

The formation of boron–carbon bonds to *closo*-decaborate(2–) and *closo*-dodecaborate(2–)

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Abstract

This review describes possibilities of introducing carbon-containing substituents into *closo*-polyhedral boron clusters by formation of boron–carbon bonds. The $B_{12}H_{12}^{2-}$ cluster can be reacted with carbocations. Reactions under Friedel–Crafts conditions with acyl halides usually lead to halogenation rather than substitution with organic residues. The CO group can be introduced readily to yield starting material for further reactions. Pd-catalyzed Grignard reactions of the monoiodo derivative of $B_{12}H_{12}^{2-}$ lead to the formation of B–C bonds. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The formation of bonds between carbon atoms and boron clusters is of potential interest for the formation of boron–organic compounds. Such compounds could be of use in boron neutron capture therapy (BNCT), but also in other applications. Especially noteworthy is the high propensity of the clusters to donate electrons to substituents.

In the past, a number of methods have been described to prepare bonds between carbon and cluster boron atoms with intervening heteroatoms such as sulfur [1], oxygen [2] and nitrogen [3]. In contrast, the formation of a direct boron–carbon bond appears to be less investigated.

In this review, work on the formation and the properties of boron–carbon bonds to the $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ clusters is summarized.

2. Chemical properties of the $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ cages

Both cages carry two negative charges, in accordance with the electron count of the entities. They exhibit a remarkable stability toward oxidation, thermal decomposition, and hydrolysis, both under acidic and under alkaline conditions. In the $B_{12}H_{12}^{2-}$ cluster, all twelve atoms are identical. Disubstitution can lead to three different isomers, trisubstitution, to five. The electron density distribution of the cluster has been calculated by the ELF method [4]. The highest electron density is found to be centered on the triangles formed by the boron atoms.

In the $B_{10}H_{10}^{2-}$ cluster, the boron atoms 1 and 10 are equivalent, but different from the other eight boron atoms. The boron atoms 1 and 10 are named apical, whereas the other eight boron atoms are named equatorial. It has been proposed that the equatorial positions 2 through 9 of the $B_{10}H_{10}^{2-}$ cluster are chemically more similar to the boron atoms of $B_{12}H_{12}^{2-}$, whereas the two apical atoms differ [5].

Sulfur is introduced rather readily into the $B_{12}H_{12}^{2-}$ cluster, by the reaction with thione derivatives such as thiourea and N-methylthiopyrrolidone, but also just

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with H_2S under pressure [6]. In all cases, either the hydronium salts of the cluster or hydronium salts of reagents are used. Monosubstitution is observed, with little or no disubstitution.

Oxygen can be introduced in a similar manner. Heating of the tetrabutylammonium salt of $\text{B}_{12}\text{H}_{12}^{2-}$ with carboxylic acids leads to O-substituted mono- and diacyloxyderivatives [7]. Disubstitution is observed, and is usually on atoms 1 and 2. Alkoxy derivatives are also obtained from ethers under acidic conditions [8].

In both cases, the cluster appears to react as electrophile. In the reaction to the amino derivative $\text{B}_{12}\text{H}_{11}\text{NH}_2^-$, the cluster attacks hydroxylamine-O-sulfonic acid as nucleophile instead. Also in the case of acid-catalyzed reactions, the first step of the reaction, namely protonation of the cage, might be considered a nucleophilic reaction of the cage, which as a consequence leads to a reduction of the electron density of the cluster which then makes the cluster more amenable to nucleophilic attack by heteroatoms. This could be the reason why reaction with hydrogen halide leads to monochlorination with HCl , but to polyfluorination with HF [9].

The $\text{B}_{10}\text{H}_{10}^{2-}$ cage is much less investigated with respect to its chemical properties.

