for the thermal rearrangement completely agrees with the experimental data. Although Lipscomb et al.[12] have assumed that the mechanism via the cuboctahedron with rotation of triangles is preferable to other mechanisms, it should be noted that the halogen rearrangement in B-halogen-o- and m-carboranes may involve both intra- and inter-molecular halogen–hydrogen exchange. Thus, on heating an equilibrium mixture of o-carborane and 1-methyl-9-iodo-o-carborane (400°C, 35 min) we have observed an iodine–hydrogen exchange which led to a mixture of B-iodo-o-carboranes, 1-methyl-B-iodo-o-carboranes, o-carboranes and 1-methyl-o-carborane[15]:

$$\underset{B_{10}H_9I}{CH_3C-CH} + \underset{B_{10}H_{10}}{HC-CH} \xrightarrow{400°C} \underset{B_{10}H_{10}}{CH_3C-CH} + \underset{B_{10}H_9I}{HC-CH}$$

An analogous exchange was taking place, although more slowly in the case of 1-methyl-9-iodo-m-carborane and m-carborane.

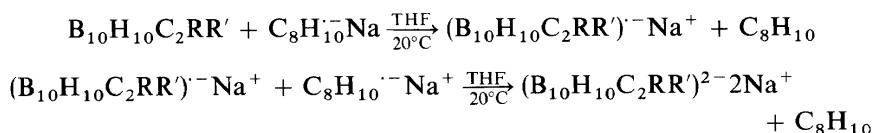### Rearrangements of carboranes through dodecahydrodicarba-*nido*-dodecaborates(2−)

In 1963 Hoffman and Lipscomb[1] predicted that when a negative charge of -2 is transmitted to the isomeric m- and p-carboranes, their stabilities should be comparable with that of o-carborane. On the other hand, although for neutral $B_{10}H_{10}C_2H_2$ the conversion of o-carborane to the m-isomer proceeds irreversibly, an equilibrium between the respective negative ions may take place to some extent. We have partially confirmed this assumption by experiment. Even in the first studies, o-[19] and m-carboranes[2] have been shown to react with two equivalents of alkali metal (M) in liquid ammonia to give the adducts $B_{10}H_{10}C_2H_2.2M$. Recently[20], two equivalents of alkali metal have also been shown to add to p-carborane in liquid ammonia yielding the adduct $B_{10}H_{10}C_2H_2M$. Actually we found that these adducts, being the alkali salts of dodecahydrodicarba-*nido*-dodecaborates(2−) $(B_{10}H_{10}C_2H_2)^{2-}2Na^+$, are formed when two electrons of the alkali metal transfer to the lowest vacant orbitals of the carborane as is the case in the reaction of alkali metals with aromatic hydrocarbons. o- and m-Carboranes reacted with alkali metals also in THF and monoglyme[22, 23]. These investi-

gations have shown that when alkali metals react with *o*- and *m*-carboranes in ethereal solution two electrons add consecutively via the anion-radical as an intermediate[22-24].

$$B_{10}H_{10}C_2RR' \xrightarrow{+e} (B_{10}H_{10}C_2RR')^{-\cdot} \xrightarrow{+e} (B_{10}H_{10}C_2RR')^{2-}$$

E.s.r. spectra of the anion-radicals of *o*-carboranes display no fine structure which is probably a result of the highly delocalized unpaired electron[23,24].

Analogous electron transfer from the aromatic hydrocarbon–alkali metal adducts is taking place to *o*- and *m*-carboranes (for example from sodium naphthalide or sodium biphenyl)[23,25].

$$B_{10}H_{10}C_2RR' + C_8H_{10}^{-\cdot}Na \xrightarrow[20°C]{THF} (B_{10}H_{10}C_2RR')^{-\cdot}Na^+ + C_8H_{10}$$

$$(B_{10}H_{10}C_2RR')^{-\cdot}Na^+ + C_8H_{10}^{-\cdot}Na^+ \xrightarrow[20°C]{THF} (B_{10}H_{10}C_2RR')^{2-}2Na^+ + C_8H_{10}$$

When 1-phenyl-*o*-carborane was reduced polarographically[24], the electron affinities of some *o*- and *m*-carboranes were determined in DMF in the presence of Et_4NClO_4[26,27].

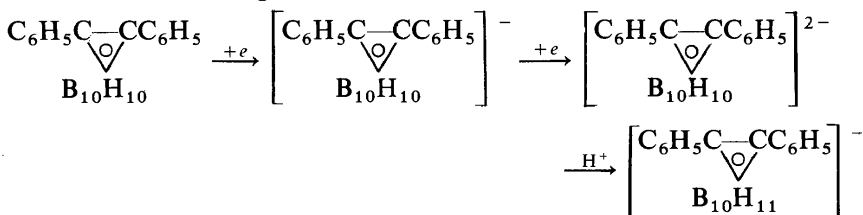The parameters of polarographic reduction of some *o*- and *m*-carboranes are listed in *Table 2*.

