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REVIEW

Synthesis and Reaction Mechanisms of Cage Organoboranes with Reactive Precursors

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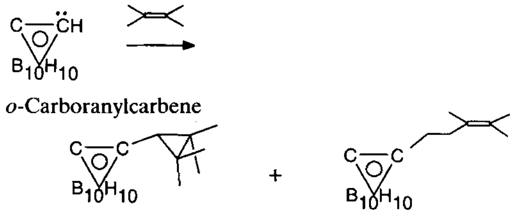
Keywords: organoboranes; cages; synthesis

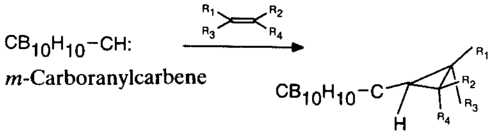
1 INTRODUCTION

The reaction of decaborane(14) with acetylenic compounds in the presence of Lewis bases has resulted in members of a class of organoboranes.[1-4] A typical reaction of 1,2-dicarba-*closo*-dodecaborane(12), $C_2B_{10}H_{12}$, and its thermal rearrangement have been well studied.[5-13] The structure of this compound shows a regular icosahedron with two carbon atoms at adjacent vertices.[14] In addition, there are two other isomers[15, 16] in the $C_2B_{10}H_{12}$ family, namely 1,7-$C_2B_{10}H_{12}$ and 1,12-$C_2B_{10}H_{12}$ (Fig. 1), which are identified as *m*-carborane and *p*-carborane. The icosahedral carboranes, 1,2-, 1,7- and 1,12-$C_2B_{10}H_{12}$ are in general use as high-boron-content materials; they are remarkably thermally stable substances, and resistant towards acids and biological reagents. Despite their cost, such properties make them suitable for various specialized applications. These include the incorporation of large concentrations of boron atoms in tumor-seeking drugs for boron neutron capture therapy (BNCT),[17-19] and the synthesis of polymers for high-temperature[20] or neutron-shielding purposes or for firing to form ceramics related to boron carbide.[21]

O-carborane and its derivatives have been described as superaromatics on the basis of extensive molecular orbital calculations.[22-25] However, it is not in as much accordance with the experimental thermodynamic stability as is the case for benzene and its derivatives.[26] The *o*-carboranes display strong electron-withdrawing character with respect to substituents attached at the carbon atoms.[27] To make a comparison between the additions of phenylcarbene and carboranylcarbenes, the additions of *o*- and *m*-carboranylcarbenes to olefins have been observed through the reactions of diazomethyl-*o*-carborane with various olefins.[28] It was concluded that the addition of *o*- and *m*-carboranylcarbenes occurs in a largely stereospecific fashion (Eqns [1] and [2]).



[1]



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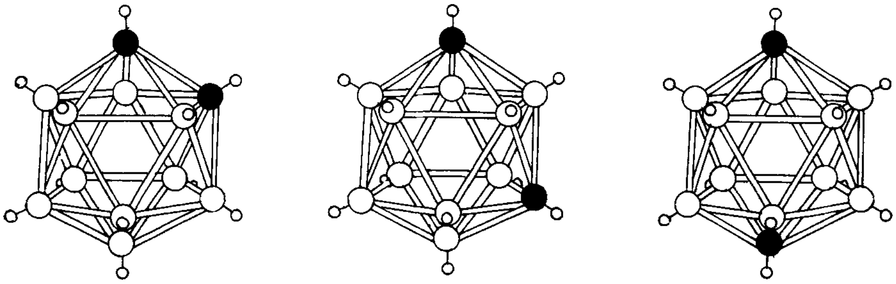

1,2-$C_2B_{10}H_{12}$ 1,7-$C_2B_{10}H_{12}$ 1,12-$C_2B_{10}H_{12}$

Figure 1 Structure of icosahedral carborane isomers.

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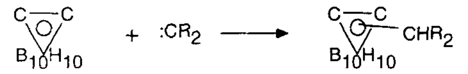
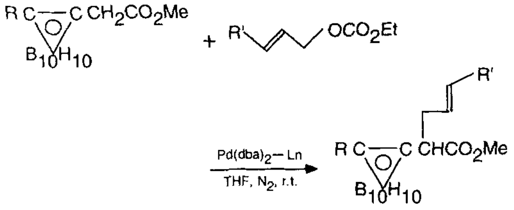
Based on another point of view, the carbene insertion products were generated by the reaction of *o*-carborane directly with the reactive carbenes (Eqn [3]).[29]



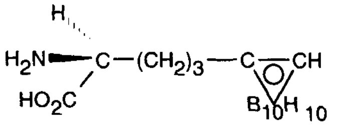
[3]