3. H^+ -catalyzed reactions of $\text{B}_{12}\text{H}_{12}^{2-}$ and $\text{B}_{10}\text{H}_{10}^{2-}$ with carbon-containing compounds

An overview of reactions leading to the formation of boron–carbon bonds with $\text{B}_{12}\text{H}_{12}^{2-}$ is found in Fig. 1.

A number of research groups (especially Muetterties and Knoth as well as Harmon) have used the hydro-

anium salt of $\text{B}_{12}\text{H}_{12}^{2-}$ and $\text{B}_{10}\text{H}_{10}^{2-}$ in reactions with a number of carbon-containing compounds. The reactions were usually carried out in aqueous solution or solution containing water from the preparation of the hydronium salts (5 mol in the case of $\text{B}_{12}\text{H}_{12}^{2-}$). In some cases, the reactions led to well-characterized compounds, whereas other reactions led to product mixtures, which were not always well characterized and separated. This is compounded by the known deficiency of elemental analysis of cluster compounds, which is disturbed by the unpredictable formation of boron carbide during analysis.

For di- and trisubstituted derivatives of $\text{B}_{12}\text{H}_{12}^{2-}$, the substitution pattern (substitutions on boron atoms 2, 7, and 12 are possible) is in most cases unknown. For $\text{B}_{10}\text{H}_{10}^{2-}$ substitution, it is in many cases not known whether only the equatorial boron atoms have reacted.

3.1. Reactions with alkenes

Styrene (3 molar equivalents) was reacted with the hydronium salt of $\text{B}_{12}\text{H}_{12}^{2-}$ (1 molar equivalent) in 2-propanol, and gave rise to tris-phenethylsubstituted $\text{B}_{12}\text{H}_{12}^{2-}$ [8]. Mono- and di-substituted products could also be detected. NMR showed that the resulting mixture contained substitution isomers with substitution of the α - and the β -carbon of the styrene entity. Hydrobromic acid could liberate ethylbenzene from the product.

Propene could be reacted directly with the hydronium salt of $\text{B}_{12}\text{H}_{12}^{2-}$. Monosubstitution was observed. Again, substitution isomers with respect to the propene moiety were obtained.

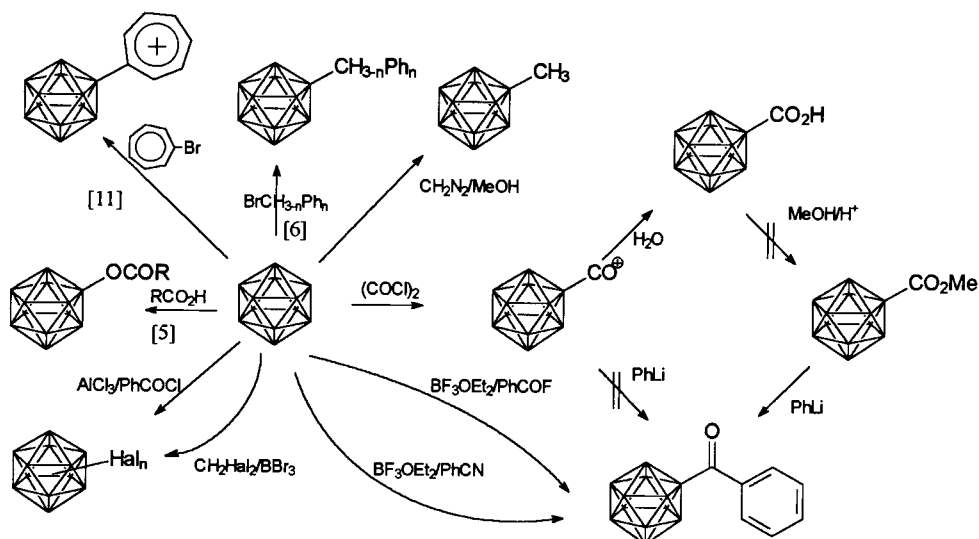


Fig. 1. Overview of reactions with $\text{B}_{12}\text{H}_{12}^{2-}$ leading to boron–carbon bonds. Referenced work is indicated in square brackets. All other reactions are by Gabel, Perleberg, Mai, unpublished.