Table 2. The parameters of polarographic reduction of some carboranes in DMF with 0.1 N Et_4NClO_4 as support

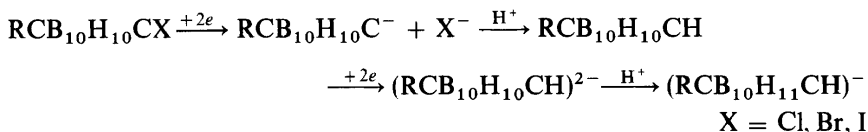| Compound	$-E_{\frac{1}{2}}$. SCE	i_d	α
o-Carborane	2.51	5.20	0.191
1-Methyl-*o*-carborane	2.44	5.10	0.200
1-Phenyl-*o*-carborane	1.95	4.89	0.197
1-Phenyl-*m*-carborane	2.45	4.80	0.224
9-Iodo-*o*-carborane	2.13	4.96	0.215
9-Bromo-*o*-carborane	2.21	5.00	0.217
9-Iodo-*m*-carborane	2.71	5.00	0.220

Under the conditions investigated, *m*-carborane, 1-methyl-*m*-carborane and *p*-carborane could not be reduced polarographically up to the discharge region of the supporting electrolyte (-2.80 V). The data in *Table 2* show that *o*-carboranes are reduced more readily and it might thus be concluded that they possess greater electron affinities with respect to *m*-carboranes. The data on polarographic reduction are in agreement with the relative rates of alkali metal addition to *o*-, *m*- and *p*- carboranes in liquid ammonia[28]. from which it follows that the electron affinities decrease in the order: *o*-carborane > *m*-carborane > *p*-carborane. It has been found[27] that the polarographic reduction of carboranes is a two-electron irreversible process leading to dodecahydrodicarba-*nido*-dodecaborate(2−) which then protonates to yield stable tridecadicarba-*nido*-dodecaborate(1−).

The polarographic reduction of *o*- and *m*-carboranes free of polarographically active groups shows one two-electron wave. 1,2-Diphenyl-*o*-carborane is, however, reduced in a stepwise fashion exhibiting two one-electron waves.

the anion-radical being the intermediate:

$$C_6H_5C\underset{B_{10}H_{10}}{\diagdown\diagup}CC_6H_5 \xrightarrow{+e} \left[C_6H_5C\underset{B_{10}H_{10}}{\diagdown\diagup}CC_6H_5\right]^{-} \xrightarrow{+e} \left[C_6H_5C\underset{B_{10}H_{10}}{\diagdown\diagup}CC_6H_5\right]^{2-}$$

$$\xrightarrow{H^+} \left[C_6H_5C\underset{B_{10}H_{11}}{\diagdown\diagup}CC_6H_5\right]^{-}$$

Polarographic reduction of 1-halogencarboranes shows two equivalent two-electron waves: the first corresponds to the reduction of the carbon—halogen bond and the second to that of the carborane nucleus. For example, the half-wave potentials $(-E_{\frac{1}{2}})$ of 1-phenyl-2-bromo-o-carborane are 0.60 and 2.30 V. Thus, polarographic reduction of 1-halogencarboranes can be depicted by the scheme:

$$RCB_{10}H_{10}CX \xrightarrow{+2e} RCB_{10}H_{10}C^- + X^- \xrightarrow{H^+} RCB_{10}H_{10}CH$$

$$\xrightarrow{+2e} (RCB_{10}H_{10}CH)^{2-} \xrightarrow{H^+} (RCB_{10}H_{11}CH)^-$$
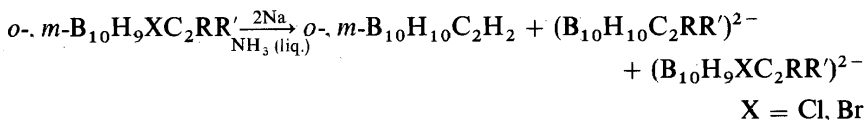
$$X = Cl, Br, I$$

Unlike 1-halogencarboranes, the polarographic reduction of 9-halogen-carboranes is a two-electron process and it does not involve reduction of the boron—halogen bond[27]:

$$RCB_{10}H_9XCH \xrightarrow{+2e} (RCB_{10}H_9XCH)^{2-} \xrightarrow{H^+} (RCB_{10}H_{10}XCH)^-$$
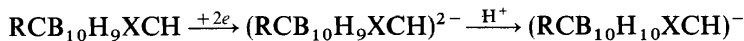
The action of alkali metals on 9-halogen o- and m-carboranes in liquid ammonia is rather complicated. Two sodium equivalents may reduce almost completely the boron—iodine bond in 9-iodocarboranes[27,29]:

$$o\text{-}, m\text{-} B_{10}H_9IC_2RR' \xrightarrow[NH_3 \text{(liq.)}]{2Na} o\text{-}, m\text{-} B_{10}H_{10}C_2RR' + NaI$$
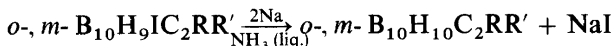
Undoubtedly, the reduction of the B—I bond with alkali metal is similar to that of the C—I bond, giving rise to the respective anion $(o\text{-}, m\text{-}B_{10}H_9C_2RR')^-$ which then undergoes protonation to o- and m-$B_{10}H_{10}C_2RR'$. Two sodium equivalents reacting with 9-chloro- and 9-bromo-o- and m-carboranes with partial reduction of the boron—halogen bond yielded also a mixture of $(B_{10}H_{10}C_2RR')^{2-}$ and $(B_{10}H_9XC_2RR')^{2-}$ with some unchanged 9-halogen-carborane. Moreover, some cleavage of the halogencarborane system also took place[27].