The strong electron-withdrawing effect of the 1-*o*-carboranyl group results in an essentially increasing acidity of functionally connected acid, hydroxy, amino and mercapto substituents.[22,30,31] The acidity of CH_2 protons in 1-methyl-2-benzyl-*o*-carborane has been shown to be higher than the acidity of the C–H bond of *o*-carborane on the same scale.[32] It would be expected that the exchange of the phenyl group in 1-methyl-2-benzyl-*o*-carborane with a more electron-withdrawing group (carbomethoxy) would promote increasing acidity of the CH_2 protons. In order to test the ability of carboranylacetic esters to form a stabilized carbanion, the palladium-catalyzed allylation of carbonucleophiles was carried out under neutral conditions using allylic carbonates (Eqn [4]).[33]



[4]

Lipophilic clusters including *closo*-carborane derivatives have been synthesized for useful medicines for boron neutron capture therapy (BNCT).[34] Hexadecyl-*o*-carborane was synthesized by the reaction of 1-octadecyne and decarborane in a solution of acetonitrile and benzene.[35] However, the yield was somewhat low (30%). A new compound for BNCT was synthesized recently, i.e. 5-(1,2-dicarba-*closo*-dodecaborane-(12)-1-yl)-2-aminopentanoic acid i.e. (**1**), which acts as a good receptor to bind cancer cells selectively by using an alkylation of the boron cage skeleton.[36] The receptor compound is obtained via alkylation of imidazolidine with a protected alkylsilyliodoalkylcarborane. Alkylsilylcarboranes are very important protecting reagents for the synthesis of receptor compounds.

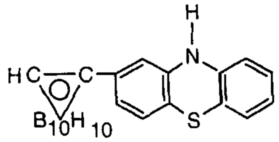


(**1**)

A new approach to the synthesis of disilacarborane has been reported, including the successful synthesis of a disilacarboranyl polymer, by the reaction of bis(dimethylamino)silanes with decarborane (Eqn [5]).[37]

$$\begin{aligned} &H_3C(H)Si[N(CH_3)_2]_2 + B_{10}H_{14} \\ &\rightarrow H_2 + (CH_3)_2NH + 6,9\text{-}[(CH_3)NH]_2B_{10}H_{12} \\ &+ B_{10}H_{10}(SiCH_3)_2 \qquad [5] \end{aligned}$$

From a large number of candidates, ^{10}B-enriched *o*-carborane derivatives were selected recently for use in clinical trials.



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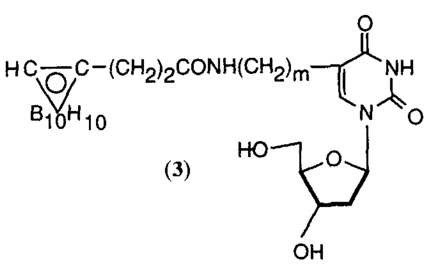

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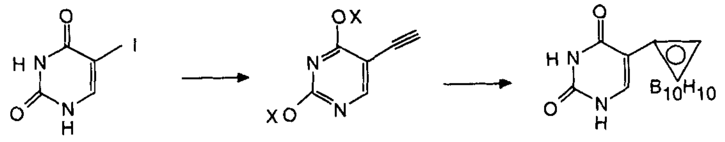


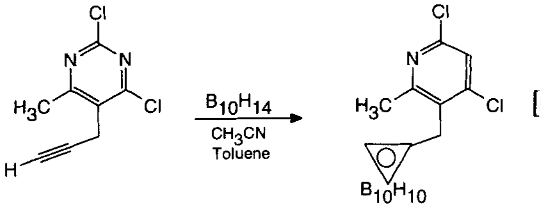
Scheme 1

Soloway *et al.* attached *o*-carboranyl cages to phenothiazine derivatives (**2**)[38] and to the 5-position in pyrimidine nucleosides[39] linked through an appropriate spacer to the 5-position of the base (**3**).

5-Carboranyluracil was synthesized as a versatile intermediate for the synthesis of a number of nucleoside analogs, starting from the commercially available 5-iodourcil, by Goudgaon *et al.* (Scheme 1).[40]

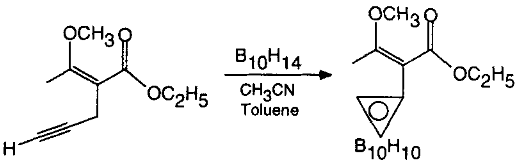
Many synthetic routes to 5-(1-*o*-carboranylmethyl)-substituted pyrimidines have been reported, including the successful synthesis of 2, 4 - dichloro - 5 - (1 - *o* - carboranylmethyl) - 6 - methyl-pyrimidine.[41–44]