3.2. Reactions with carbonyl compounds

CO can be introduced as substituent in the apical positions 1 and 10 of $B_{10}H_{10}^{2-}$, by reaction of the corresponding bis-diazonium derivative [10]. The latter is prepared from $B_{10}H_{10}^{2-}$ with a large excess of aqueous nitrous acid followed by a reduction of the intermediate with $NaBH_4$ or Zn/HCl . Exchange to CO is achieved with CO at high pressure and high temperature, using no solvent. When cyclohexane is used as solvent, the corresponding mono- and bis-cyclohexyl dicarbonyls are formed.

Similarly, the $B_{12}H_{12}^{2-}$ cluster can be converted to the mono- and di-carbonyl derivatives with CO, with temperatures of 70 and 130°C, respectively [11].

Under acidic conditions, CO can react with the $B_{12}H_{12}^{2-}$ cluster directly, yielding a mixture of both mono- and di-substituted products [10]. The latter consist of at least two isomers. Clean mono-substitution can be obtained by reacting the TBA salt of $B_{12}H_{12}^{2-}$ in CH_2Cl_2 with equimolar amounts of $(COCl)_2$ (Mai and Gabel, unpublished).

With $B_{10}H_{10}^{2-}$, $(COCl)_2$ leads to the apically substituted mono-carbonyl derivative in high yields [12].

Benzoyl chloride reacts with the hydronium salt of $B_{10}H_{10}^{2-}$ to a benzoyl-substituted cage [8]. The substitution is predominantly equatorial. The ketone is a rather strong base; the acidic form has a dark red color, whereas the deprotonated form is light yellow. The carbonyl stretching frequency (1570 cm^{-1}) is abnormal for benzoyl derivatives (normally found at $1670\text{--}1660\text{ cm}^{-1}$). Nevertheless, semicarbazides can be formed, and the compound can be oxidized in a Baeyer–Villiger reaction to the benzoyl ester of $B_{10}H_9OH^{2-}$.

In contrast, the reaction of benzoyl chloride with the hydronium salt of $B_{12}H_{12}^{2-}$ yields the benzoyl derivative of $B_{12}H_{11}OH^{2-}$ as the major product.

3.3. Reactions with stable carbonium ions

A most interesting reaction was observed by Harmon and Harmon [13]. Reaction of $B_{10}H_{10}^{2-}$ or $B_{12}H_{12}^{2-}$ under acidic conditions (the counter-ions being hydronium) with tropylium bromide leads to the formation of a B–C bond. In the case of $B_{12}H_{12}^{2-}$, monosubstitution is observed. For $B_{10}H_{10}^{2-}$, both mono- and disubstituted products are found. The mono-substituted product carries the substituent on an equatorial boron atom. The hydride from that atom is transferred to a tropylium ion to yield equimolar amounts of cycloheptatriene.

3.4. Halogenation

The use of CF_3COOH in dihalomethane leads to the formation of mixtures of reaction products, from which

mono-halogenated derivatives can be isolated [14]. This procedure is an improvement over the reactions with elemental halogen previously described [15]. The mechanism formulated by the authors implies the formation of a monohalomethyl ester of CF_3COOH ; its formation has, however, not been investigated.

4. Lewis-acid catalyzed reactions

In contrast to the proton-catalyzed reactions of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$, Lewis acids have not been explored extensively as catalysts for reactions involving these boron clusters. Reactions under Friedel–Crafts conditions could be expected to lead to C-substitution of the cluster in analogy to the substitution chemistry on organic aromatic compounds. We wish to report here about the reactions of different Lewis acids with the $B_{12}H_{12}^{2-}$ cluster, leading to unexpected products.