$$o\text{-}, m\text{-}B_{10}H_9XC_2RR' \xrightarrow[NH_3 \text{(liq.)}]{2Na} o\text{-}, m\text{-}B_{10}H_{10}C_2H_2 + (B_{10}H_{10}C_2RR')^{2-}$$

$$+ (B_{10}H_9XC_2RR')^{2-}$$

$$X = Cl, Br$$

Confirmation that dodecahydrodicarba-$nido$-dodecaborates (resulting after addition of two electrons to o- and m-carboranes) produce tridecahydrodi-carba-$nido$-dodecaborates $(1-)$ upon protonation has been obtained independently[21 23]. $(B_{10}H_{10}C_2RR')^{2-}$ evolved no hydrogen when it dissolved in water but produced stable $(B_{10}H_{11}C_2RR')^-$ which could be precipitated in

the form of ammonium or phosphonium salts from the aqueous solution.

$$(B_{10}H_{10}C_2RR')^{2-} 2Na^+ \xrightarrow{H_2O} (B_{10}H_{11}C_2RR')^- Na^+ + NaOH$$
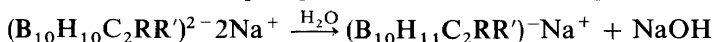
Unlike dodecahydrodicarba-*nido*-undecaborates$(1-)(B_9H_{10}C_2RR')^-$ which are stable on being heated in aqueous solutions, the anion $(B_{10}H_{11}C_2RR')^{2-}$ readily hydrolyses under the same conditions evolving hydrogen and cleaving the boron skeleton to boric acid. For example, hydrolysis of $(B_{10}H_{11}C_2Ph_2)^{2-}$ occurs in accordance with the scheme[21]:

$$\xrightarrow[100°C]{H_2O} 2C_6H_5CH_3 + H_2 + B(OH)_3$$
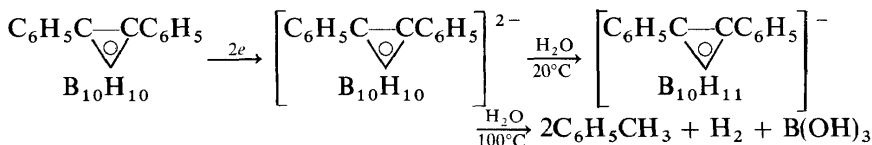
In the study of the properties of $(B_{10}H_{11}C_2RR')^{2-}$ prepared from *o*-carboranes it has been found that these compounds can be oxidized reversibly to *o*-carboranes[21, 23, 25]. It is obvious that oxidation involves formation of the respective anion-radical intermediate.

$$(o\text{-}B_{10}H_{10}C_2RR')^{2-} \xrightarrow{-e} (o\text{-}B_{10}H_{10}C_2RR')^- \xrightarrow{-e} o\text{-}B_{10}H_{10}C_2RR'$$
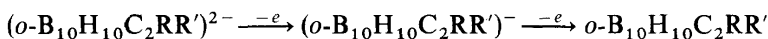
m-Carboranes have not been detected in the reaction mixture. Air, oxygen, transition metal salts ($CuCl_2$ etc.), potassium permanganate, and some organic electron acceptors can be used as oxidants. Benzophenone and fluorenone react with $(o\text{-}B_{10}HC_2RR')^{2-}$ by electron transfer.
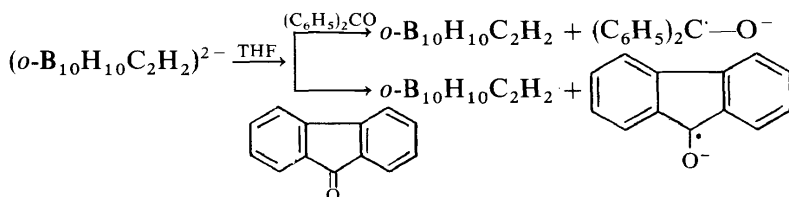
$(o\text{-}B_{10}H_{10}C_2H_2)^{2-}$ may easily transfer its electrons to *p*-quinone and nitrobenzene (giving respectively *o*-carborane–semiquinone and the anion-radical of nitrobenzene) and to the C—Hal bond of $CHBr_3$ or CBr_4.

$$(o\text{-}B_{10}H_{10}C_2H_2)^{2-} + CHBr_3 \rightarrow o\text{-}B_{10}H_{10}C_2H_2 + (CHBr_3)^-$$
$$\rightarrow (CHBr_2)^- + Br^-$$
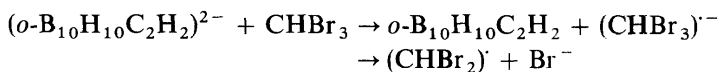
It has been also shown that, depending upon electron affinities, the electrons of dicarbadodecaborane(14) may transfer to some other substituted *o*-carborane. For example:

$$(o\text{-}B_{10}H_{10}C_2H_2)^{2-} + o\text{-}B_{10}H_{10}C_2RR' \rightarrow o\text{-}B_{10}H_{10}C_2H_2$$
$$+ (o\text{-}B_{10}H_{10}C_2RR')^{2-}$$

$$(1) \quad R = H, R' = C_6H_5$$
$$(2) \quad R = H, R' = CH=CH_2$$
$$(3) \quad R = R' = C_6H_5$$

Electron transfer from $(o\text{-}B_{10}H_{10}C_2H_2)^{2-}$ to anthracene and stilbene has not been detected.

