Review

Synthesis and Reactivity of Cyclic Oxonium Derivatives of *nido*-Carborane: A Review

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Abstract: Nucleophilic ring-opening reactions of cyclic oxonium derivatives of anionic boron hydrides are a convenient method of their modification which opens practically unlimited prospects for their incorporation into various macro- and biomolecules. This contribution provides an overview of the synthesis and reactivity of cyclic oxonium derivatives of *nido*-carborane as well as half-sandwich complexes based on it.

Keywords: *nido*-carborane; half-sandwich complexes; oxonium derivatives; ring-opening reactions; functionalization

1. Introduction

The 7,8-Dicarba-*nido*-undecaborante anion $[7,8\text{-}C_2B_9H_{12}]^-$ (*nido*-carborane) belongs to a family of polyhedral boron compounds, the discovery of which in the middle of the last century became one of the most significant events in the history of modern inorganic chemistry [1]. This anionic boron cluster with an open pentagonal face was synthesized for the first time by M. F. Hawthorne more than 50 years ago by deboronation of 1,2-dicarba-*closo*-dodecaborane (*ortho*-carborane) with potassium hydroxide in methanol [2,3]. Later various milder deboronating agents including amines [4–7] and fluoride ion [8–11] were proposed. Deprotonation of *nido*-carborane with strong bases results in the dicarbollide dianion $[7,8\text{-}C_2B_9H_{11}]^{2-}$, which was recognized as an isolobal analogue of the cyclopentadienyl anion [12]. Due to this, the dicarbollide dianion is considered as an unusual three-dimensional π-ligand for the synthesis of metal complexes [13–15], which can be used as catalysts in a variety of chemical processes [16,17]. Another important area of use for *nido*-carborane derivatives as water-solubilizing boron moieties is the design of potential drugs for boron neutron capture therapy of cancer [18–23]. In addition, based on *nido*-carborane derivatives, it is possible to obtain reagents for radioimaging of tumors [24–28], new optical and luminescent materials [29–37], ionic liquids [38,39], etc. Thus, the development of convenient approaches to the modification of the *nido*-carborane cluster remains highly relevant.

Currently the main approach to the synthesis of *nido*-carborane derivatives is based on the deboronation of the corresponding *ortho*-carborane derivatives. This approach is widely used for the synthesis of *C*-substituted derivatives of *nido*-carborane, as well as derivatives containing substituents at the lower belt of the *nido*-carborane cage [40]. There are several general methods for the synthesis of *B*-substituted derivatives with substituents in the upper belt of the *nido*-carborane cage; however, most of them are used to obtain asymmetrically substituted derivatives $[9\text{-}X\text{-}7,8\text{-}C_2B_9H_{11}]^-$ [41–49].

Several approaches to the synthesis of symmetrically substituted derivatives of *nido*-carborane $[10\text{-}X\text{-}7,8\text{-}C_2B_9H_{11}]^-$ with boron–sulfur [50,51] and boron–nitrogen [52–55] bonds have also been developed recently; however, the greatest interest is the functionalization of *nido*-carborane via its cyclic oxonium derivatives. Previously, this approach was successfully used for the synthesis of numerous derivatives of *closo*-decaborate and

closo-dodecaborate anions [56,57], as well as sandwich bis(dicarbollide) transition metal complexes [58]. In this contribution synthesis and properties of cyclic oxonium derivatives of *nido*-carborane as well as half-sandwich complexes based on it will be reviewed.