Benzoyl chloride in acetonitrile, with $AlCl_3$ as catalyst, does not yield the benzoyl derivative expected, nor the benzoate of $B_{12}H_{11}OH^{2-}$ described by Knoth [8]. Instead, chlorination is observed. The predominant product is the monochloro derivative.

BCl_3 in acetonitrile leads to a reaction of the cluster with the solvent, resulting in the formation of the acetyl derivative of $B_{12}H_{12}^{2-}$. In CH_2Cl_2 in the absence of additional halogen-containing compounds, chlorination is observed, to yield a mixture of mono- and higher-substituted products. The same is observed with $AlCl_3$ and $TiCl_4$. When BX_3 ($X = Cl, Br, I$) is allowed to react with $B_{12}H_{12}^{2-}$ in CH_2X_2 , halogenation is observed, with no adequate control over the degree of substitution. In cross-experiments with BBr_3 or $BF_3 \cdot OEt_2$ in CH_2Cl_2 , chlorination is observed exclusively, but no bromination or fluorination.

With $BF_3 \cdot MeOH$ in acetonitrile, benzoyl chloride leads to both the chlorinated and the benzoylated derivatives of $B_{12}H_{12}^{2-}$. Clean benzoylation is observed with $BF_3 \cdot MeOH$ in benzoyl chloride as reactant and solvent, or with $BF_3 \cdot MeOH$ and benzoyl fluoride in acetonitrile.

In analogy to the reaction of $B_{12}H_{12}^{2-}$ with BCl_3 in acetonitrile, the same Lewis acid in benzonitrile leads to the formation of the benzoyl derivative of $B_{12}H_{12}^{2-}$. The carbonyl stretching frequency at 1635 cm^{-1} is not shifted as much as in the $B_{10}H_{10}^{2-}$ derivative (see above), although still outside what is normally observed for benzoyl derivatives.

5. Reactions with Grignard reagents

Recently, Peymann et al. [16] reported the reaction of $B_{12}H_{12}^{2-}$ with Grignard reagents in the presence of Pd catalysts. The monoiodo derivative of the cluster reacts

with the appropriate Grignard reagent (methyl, phenyl or octadecyl) in the presence of *trans*-dichlorobis-(triphenylphosphine)palladium to the corresponding B–C-connected species. Yields are in the order of 50–80%. The methyl and phenyl derivatives could be crystallized; X-ray structure analysis could be obtained.

Reactions with unsaturated hydrocarbon reagents were not successful.

6. Reactions with carbocations

In the reaction of derivatives of $B_{12}H_{12}^{2-}$ with carbocations, substitution of the cluster was observed. These observations were made in the course of preparing derivatives of the $B_{12}H_{12}^{2-}$ cluster for use in BNCT. We found that trityl bromide (intended as a protecting group for primary alcohols) reacted with the cluster (acetonitrile as solvent and catalytic amounts of *N,N*-dimethylaminopyridine), forming compounds with a mass corresponding to mono-substituted products (Perleberg, Dissertation, U. of Bremen, 1997). Separation of the product from excess cluster could not yet be achieved. Similar reactions occur with dimethoxytrityl bromide at an even faster rate. Reactions with diphenylmethyl bromide and benzyl bromide occur, but are much slower. With ethyl bromide, no reaction is found even after prolonged reaction times.

When $B_{12}H_{12}^{2-}$ is allowed to react with an excess of diazomethane in methanol, part of the cluster reacts to the monomethyl product (Mai, Dissertation, U. of Bremen, 1997). Also here, separation from the unreacted cluster could not yet be achieved.

7. Mechanism of the reactions

Not all of the reaction mechanisms of the above reactions have been fully understood so far. In principle, there are several ways how the cluster can be attacked directly. In addition, intermediates are possible which might be responsible for the observed products.