The various reaction procedures by which pyrimidines and their nucleosides are utilized in the cell make these bioactive molecules a particularly attractive target for boronation in order to concentrate ^{10}B in actively replicating tissue. Furthermore, a successful approach provides a strategy for the synthesis of 2,4-dichloro-5-(1-*o*-carboranylmethyl)-6-methylpyrimidine (Eqn [6]).[45]



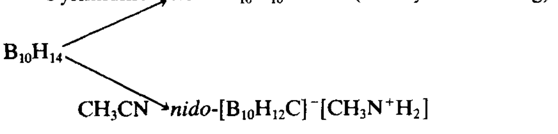
[6]

Though decarborane reacts on pentanoate derivatives (Eqn [7]), the reaction has been shown to be depended on the acetonitrile concentration.



[7]

A parallel second-order reaction was observed by the reaction of *nido*-$B_{10}H_{14}$ with alkynylpyrimidines.[46] Competitive generation of *nido*-$[B_{10}H_{12}C]^{-}[MeN^{+}H_2]$ and *closo*-$B_{10}H_{10}CHCR$ is observed from the reaction (Scheme 2).



Scheme 2

Other *closo*-$C_2B_{n-2}H_n$ carboranes, with $n = 6–12$, were synthesized.[47] These carborane molecules react with organic molecules, and isomers can be generated by movement of the polyhedral carbon atoms relative to each other over the polyhedral surface.[1, 48]

Synthesis of a molecule which contains both an *o*-carborane and an organic molecule such as pyrimidine is especially difficult because *o*-carborne is a quite stable solid. Furthermore, its *o*-carboranyl anion is a weak nucleophile. This behavior suggests that the S_N2 reaction of the *o*-carboranyl anion with primary alkyl halides will not occur easily. S_N2 reaction with a sterically encumbered molecule such as a tertiary alkyl halide will not give an *o*-carboranyl compound.

We have now investigated the possibilities of a new synthesis of *o*-carborane derivatives using very rective precursors (carbenes) and describe in the next section the synthesis and the reaction mechanism.

2 BORON CLUSTER EXPANSION REACTIONS

Our original interest in the chemistry of boron cluster expansion reactions grew out of our studies of the reactions of carbene precursors with polyhedral boranes. In particular, we were interested in the development of new methods of promoting carbene insertion reactions on boron clusters. Boron cluster expansion by reaction of decaborane with nitriles has usually involved initial electrophilic addition at nitrogen to produce carboranylnitriles (Eqn [8]).[51–54]

$$2RC{\equiv}N + B_{10}H_{14} \rightarrow 6,9\text{-}(RCN)_2B_{10}H_{12} + H_2 \quad [8]$$

We felt that *nido*-decaborane ($B_{10}H_{14}$) might also be able to undergo similar types of expansion reaction using reactive intermediates such as carbenes. Reactive carbenes act as electrophiles, nucleophiles or ambiphiles.[55–57] Dihalocarbenes ($:CCl_2$, $:CBr_2$) seem to behave as electrophiles. The relative reaction rates decrease continuously with decrease in the π-electron donor ability of the olefines.[55, 56, 58–62]

Dihalocarbenes can react with both electron-rich and electron-poor alkenes, but the reactivity depends on the nature of the alkene. Two borons at the 6- and 9-positions in decaborane might behave as electrophilic centers for reaction with dihalocarbenes, and then undergo intramolecular rearrangements to yield the expansion cluster

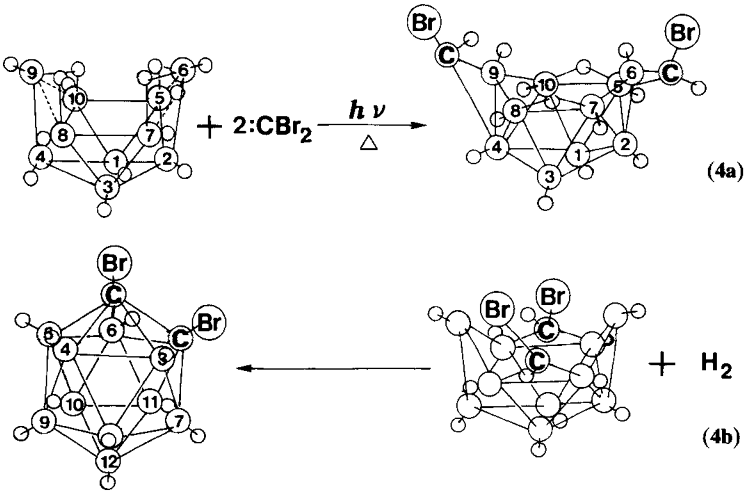


Figure 2 Mechanism for formation of 1,2-$Br_2C_2B_{10}H_{10}$.