2. Synthesis of Oxonium Derivatives of *nido*-Carborane

To date, oxonium derivatives of *nido*-carborane have been synthesized with all cyclic ethers used as common solvents, including tetrahydrofuran, 1,4-dioxane, and tetrahydropyran. The first oxonium derivative was obtained as early as 1969 by the reaction of the potassium salt of *nido*-carborane with $FeCl_3$ in a mixture of benzene and tetrahydrofuran. The reaction gave a mixture of asymmetric $9\text{-}(CH_2)_4O\text{-}7,8\text{-}C_2B_9H_{11}$ and symmetric $10\text{-}(CH_2)_4O\text{-}7,8\text{-}C_2B_9H_{11}$ which were separated by column chromatography in benzene. Similar mixture of isomers was obtained for the *C,C*-dimethyl derivative of *nido*-carborane as well [59] (Scheme 1).
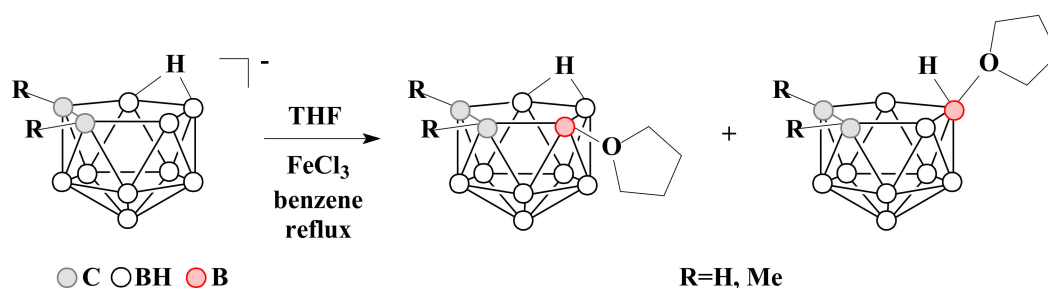
Scheme 1. The synthesis of $9\text{-}(CH_2)_4O\text{-}7,8\text{-}C_2B_9H_{11}$ and $10\text{-}(CH_2)_4O\text{-}7,8\text{-}C_2B_9H_{11}$ by the reaction of *nido*-carborane with $FeCl_3$ in a THF–benzene mixture.

The proposed mechanism of this reaction includes the initial abstraction of hydrogen hydride from position 9 by iron(III) chloride as a Lewis acid with the formation of a quasi-borinium cation. In the absence of strong nucleophiles, this intermediate can be isomerized to a more stable symmetric form with a quasi-electrophilic center at position 10, which is then attacked by an ether solvent molecule as a weak but most accessible nucleophile. As a result, a mixture of 9- and 10-substituted isomers is formed [60]. This mechanism is known as electrophile-induced nucleophilic substitution (EINS) and is considered as one of the main mechanisms of substitution of hydrogen atoms in polyhedral boron hydrides.

Later, it was found that the reaction of *nido*-carborane with $HgCl_2$ in tetrahydrofuran leads to the selective formation of the symmetrically substituted product $10\text{-}(CH_2)_4O\text{-}7,8\text{-}C_2B_9H_{11}$ [60,61]. In a similar way, the derivatives with 1,4-dioxane $10\text{-}O(CH_2CH_2)_2O\text{-}7,8\text{-}C_2B_9H_{11}$ [60] and tetrahydropyran $10\text{-}(CH_2)_5O\text{-}7,8\text{-}C_2B_9H_{11}$ [62,63] were synthesized.

It is assumed that the selectivity of the reactions in these cases is determined by the fact that the endo-polyhedral hydrogen atom of *nido*-carborane cage is replaced at the first stage of the reaction by a mercury atom with the formation of η^1-metallacarborane, in which mercury is bound to the B(10) atom of the dicarbollide ligand [64–67]. Heating of this complex results in elimination of mercury and generation of quasi-electrophilic center at position 10 followed by its attack by the nucleophile [60].

Another convenient method for the synthesis of 1,4-dioxane derivative of *nido*-carborane is to heat in 1,4-dioxane the protonated form of *nido*-carborane $7,8\text{-}C_2B_9H_{13}$, which is formed by treating a suspension of the triethylammonium salt of *nido*-carborane with concentrated sulfuric acid in toluene [68].

The symmetrically substituted tetrahydrofuran derivative $10\text{-}(CH_2)_4O\text{-}7,8\text{-}C_2B_9H_{11}$ can be obtained by the reaction of tetramethylammonium salt of *nido*-carborane with $AlCl_3$ in a mixture of tetrahydrofuran and acetone [69]. The symmetrically substituted tetrahydrofuran and 1,4-dioxane derivatives of *nido*-carborane were also synthesized by the reactions of *nido*-carborane with the corresponding ethers in the presence of acetaldehyde or formaldehyde and hydrochloric acid in a mixture of water and toluene [70]. The

methods of synthesis of symmetrically substituted oxonium derivatives of *nido*-carborane are summarized in Scheme 2.