For the reaction of $B_{10}H_{10}^{2-}$ with benzoyl bromide under proton acidic conditions, a reaction mechanism similar to an electrophilic substitution of aromatic compounds may be postulated. In this case, however, the protonation of the cluster rather than the protonation of the carbonyl oxygen might be the initial step, as the cluster reacts as a strong acid with a pK_a value of around 0.

In the case of the $B_{12}H_{12}^{2-}$ cluster, benzoyl chloride reacts under proton acidic conditions to the O-bonded derivative, in which the cluster reacts more probably as an electrophile. Also the reaction with neat acids [7] can be understood in this way. Nevertheless, in both cases the high electron-donating properties of the cluster must be overcome. Tolpin et al. [6] have interpreted the reaction

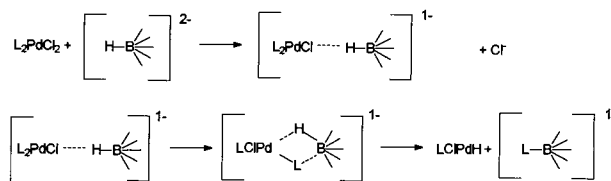


Fig. 2. Reaction of $B_{12}H_{12}^{2-}$ with Pd reagents [17].

of $B_{12}H_{12}^{2-}$ with sulfur-containing compounds such that the cluster reacts as an electrophile. They also report, however, reactions where the cluster might be considered a nucleophile.

Our own results on the reaction of $B_{12}H_{12}^{2-}$ with carbocationic species are most easily interpreted as reactions of the cluster as nucleophile. In this case, the centers of the cluster triangles that possess the highest electron density [4] could interact with carbocations directly, with subsequent coordination migration of the carbocation to an apex of the cluster and the migration of a proton from the apex to its neighboring triangle.

The interaction of protons with the cluster (under the proton acidic conditions under which many of the above reactions have been carried out) could be expected to reduce the overall electron density of the cluster, thus enabling the secondary attack of a nucleophile especially on $B_{12}H_{12}^{2-}$.

For the halogenation of clusters under Lewis acidic conditions, a different mechanism appears more likely. Reactions of $B_{12}H_{12}^{2-}$ with Pd reagents of the type L_2PdCl_2 (with $L = PMe_2Ph$) lead to neutral, phosphorus-containing compounds [17] (see Fig. 2). The postulated reaction mechanism involves a 2-electron 3-center bonding in which ligand exchange between boron and palladium can occur. A similar mechanism is proposed for the reaction of Grignard reagents under Pd catalysis [16]. The halogenation of the cluster in dihalomethane with Lewis acids, observed by us, cannot occur in this manner; if that were the case, the halogen would have to come from the Lewis acid. Rather, the halogen originates from the solvent.

We therefore postulate a different reaction mechanism, in which the initial step is the interaction of the Lewis acid with the cluster (see Fig. 3). As a consequence,

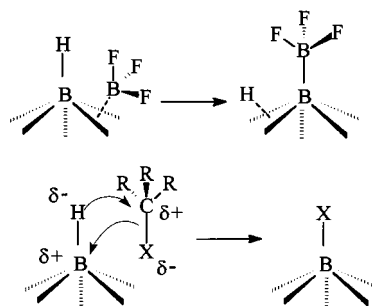


Fig. 3. Postulated interaction of the cluster with Lewis acids.

the overall electron density of the cluster would be reduced, allowing the interaction of the dihalomethane with the cluster, at a different boron atom, under hydrogen–halogen exchange. The other product would then be the monohalomethane. Preetz et al. [14] have postulated that the reaction with halogenated solvents in the presence of trifluoroacetic acid would result in molecular hydrogen. Neither of these hypotheses has as yet been proven experimentally.

Similarly, when an acyl halide is offered to the cluster under such conditions, a similar exchange could take place to the resulting halogenated cluster; this would result in the formation of an aldehyde. The reaction of benzoyl tosylate with $B_{12}H_{12}^{2-}$ [8], which results in the benzyloxy-substituted cluster, has been postulated to involve benzaldehyde and a (hypothetical) $B_{12}H_{11}^-$. Alternatively, this reaction might well occur according to the above acid-catalyzed reaction.