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Dodecahydrodicarba-*nido*-dodecaborates(2−) obtained by the action of the alkali metals on *m*-carborane and its derivatives in liquid ammonia or THF and DME do not form *m*-isomers by oxidation but produce the respective *o*-carboranes[23, 25]. In accordance with Hoffman and Lipscomb's prediction[1], this result has been interpreted as a rearrangement of (*m*-$B_{10}H_{10}C_2RR')^{2-}$ (generated during transfer of two electrons to a *m*-carborane) to the *o*-isomer (generated when two electrons add to *o*-carboranes). The rearrangement of (*m*-$B_{10}H_{10}C_2RR')^{2-}$ to (*o*-$B_{10}H_{10}C_2RR')^{2-}$ proceeds to completion. Thus, the rearrangement of *m*- to *o*-carboranes should be regarded as a three-step process:

(a) Reduction (addition of two electrons);
(b) Rearrangement of the dianion;
(c) Oxidation (removal of two electrons).

$$m\text{-}B_{10}H_{10}C_2RR' \xrightarrow{+2e} (m\text{-}B_{10}H_{10}C_2RR')^{2-} \xrightarrow{\text{rearrangement}}$$
$$(o\text{-}B_{10}H_{10}C_2RR')^{2-} \xrightarrow{-2e} o\text{-}B_{10}H_{10}C_2RR'$$

A specific feature of the rearrangement of *m*-dianions to *o*-dianions is the great ease of the process. The reaction is fast even at −70°C, while thermal rearrangement of *o*- to *m*-carborane requires prolonged heating at 500°C. The identity of $(B_{10}H_{10}C_2RR')^{2-}$, generated on addition of two electrons to *o*- and *m*-carboranes, has been confirmed also by the identity of the salts of $(B_{10}H_{11}C_2RR')^-$. Earlier, Grafstein and Dvorak reported[2] that, unlike *o*-carborane, the *m*-isomer reacts with sodium in liquid ammonia in a stepwise fashion: at first, one sodium equivalent adds rapidly giving the adduct $B_{10}H_{10}C_2H_2$.Na, and then the second sodium equivalent reacts slowly producing $B_{10}H_{10}C_2H_2$.2Na. Both adducts differ in their hydrolysis in an argon atmosphere. $B_{10}H_{10}C_2H_2$.Na gives dicarborate which is soluble in water together with *o*-carborane (16 per cent), while $B_{10}H_{10}C_2H_2$.2Na leads only to the former product. As was shown above, we also prepared from two sodium equivalents and *m*-carborane in liquid ammonia the adduct $B_{10}H_{10}C_2H_2$.2Na which is the sodium salt of dodecahydrodicarba-*nido*-dodecaborate(2−). We failed, however, to reproduce the data of Grafstein and Dvorak on the formation of $B_{10}H_{10}C_2H_2$.Na. The action of one sodium equivalent on *m*-carborane in liquid ammonia always resulted in half the quantity of unreacted *m*-carborane together with $(B_{10}H_{10}C_2H_2)^{2-}$ 2Na$^+$, hydrolysis led only to *m*-carborane, while oxidation with $KMnO_4$ yielded a mixture of equal amounts of *o*- and *m*-carboranes[23]. It is not clear, however, how *o*-carborane was formed from the *m*-isomer under the conditions used by Grafstein and Dvorak[2] since transformation of the anion to the neutral *o*-carborane requires the presence of electron acceptors which were not present in the author's experiment.

To obtain information on the electron density distribution in dodecahydrodicarba-*nido*-dodecaborate(2−), we synthesized (*o*-$B_{10}H_{10}C_2HC_6H_4F$-*m, p*)$^{2-}$ and measured its ^{19}F chemical shifts in THF, using fluorobenzene as a standard[31].

We also measured the ^{19}F chemical shifts for (*p*- and *m*-fluorophenyl)-tridecahydrodicarba-*nido*-dodecaborate(1 −). The ^{19}F chemical shifts and the σ_i and σ_R^0 constants estimated from the equations of Taft *et al.*[32] are given in *Table 3*. It is concluded[31] that a considerable electron-releasing (both inductive and mesomeric) effect of the $(B_{10}H_{10}C_2H)^{2-}$ group indicates that a doubly occupied molecular orbital extends over the 1,2 and 3 or 6 atoms.