compound. Indeed, we found that decarborane, $B_{10}H_{15}$, reacts with dibromocarbene, $:CBr_2$, to give 1,2-dibromo-*o*-carborane (Eqn [9]).[63]

$$nido\text{-}B_{10}H_{14} + 2\ :CBr_2 \rightarrow 1,2\text{-}Br_2C_2B_{10}H_{10} \quad [9]$$

The dibromocarbene precursor, phenyltribromomethylmercury, was prepared by Seyferth's method (Eqn [10]).[64-65]

$$C_6H_5HgBr + CHBr_3 + t\text{-}BuOK$$
$$\rightarrow C_6H_5HgCBr_3 + KBr + t\text{-}BuOH \quad [10]$$

Phenyltribromomethylmercury produces dibromocarbene by photolysis or thermal decomposition (Eqn [11]).[65-68]

$$C_6H_5HgCBr_3 \xrightarrow[\Delta]{h\nu} :CBr_2 + C_6H_5HgBr \quad [11]$$

nido-$B_{10}H_{14}$ did not react with the phenylmercuric species but reacted selectively with $:CBr_2$. The yield of 1,2-$Br_2C_{10}H_{10}$ increased from 45% to 70% when $:CBr_2$ was produced in the presence of NaI in a solution of CCl_4 and C_6F_6, more than in the presence of *t*-BuOK (Eqn [12]).

$$nido\text{-}B_{10}H_{14} + 2C_6H_5HgCBr_3 + 2NaI$$
$$\xrightarrow[CCl_4,\ C_6F_6]{h\nu,\ \text{reflux}} 1,2\text{-}Br_2C_2B_{10}H_{10} + 2C_6H_5HgBr$$
$$+ 2NaBr + 2HI + H_2 \quad [12]$$

The product, 1,2-$Br_2C_2B_{10}$, was characterized by a combination of ^1H, ^{11}B and ^{13}C NMR, IR and Mass Spectrometry.[63]

The ^{11}B NMR spectrum ($CDCl_3$) showed four peaks at δ_B −2.79, −1.04, 1.25 and 8.10 ppm. The B—H proton peaks for the positions, 4,5,7,11 appeared at δ_H 2.83, B—H positions for 8,9,10,12 at δ_H 2.01, and the 3,6 B—H positions at δ_H 3.62 in the ^1H NMR ($CDCl_3$). One peak corresponding to the two C—Br in 1,2-$Br_2C_2B_{10}H_{10}$ appeared at δ_C 81.6.

The observed formation of 1,2-$Br_2C_2B_{10}H_{10}$ as one produce by the reaction of $B_{10}H_{14}$ with a unique carbene was unexpected and its reaction mechanism seems to be complicated. However, a reasonable mechanism for formation of 1,2-$Br_2C_2B_{10}H_{10}$ might be explained from this work as shown in Fig. 2.

The first step in this reaction (Eqn [9]) is the addition of two molar equivalents of dibromocarbene produced from phenyltribromomethyl mercury to *nido*-$B_{10}H_{14}$, which then generates the produce through loss of H_2. The ten boron atoms of the *nido* structure remain in a fixed state in their polyhedral arrangement before the cluster expansion.[63]

The insertion of $:CBr_2$ in *nido*-$B_{10}H_{14}$ probably proceeds through deprotonation of the acidic centers of B(9) and B(6) of *nido*-$B_{10}H_{14}$ by the lone electron pair of the carbene.

After deprotonation, the cluster rearrangement from **4a** to **4b** occurs rapidly and then a new neutral bond between the two carbon atoms forms to give the final product, as shown in Fig. 2.

1,2-$Br_2C_2B_{10}H_{10}$ is very unstable at room temperature and is stable in methanol. The potassium salt of $1,2\text{-}Br_2C_2B_{10}H_{10}$, however, is stable in water.

Irradiation of decaborane with trimethylsilyldiazomethane (**5**) generated *closo*-compound **6**, which was isolated as an air-stable, white, solid product (Eqn [13]).[69] As well as the product (**6**), $6,9\text{-}(N_2CH_2SiMe_3)_2B_{10}H_{12}$ (**7**) was formed concurrently as minor component (Eqn [14]).