8. Reactions of CO on clusters

Due to the fact that cluster-bound carbonyl compounds are relatively easy to prepare, some chemical properties of the CO-groups have been investigated. Whereas some reactions proceed as in their organic counterparts, some other reactions are not possible.

The benzoyl derivative of $B_{10}H_{10}^{2-}$ can be reacted to a semicarbazone, and can be oxidized with hydrogen peroxide to $B_{10}H_9OCOC_6H_5^{2-}$ similar to a Baeyer–Villiger reaction. Hydrolysis leads to the corresponding $B_{10}H_9OH^{2-}$.

$B_{10}H_9CO^-$ reacts with organomercurials to the corresponding acyl derivatives (cited in Ref. [18]). With *N,N*-dimethylaminoaniline, electrophilic substitution of the aromatic ring is observed. Reaction of $B_{10}H_9CO^-$ with $B_{10}H_{10}^{2-}$ or its derivatives leads to a keto-linkage between the two clusters.

The monocarbonyl derivative of $B_{12}H_{12}^{2-}$ can be reacted to the methyl ester by basic work-up of the carbonylation reaction. Methylation of the acid with diazomethane is not successful, also due to the side reaction described above. $B_{12}H_{11}COOCH_3^{2-}$ reacts with phenyl lithium to the benzoyl derivative; $B_{12}H_{11}CO^-$ reacts with phenyl lithium to other products, so far unidentified. This reaction proceeds probably via radicals, as a transient blue color is observed. The methyl ester does not form from the carboxyl derivative with methanol under acidic conditions.

9. Detection and purification

The ionic nature of the *closo*-cluster compounds of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ make the detection and separation

of new compounds from their precursors a challenging task.

^{11}B -NMR can be used to detect new compounds formed from the unsubstituted $B_{12}H_{12}^{2-}$ cluster, whose resonance is a singlet in a proton-decoupled spectrum. For the $B_{10}H_{10}^{2-}$ cluster, two resonances are found already in the unsubstituted material. When mixtures of unsubstituted and substituted clusters are present, no definite interpretation of the resulting spectra can usually be given. Proton NMR is even more difficult to use in the case of mixtures, as the cluster protons tend to have a broad range of resonances (2–0 ppm in the case of $B_{12}H_{12}^{2-}$).

Mass spectrometry of the clusters is not trivial, owing to the negative charge carried by the cluster. Several compounds are, however, not detectable in mass spectrometry. In our experience, the use of fast atom bombardment results in ions of the substance and of fragmentation products. In the case of doubly negatively charged compounds, either counter ions can be present or a hydride is removed together with a proton from the solvent, resulting in an apparent mass discrepancy. For most counterions, glycerol is a better matrix than nitrobenzyl alcohol. Nevertheless, a number of compounds do not yield ion currents useful for detection and identification. Direct chemical ionization with NH_3 is also possible. Here, fragmentation is less pronounced, but often multiple peaks are observed due to the formations of adducts with NH_3 . In both cases, and especially when boron in its natural isotope abundance is used, differences between the observed and the calculated masses might occur.

Purification of the compounds is problematic. Most cluster derivatives precipitate from aqueous solutions with quaternary ammonium salts, and from methanolic solutions as cesium salts. It is, however, usually impossible to separate cluster derivatives in this manner. Chromatography for analytical purposes is most conveniently carried out under reversed-phase conditions [19]. Although this can be done in semi-preparative or preparative methods, the limited capacity (owing to the required presence of ion pair reagents) makes this a tedious and laborious procedure. Ion-exchange chromatography on DEAE-cellulose can be used [20]. Here, the elution of the compounds from the column can require large volumes of eluent.

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