○ **CH** ○ **BH** ○ **B**
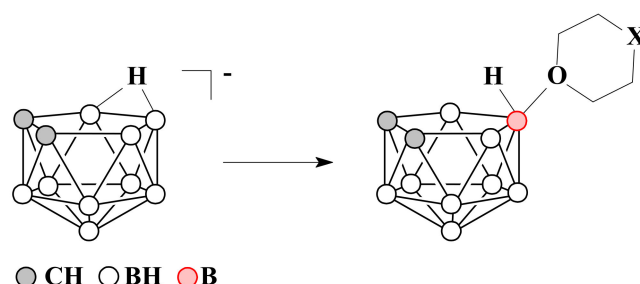
Reagents and conditions:

X = - : HgCl$_2$, THF, benzene, reflux [60,61];
AlCl$_3$, acetone, THF, reflux [69];
HC(O)H or MeC(O)H, HCl, THF, toluene, *r.t.* [70]

X=O: HgCl$_2$, 1,4-dioxane, benzene, reflux [60];
H$_2$SO$_4$, toluene, *r.t.*; 1,4-dioxane, reflux [68];
HC(O)H, HCl, 1,4-dioxane, toluene, *r.t.* [70]

X=CH$_2$: HgCl$_2$, THP, benzene, reflux [62,63]

Scheme 2. The different synthetic pathways to the 10-(CH$_2$)$_4$O-7,8-C$_2$B$_9$H$_{11}$, 10-O(CH$_2$CH$_2$)$_2$O-7,8-C$_2$B$_9$H$_{11}$ and 10-(CH$_2$)$_5$O-7,8-C$_2$B$_9$H$_{11}$.

The molecular structure of the 1,4-dioxane derivative of *nido*-carborane was determined by single crystal X-ray diffraction [71] (Figure 1).
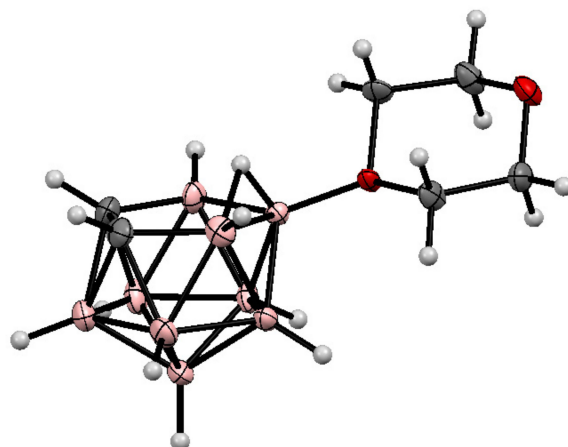

Figure 1. The molecular structure of 10-O(CH$_2$CH$_2$)$_2$O-7,8-C$_2$B$_9$H$_{11}$.

It should be noted that, in addition to cyclic oxonium derivatives of *nido*-carborane, some acyclic oxonium derivatives such as the dimethyloxonium 9-Me$_2$O-7,8-C$_2$B$_9$H$_{11}$ and 10-Me$_2$O-7,8-C$_2$B$_9$H$_{11}$ [72] and the diethyloxonium 9-Et$_2$O-7,8-C$_2$B$_9$H$_{11}$ [73] and 10-Et$_2$O-7,8-C$_2$B$_9$H$_{11}$ [70,73,74] derivatives are known as well. The molecular structure of the 10-diethyloxonium derivative of *nido*-carborane was determined by single crystal X-ray diffraction [73] (Figure 2). The formation of the 1,2-dimethoxyethane derivatives 9-MeOCH$_2$CH$_2$(Me)O-7,8-C$_2$B$_9$H$_{11}$ and 10-MeOCH$_2$CH$_2$(Me)O-7,8-C$_2$B$_9$H$_{11}$ was also reported, however they have low stability and easily lose the methyl group, giving the corresponding alkoxy derivatives [75].
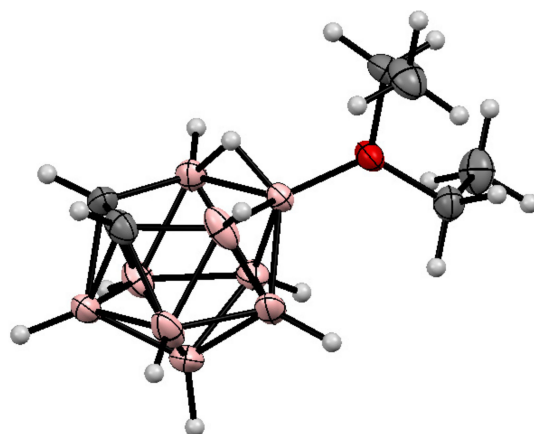
Figure 2. The molecular structure of 10-Et$_2$O-7,8-C$_2$B$_9$H$_{11}$.