$$\textit{nido}\text{-}B_{10}H_{14} + 4\underset{\mathbf{5}}{(CH_3)_3SiCHN_2} \xrightarrow[C_6H_5CH_3]{h\nu,\ \text{reflux}} \underset{\mathbf{6}}{\textit{closo}\text{-}1,2\text{-}(SiMe_3)_2C_2B_9H_{11}} + HB(N_2CHSiMe_3)_2 + 2N_2 + 2H_2 \qquad [13]$$

$$\textit{nido}\text{-}B_{10}H_{14} + 2\underset{\mathbf{5}}{(CH_3)_3SiCHN_2} \xrightarrow[C_6H_5CH_3]{h\nu,\ \text{reflux}} \underset{\mathbf{7}}{\textit{nido}\text{-}6,9\text{-}(N_2CH_2SiMe_3)_2B_{10}H_{12}} \qquad [14]$$

The yield of products **6** and **7** vary with duration of irradiation or heating conditions, as shown in Table 1.[69] Irradiation of diazo compound **5** can lead to a reactive carbene intermediate, e.g. $Me_3SiCH{:}$, but thermal reaction in the dark gives a less reactive azine intermediate, $Me_3SiCH{=}N{-}N{=}CHSIMe_3$.[70] Compound **7** is soluble only in solvents such as *N,N*-dimethylformamide and dimethyl sulfoxide.

Compound **7** melted with decomposition above 198 °C. This results from weaker B–N bonding in the *nido* structure. However, when *nido*-$B_{10}H_{14}$ was reacted with the diazo compound (**5**) with irradiation in toluene, a white precipitate was formed after a 10 h reflux. The structures of the reaction products **6** and **7** are shown in Fig. 3.

Table 1 Relative yields of reaction of decaborane with trimethylsilyldiazomethane[69]

	Conditions			
Product	Temp. (K)	Radiation	Yield (%)	Relative yield
6	383	*hν*	37	1.00
	323	*hν*	19	0.52
	293	*hν*	5	0.14
	383	(Dark)	0	0.00
7	383	*hν*	34	1.00
	383	(Dark)	34	1.00
	293	*hν*	18	0.53
	293	(Dark)	18	0.53

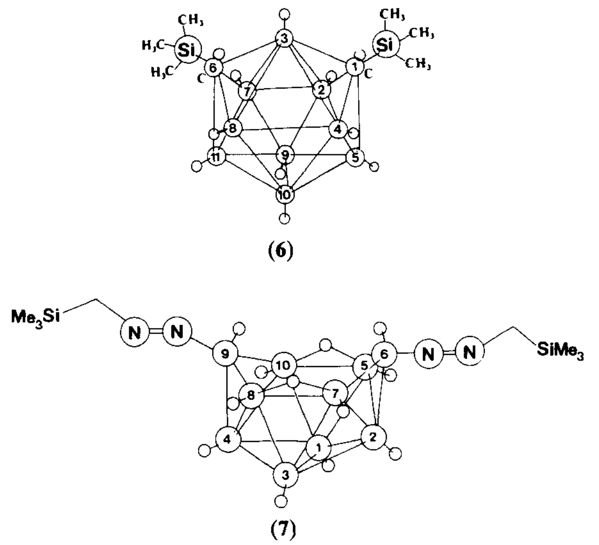


Figure 3 Structure of *closo*-$1,2\text{-}(SiMe_3)_2C_2B_9H_{11}$ (**6**) and *nido*-$6,9\text{-}(N_2CH_2SiMe_3)_2B_{10}H_{12}$ (**7**).

Product analysis and geometry-optimized calculations indicate that **6** has a deltahedral structure.[69] Two C—Si(Me)$_3$ vertices are substituted for two B—H vertices of *nido*-decaborane. Neighboring, similarly charged, C—Si(Me)$_3$ vertices repel each other so that charge smoothing tends to favor *closo*-carborane wherein the two carbons are separated as nonadjacent sites.[51,71] The Si–C bond distances (1.827 Å, on the average) in **6** are very close to those of 1,2-dimethyl-1,2-disila-*closo*-dodecaborane(12). The B–B bond distances in **6** are very similar to the *closo*-carborane structures, supported by the fact that the C–Si bond distance is within the normal C–Si single-bond range.[73] Compound **6** is a *closo* structure with four aberrant open faces, as shown in Fig. 3. However, the structure of **7** is of a four open-faced *nido*-form.