Table 3. The ^{19}F chemical shifts in $(o\text{-}B_{10}H_{10}C_2HC_6H_4F\text{-}m.p)^{2-}$ and $(o\text{-}B_{10}H_{11}C_2HC_6H_4F\text{-}m.p)^-$ (in THF). σ_i and σ_R^0 constants

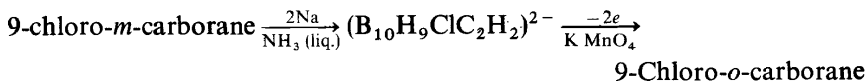| Derivative	^{19}F chemical shift. p.p.m.	σ_i	σ_R^0
$(p\text{-}FC_6H_4C_2HB_{10}H_{10})^{2-}$	10.15	− 0.54	− 0.19
$(m\text{-}FC_6H_4C_2HB_{10}H_{10})^{2-}$	4.44		
$(p\text{-}FC_6H_4C_2HB_{10}H_{10})^-$	8.40		
		− 0.39	− 0.17
$(p\text{-}FC_6H_4C_2\,HB_{10}H_{11})^-$	3.38		

Rearrangement of *p*-carborane via $(B_{10}H_{10}C_2H_2)^{2-}$ under conditions analogous to those used during the rearrangement of *m*-carborane was somewhat unexpected. *p*-Carborane has been found to react with two sodium equivalents in liquid ammonia to give $(p\text{-}B_{10}H_{10}C_2H_2)^{2-}$ which rapidly rearranges to $(m\text{-}B_{10}H_{10}C_2H_2)^{2-}$ at − 45°C. The latter was oxidized with $KMnO_4$ to *m*-carborane.
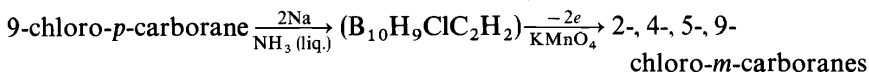
$$p\text{-}B_{10}H_{10}C_2H_2 \xrightarrow[\text{NH}_3 \text{ (liq.)}]{2\text{Na}} (p\text{-}B_{10}H_{10}C_2H_2)^{2-} \xrightarrow[45]{\text{rearrangement}} (m\text{-}B_{10}H_{10}C_2H_2)^{2-}$$
$$\xrightarrow[\text{KMnO}_4]{-2e} m\text{-}B_{10}H_{10}C_2H_2$$
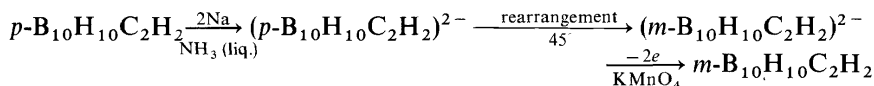
Under the reaction conditions used no subsequent rearrangement of $(m\text{-}B_{10}H_{10}C_2H_2)^{2-}$ to $(o\text{-}B_{10}H_{10}C_2H_2)^{2-}$ has been observed. On the basis of our data on the rearrangement of *m*- to *o*- and *p*- to *m*-carboranes proceeding through the formation of $(B_{10}H_{10}C_2H_2)^{2-}$, one may assume at least two isomers for $(m\text{-}B_{10}H_{10}C_2H_2)^{2-}$ differing in their stabilities. One of the isomers evidently isomerizes rapidly to $(o\text{-}B_{10}H_{10}C_2H_2)^{2-}$ while the other is stable.

In discussing possible mechanisms for the rearrangements of *m*- to *o*- and *p*- to *m*- carboranes through $(B_{10}H_{10}C_2H_2)^{2-}$, mutual repulsion of the negative charges should be assumed to be the driving force of these rearrangements. On the basis of known properties of $(o\text{-}B_{10}H_{10}C_2H_2)^{2-}$, it follows that the density of its two electrons is generally localized at the 3 and 6 positions of the carborane nucleus, i.e. two electrons add to the *o*-carboranes at the most electron-deficient centres. Thus, two electrons might be assumed to add to *m*-carborane also at the sites of lowest electron density, that is at positions 2 and 3. In *m*-carborane these positions are vicinal, so that the mutual repulsion of negative charges makes the anion $(m\text{-}B_{10}H_{10}C_2H_2)^{2-}$ unstable, and it isomerizes to the more stable $(o\text{-}B_{10}H_{10}C_2H_2)^{2-}$ with separated negative charges (its 3 and 6 positions not being vicinal). One might also suggest that two electrons would add to *p*-carborane giving $(p\text{-}B_{10}H_{10}C_2H_2)^{2-}$ in which the highest electron density is localized at

the vicinal positions. Then rearrangement gives $(m\text{-}B_{10}H_{10}C_2H_2)^{2-}$ with separated negative charges, which differs from the anion $(m\text{-}B_{10}H_{10}C_2H_2)^{2-}$ formed by the addition of two electrons to m-carborane. Taking these assumptions into account, the data on the rearrangements obtained for $(B_{10}H_{10}C_2H_2)^{2-}$ are best explained by the following mechanisms: (a) rotation of pentagonal pyramids; or (b) via the cuboctahedral structure, with and without rotation of triangles. In the case of rearrangement through the dianion, 9-halogen-m-carborane should give 9-halogen-o-carborane or a mixture of 9- and 8-halogen o-carboranes, while halogen-p-carborane should give 2-, 4-, 5- and 9-halogen-m-carboranes. In the reaction of two equivalents of sodium with 9-chloro-m-carborane in liquid ammonia followed by oxidation with $KMnO_4$, we obtained 9-chloro-o-carborane together with some o-carborane:

$$9\text{-chloro-}m\text{-carborane} \xrightarrow[\text{NH}_3 \text{ (liq.)}]{2\text{Na}} (B_{10}H_9ClC_2H_2)^{2-} \xrightarrow[\text{K MnO}_4]{-2e}$$
$$9\text{-Chloro-}o\text{-carborane}$$