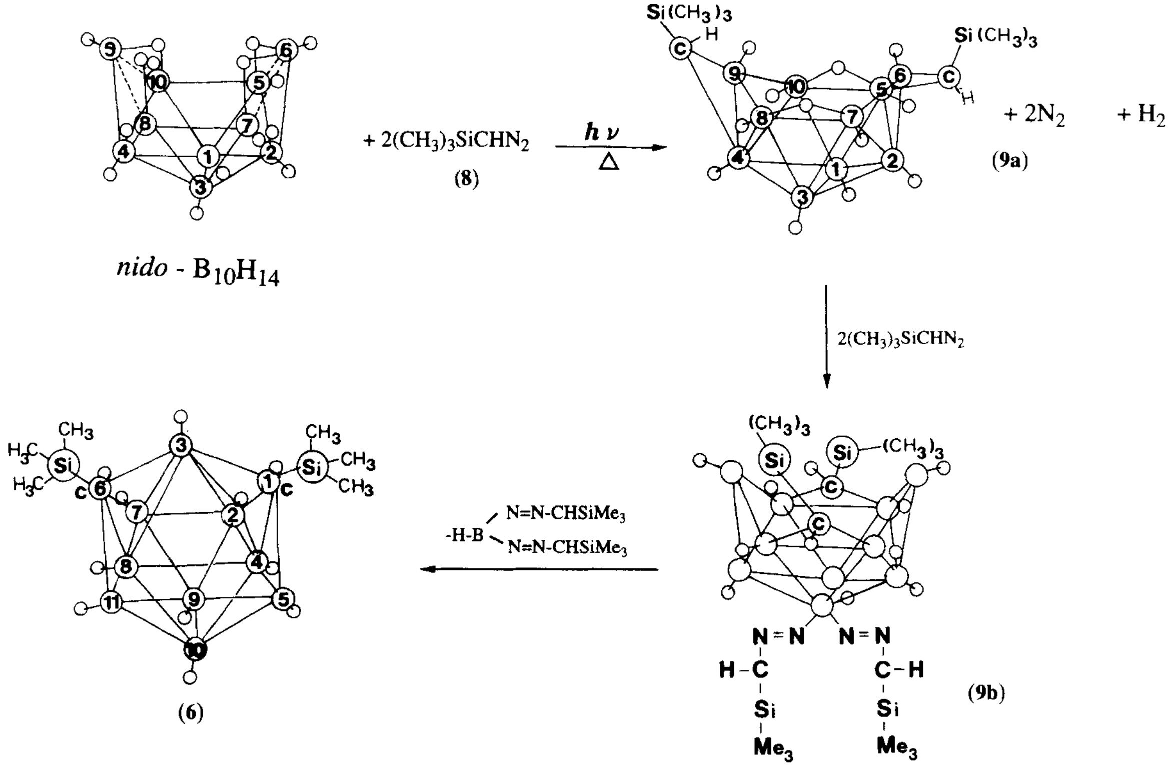
Other B–B–B and B–B–C bond angles in **6** are similar to those in other four-faced *closo*-carborane compounds.[74] The ^{11}B NMR spectrum, taken in $CDCl_3$ solution, shows the five peaks at δ_B −7.84, −7.51, −12.3, −16.7 and −22.9 ppm. The $SiMe_3$ peak appears at δ 0.053–1.22 ppm in the ^1H NMR spectrum of **6** in $CDCl_3$, moving downfield in CD_2Cl_2 to 0.69–1.28 ppm. The IR spectrum of **6** was measured in the region 450–3500 cm^{-1} and its Raman spectrum was also obtained in the region 400–3600 cm^{-1}.

Polarization measurements of Raman lines were carried out in a saturated solution in benzene.

The most prominent features of the vibrational spectra of all cage *closo*-boranes are the ν(BH) multiplet in the region 2490–2520 cm^{-1} and the polyhedron 'breathing' mode near 781 cm^{-1}. In the case of **6** the ν(BH) medium bands show near 2519 cm^{-1}. In the case of **6** the ν(BH) medium bands show near 2519 cm^{-1} and the breathing mode comes near 695 cm^{-1}, both features being markedly shifted to lower frequencies compared with the *closo*-carboranes. The frequency shifts seem to be caused by weakening of molecular bonding in **6** as compared with that in *closo*-carborane. The most intense peak in the Raman spectrum is the strongly polarized 912 cm^{-1} band, which corresponds to the ν(C—B) mode of alkylboranes.[75]

The polarized Raman line at 705 cm^{-1} seems to be the symmetrical stretch of the exo-polyhedral Si—C bands. This frequency lies in the usual range of Si—C bonds and is similar to that of the ν(Si—C) mode in $Si(CH_3)_4$[76] and $(CH_3)_3SiCl$.[77]

The formation of **6** as one product of the reaction of decaborane with a diazo compound (**5**) was unexpected and its reaction of decaborane with a diazo compound (**5**) was unexpected and its reaction mechanism seems to be complicated. A reasonable interpretation of the formation of **6** is under investigation. However, a reaction mechanism for the formation of **6** is proposed as follows. The first step in this reaction is the addition of two molar equivalents of **8**, a Lewis base, to *nido*-$B_{10}H_{14}$. Adduct **9a** was generated through loss of H_2 and N_2 as shown in Scheme 3. The ten boron atoms of the *nido* structure remain in a fixed state in the polyhedral arrangement during the cluster expansion. The formation of adduct **9a** proceeds through deprotonation of the acidic center of B(9) and B(6) by intermolecular attack of the lone electron pair of the carbene, :$CHSiMe_3$. Rapid rearrangement of the neutral $BBCHSiMe_3$ bond from **9a** occurs to produce **9b** as depicted in Scheme 3. Additional $(CH_3)_3SiCHN_2$ reacts with the B—H (3-position) of **9a** to remove the carbon atom from the adduct **9b**. In the final step, which results in the formation of **6**, there is an intramolecular rearrangement to make a new bond to form the final *closo* compound.



Scheme 3

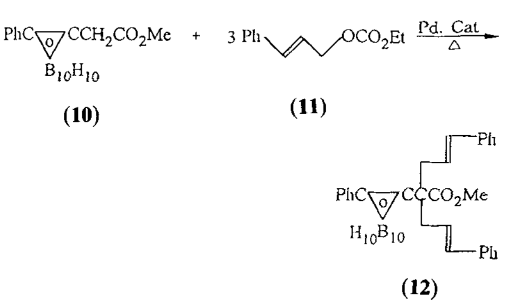
3 ALLYLATION OF *o*-CARBORANYL ESTERS

There has been considerable interest in the synthesis of mono- or di-substituted icosahedral 1,2-$C_2B_{10}H_{12}$ carborane derivatives. However, many of the complex organic structures desired are not always possible to attain through known synthetic methods for *C*-substituted *o*-carborane species. A limited number of *C*-substituted *o*-carborane derivatives have been synthesized by using monolithiation[78] of *o*-carborane and the conversion reaction[79] of *t*-butyldimethylsilyl chloride with *o*-carborane.

We have investigated the synthesis of new types of *C*-substituted *o*-carborane derivatives using stabilized carbonucleophiles based on the strong electron-withdrawing effect of the *cage*-carboranyl group.

To test the ability of carboranylacetic esters to form stabilized carbanions, palladium-catalyzed *C*-allylation of carbonucleophiles has been carried out under neutral conditions using allylic carbonates.[80] The strongly electron-deficient *cage*-carborane 1-*o*-$C_2B_{10}H_{11}$ results in an essentially increasing acidity for connecting with basic substituents.[31, 81]

Treatment of methyl 2-(2-phenyl-*o*-carboran-1-yl)acetate (**10**) with excess (about 3 mol) of ethyl cinnamylcarbonate(**11**), bis(dibenzylideneacetone ($Pd(dba)_2$) and 1,2-bis(diphenylphosphino)-ethane (DPPE) in THF at 60 °C under nitrogen for 5 h, gave the corresponding disubstituted *C*-allylated product **12** in good to excellent yields (Eqn [15].[82]

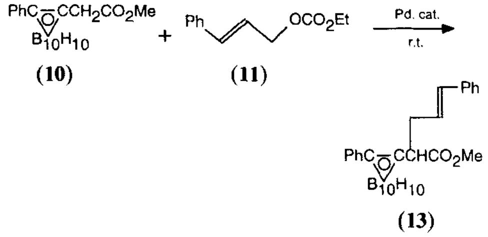


[15]

Palladium-catalyzed *C*-allylation of the *o*-carboranylacetic ester **10** with the corresponding carbonates in THF was very sensitive to the CH-acidity of the carbonucleophiles. To find optimum conditions for *C*-allylation of **10**, the molar ratio of palladium catalysts has been investigated. The yield of disubstituted *C*-allylated product **12** was affected significantly by the reaction conditions. The yield of **12** was influenced by the molarity of $Pd(dba)_2$ and by the reaction temperature.

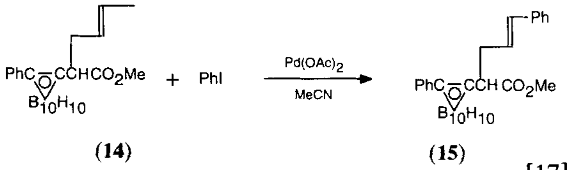
A small amount of the catalyst, below 2 mol%, gave poor yields (about 50%); however, increasing the molar ratio of $Pd(dba)_{21}$ to 3–10 mol% enhanced the yield of product **12** to 80–90%. The most effective amount of reaction catalyst was about 5 mol%.[82]

The reaction of methyl 2-(2-phenyl-*o*-carboran-1-yl)acetate (**10**) with 1 mol of ethyl cinnamylcarbonate (**11**) in the presence of $Pd(dba)_2$ and DPPE in THF at room temperature gave the mono-*C*-allylated product (**13**) as previously reported (Eqn [16]).[83]