Reaction of two equivalents of sodium with chloro-p-carborane in liquid ammonia and oxidation with $KMnO_4$ gave, as well as some m-carborane, a mixture of 2-, 4-, 5- and 9-chloro-m-carboranes.

$$9\text{-chloro-}p\text{-carborane} \xrightarrow[\text{NH}_3 \text{ (liq.)}]{2\text{Na}} (B_{10}H_9ClC_2H_2) \xrightarrow[\text{KMnO}_4]{-2e} 2\text{-}, 4\text{-}, 5\text{-}, 9\text{-}$$
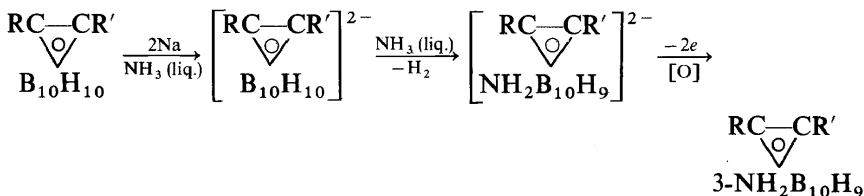$$\text{chloro-}m\text{-carboranes}$$

Analogous results have been obtained by Stanko et al.[34] for the rearrangement of chloro-p-carborane.

Our data are in excellent agreement with a mechanism involving rearrangement via an intermediate cuboctahedron with rotation of triangles by 120 degrees.
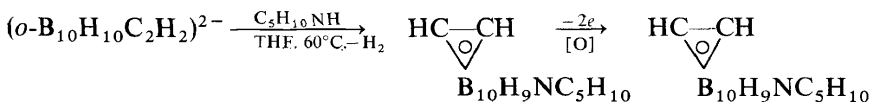
Synthesis of 3-amino-o-carboranes from dodecahydro-1,2-dicarba-$nido$-dodecaborates(2−)

We have shown that dodecahydro-1,2-dicarba-$nido$-dodecaborates(2−) and liquid ammonia react at low temperatures to give hydrogen and B-amino derivatives, the oxidation of which (by $KMnO_4$, $CuCl_2$ etc.) results in high yields of 3-amino-o-carboranes[35, 36]:
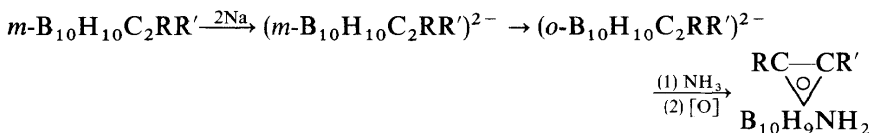
$$\begin{array}{c} RC\!\!-\!\!CR' \\ \diagdown O \diagup \\ B_{10}H_{10} \end{array} \xrightarrow[\text{NH}_3 \text{ (liq.)}]{2\text{Na}} \left[\begin{array}{c} RC\!\!-\!\!CR' \\ \diagdown O \diagup \\ B_{10}H_{10} \end{array}\right]^{2-} \xrightarrow[-\text{H}_2]{\text{NH}_3 \text{ (liq.)}} \left[\begin{array}{c} RC\!\!-\!\!CR' \\ \diagdown O \diagup \\ NH_2B_{10}H_9 \end{array}\right]^{2-} \xrightarrow[\text{[O]}]{-2e}$$

$$\begin{array}{c} RC\!\!-\!\!CR' \\ \diagdown O \diagup \\ 3\text{-}NH_2B_{10}H_9 \end{array}$$

$(o\text{-}B_{10}H_{10}C_2RR')^{2-}$ and the amines have also been found to produce N-substituted 3-amino-o-carboranes. Thus, the heating of a mixture of $(o\text{-}B_{10}H_{10}C_2H_2)^{2-}.2Na^+$ with piperidine in THF and subsequent oxidation

yielded N-3-piperidino-o-carborane[36].

$$(o\text{-}B_{10}H_{10}C_2H_2)^{2-} \xrightarrow[\text{THF. } 60°C.-H_2]{C_5H_{10}NH} \quad \underset{B_{10}H_9NC_5H_{10}}{HC\text{—}CH} \xrightarrow[\text{[O]}]{-2e} \quad \underset{B_{10}H_9NC_5H_{10}}{HC\text{—}CH}$$
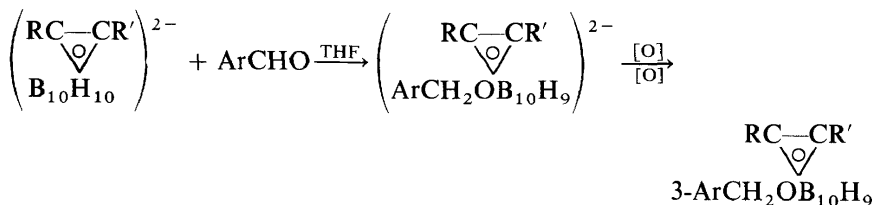
In our new reaction, one NH_2 group enters the carborane nucleus producing only 3-amino-o-carboranes. When applied to m-carboranes this reaction yields 3-amino-o-carboranes instead of B-amino-m-carboranes since, as was shown above, under the reaction conditions $(m\text{-}B_{10}H_{10}C_2RR')^{2-}$ rearranges to $(o\text{-}B_{10}H_{10}C_2RR')^{2-}$