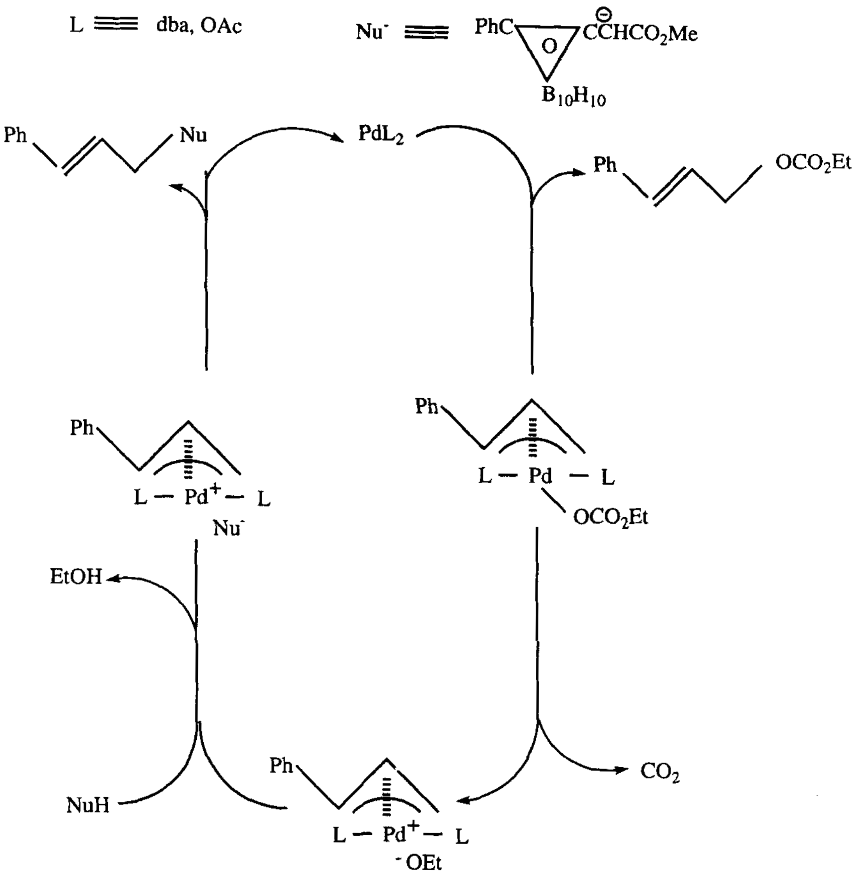
[16]

A very simple additional allylation of carbonucleophile **10** occurred easily by the reaction of the *C*-allylated compound, methyl 2-(2-phenyl-*o*-carboran-1-yl)-2-allylacetate (**14**), with iodobenzene in the presence of $Pd(OAc)_2$ in acetonitrile (Eqn [17]).[82]

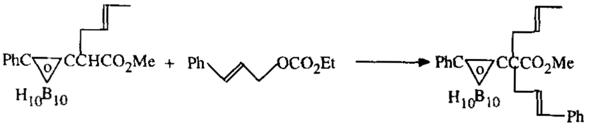


[17]

This reaction has limited utility because of the need to use a stoichiometric quantity of $Pd(OAc)_2$. When the molar ratio of $Pd(OAc)_2$ to **14** was 4 mol%, the most effective reaction time was 6 h for the formation of methyl 2-(2-phenyl-*o*-carboran-1-yl)-2-cinnamylacetate (**15**). The corresponding di-substituted *C*-allylated *o*-carborane derivatives were prepared from mixtures of methyl 2-(2-phenyl-*o*-carboran-1-yl)-2-allylacetate (**14**), ethyl cinnamylcarbonate (**11**), $Pd(dba)_2$ and DPPE in THF at room temperature (Eqn [18]).



Scheme 4



(14) (11) (16) [18]

In this reaction the starting material, **14**, was prepared by the synthetic route for **13**. Mono- or di-substituted *C*-allylations of *o*-carborane derivatives using palladium catalysts can be explained by a previously proposed mechanism[84, 85] as shown in Scheme 4.

Oxidative addition of the ethyl allyl carbonate (in this case the cinnamyl carbonate) to the palladium(0)–phosphine complex gives the π-allylpalladium carbonate, which undergoes decarboxylation to form a π-allylpalladium ethoxide. As soon as the ethoxide anion is formed, abstraction of an active hydrogen from an active methylene on the carboranylacetic ester occurs to generate a carbanion. The carbanion forms without addition of bases when allylation occurs with allylic carbonates. Finally, nucleophilic attach of the carbanion on the π-allylpalladium gives the allylated product and palladium(0)–phosphine is regenerated.

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