$$m\text{-}B_{10}H_{10}C_2RR' \xrightarrow{2Na} (m\text{-}B_{10}H_{10}C_2RR')^{2-} \rightarrow (o\text{-}B_{10}H_{10}C_2RR')^{2-}$$

$$\xrightarrow[\text{(2) [O]}]{\text{(1) } NH_3} \quad \underset{B_{10}H_9NH_2}{RC\text{—}CR'}$$

Dodecahydrodicarba-*nido*-dodecaborate(2 −) obtained from p-carborane and sodium in liquid ammonia did not react with ammonia[33].

We propose the following mechanism for amination of $(o\text{-}B_{10}C_{10}C_2RR')^{2-}$ anions. In this dianion a considerable part of the electron density extends over the 3 or 6 boron atoms. This increased electron density enhances the mobility of hydrogen atoms bound to these boron atoms. Thus, in the reaction with ammonia and amines the hydride ion is replaced by the amino group to form B—N-bonding and hydrogen[36]. Stanko and Gol'tyapin[37] have suggested that attack by an amide ion rather than by ammonia is more probable.

The fact that the mobility of the hydride ion in the B—N bond is higher at the 3 and 6 positions of $(o\text{-}B_{10}H_{10}C_2H_2)^{2-}$ is also shown by our newly discovered reaction between the anion and aromatic aldehydes resulting in 3-benzyloxy-o-carboranes[38]:

$$\left(\underset{B_{10}H_{10}}{RC\text{—}CR'} \right)^{2-} + ArCHO \xrightarrow{THF} \left(\underset{ArCH_2OB_{10}H_9}{RC\text{—}CR'} \right)^{2-} \xrightarrow[\text{[O]}]{\text{[O]}}$$

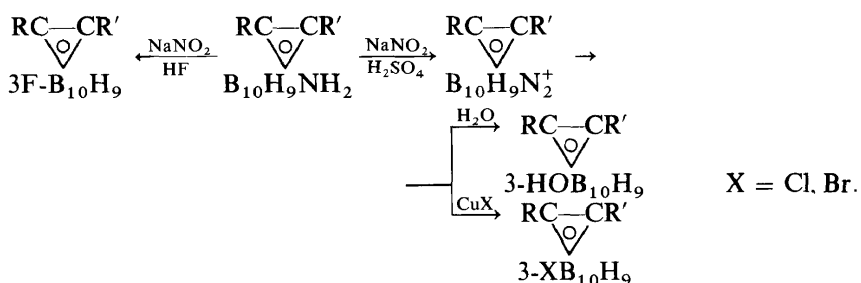$$\underset{3\text{-}ArCH_2OB_{10}H_9}{RC\text{—}CR'}$$

3-Amino-o-carboranes represent an interesting class of compounds which have not been studied before. They provide the route to otherwise unavailable B-functional o-carboranes. 3-Amino-o-carboranes are stable in air. Their properties are similar to those of aliphatic and aromatic amines. They are comparatively weak bases. Basicities of some 3-amino-o-carboranes in 50 per cent alcohol are listed in *Table 4*.

We have investigated in detail the properties of 3-amino-o-carboranes[36, 38]. The conversion of amines to other derivatives is most interesting. Diazotization of 3-amino-o-carboranes with nitrous acid led to the unstable diazonium salt which then decomposed in water to yield 3-hydroxy-o-carboranes. In the presence of CuCl and CuBr or liquid HF, the diazonium salts cleaved
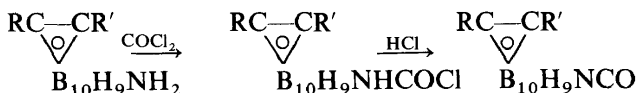
Table 4. pK_a values for *o*-carborane-3-ammonium salts in
50 per cent ethanol

$$\underset{B_{10}H_9NH_3^+}{RC\!\!-\!\!CR'}$$

Amines	pK_a
3-Amino-*o*-carborane	3.17
1-Methyl-3-amino-*o*-carborane	3.00
1-Ethyl-3-amino-*o*-carborane	2.93
1.2-Dimethyl-3-amino-*o*-carborane	2.53
1-Phenyl-3-amino-*o*-carborane	2.70
p-Chloroaniline	3.98

to give the respective 3-halogen-*o*-carboranes:

$$\underset{3F\text{-}B_{10}H_9}{RC\!\!-\!\!CR'} \xleftarrow[HF]{NaNO_2} \underset{B_{10}H_9NH_2}{RC\!\!-\!\!CR'} \xrightarrow[H_2SO_4]{NaNO_2} \underset{B_{10}H_9N_2^+}{RC\!\!-\!\!CR'} \rightarrow$$

$$\xrightarrow{H_2O} \underset{3\text{-}HOB_{10}H_9}{RC\!\!-\!\!CR'} \qquad X = Cl, Br.$$

$$\xrightarrow{CuX} \underset{3\text{-}XB_{10}H_9}{RC\!\!-\!\!CR'}$$

Action of $COCl_2$ on 3-amino-*o*-carboranes in boiling chlorobenzene gave *o*-carboran-3-yl-isocyanates.

$$\underset{B_{10}H_9NH_2}{RC\!\!-\!\!CR'} \xrightarrow{COCl_2} \underset{B_{10}H_9NHCOCl}{RC\!\!-\!\!CR'} \xrightarrow{HCl} \underset{B_{10}H_9NCO}{RC\!\!-\!\!CR'}$$

Reaction of $POCl_3$ with *N*-formylamino-*o*-carboranes in the presence of pyridine gave *o*-carboran-3-yl-isonitriles in a smooth reaction.

$$\underset{B_{10}H_9NH_2}{RC\!\!-\!\!CR'} \xrightarrow{HCOOH} \underset{B_{10}H_9NHCHO}{RC\!\!-\!\!CR'} \xrightarrow[C_5H_5N]{POCl_3} \underset{B_{10}H_9NC}{RC\!\!-\!\!CR'}$$
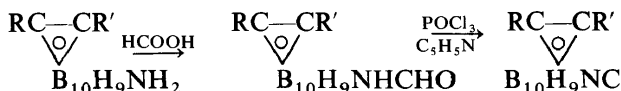
At 200°C in decalin, these isonitriles completely rearranged to the respective *o*-carboran-3-yl-nitriles.

$$\underset{B_{10}H_9NC}{RC\!\!-\!\!CR'} \xrightarrow{200°C} \underset{B_{10}H_9CN}{RC\!\!-\!\!CR'}$$
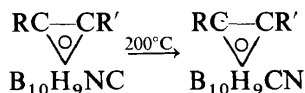
A two-step hydrolysis of the nitriles gave high yields of 3-*o*-carborane carboxylic acids[39]:

$$\underset{B_{10}H_9CN}{RC\!\!-\!\!CR'} \xrightarrow[CH_3COOH]{H_2SO_4} \underset{B_{10}H_9CONH_2}{RC\!\!-\!\!CR'} \xrightarrow[H_2SO_4]{NaNO_2} \underset{B_{10}H_9COOH}{RC\!\!-\!\!CR'}$$

These acids have properties analogous to those of the aliphatic and aromatic

carboxylic acids. They are, however, weaker acids than the corresponding 1-*o*-carborane acids.

Table 5 shows the pK_a values for some *o*- and 3-*o*-carborane carboxylic acids in 50 per cent ethanol[40].
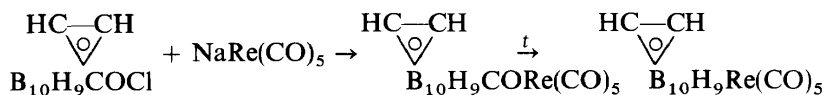
Table 5. pK_a values for 1-*o*- and 3-*o*-carborane carboxylic acids in 50 per cent ethanol at 25°C

Acid	pK_a
HC—CH $B_{10}H_9COOH$	5.38
CH_3C—CH $B_{10}H_9COOH$	5.47
HC—C—COOH $B_{10}H_{10}$	2.60

3-*o*-Carboranecarboxylic acids provide attractive possibilities for the synthesis of *B*-substituted *o*-carboranes. In particular, we have prepared derivatives of transition metals containing a transition metal–boron bond[41] starting from 3-*o*-carborane carboxylic acid

HC—CH
$B_{10}H_9COCl$ + $NaFe(CO)_2C_5H_5\pi$ → HC—CH
$B_{10}H_9COFe(CO)_2C_5H_5\pi$

→ HC—CH
$B_{10}H_9Fe(CO)_2C_5H_5\pi$
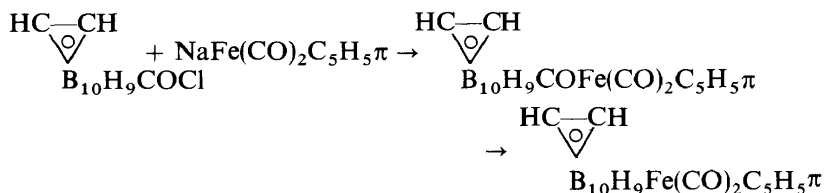
Metal carbonyl derivatives have also been synthesized.

HC—CH
$B_{10}H_9COCl$ + $NaRe(CO)_5$ → HC—CH
$B_{10}H_9CORe(CO)_5$ $\xrightarrow{t}$ HC—CH
$B_{10}H_9Re(CO)_5$

Studies of various *o*-carborane *B*-derivatives have shown that the behaviour of boron in the carborane nucleus is very similar to the behaviour of carbon in purely organic compounds.

ACKNOWLEDGEMENT

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