### 3. Properties of Oxonium Derivatives of *nido*-Carborane. Reactions with Nucleophiles

The use of ring opening reactions of cyclic oxonium derivatives of polyhedral boron hydrides under the action of nucleophiles for the preparation of their various derivatives is well known [56–58]. In the case of *nido*-carborane, this method has several advantages. First of all, the substituent is symmetrically located at position 10 of the boron cluster. This avoids the formation of racemic and diastereomeric mixtures of products and greatly facilitates the identification of compounds by NMR, which is one of the main methods for characterization of this type of compounds. Another advantage is that the yield of the target product is in most cases very high or nearly quantitative. In addition, the variety of oxonium derivatives makes it possible to obtain products with different lengths of the spacer between the *nido*-carborane cage and the substituent.

Thus, by the ring-opening reactions of tetrahydrofuran and 1,4-dioxane derivatives of *nido*-carborane with phenolates a series of *nido*-carborane-based carboxylic acids with different spacer lengths between *nido*-carborane cage and functional group was prepared. Phenolates were generated by the treatment of hydroxybenzoic acids with K$_2$CO$_3$ in acetonitrile [60] (Scheme 3). The reaction of the 1,4-dioxane derivative of *nido*-carborane with methyl ether of *p*-hydroxybenzoate in the same conditions led to the corresponding K[10-(4-CH$_3$OOCC$_6$H$_4$O)-CH$_2$CH$_2$OCH$_2$CH$_2$O-7,8-C$_2$B$_9$H$_{11}$] [76].
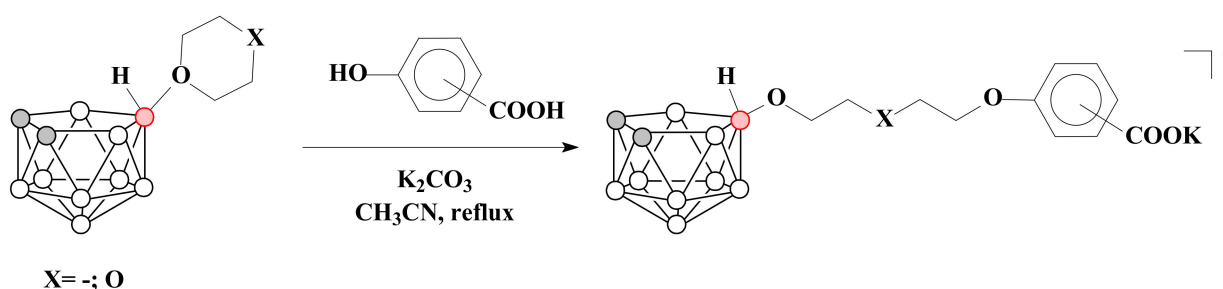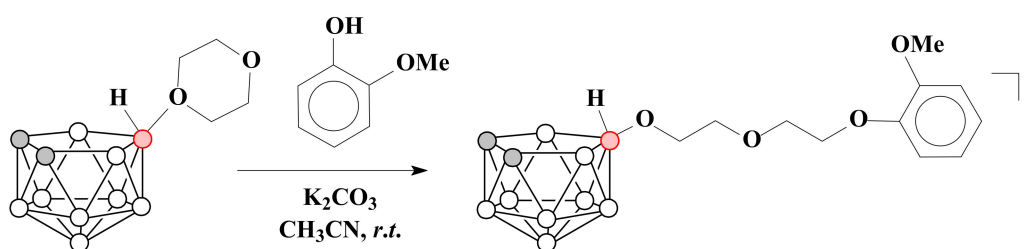

Scheme 3. The synthesis of *nido*-carborane derivatives with terminal carboxylic group.

The obtaining of 10-substituted derivatives of *nido*-carborane in the case of oxonium derivatives and products of their ring-opening reactions leaves free the positions 9 and 11 of *nido*-carborane cage. This can be used for the following substitution, such as, for example, the halogenation, which was carried out for K[1 0-(4-HOOCC$_6$H$_4$O)-C$_4$H$_8$O-7,8-C$_2$B$_9$H$_{11}$], K[10-(4-HOOCC$_6$H$_4$O)-CH$_2$CH$_2$OCH$_2$CH$_2$O-7,8-C$_2$B$_9$H$_{11}$] and K[10-(4-CH$_3$OOCC$_6$H$_4$O)-CH$_2$CH$_2$OCH$_2$CH$_2$O-7,8-C$_2$B$_9$H$_{11}$] [76] (Scheme 4). The obtained halogenated compounds can find application in the design of drugs for radionuclide imaging and boron neutron capture therapy of cancer.
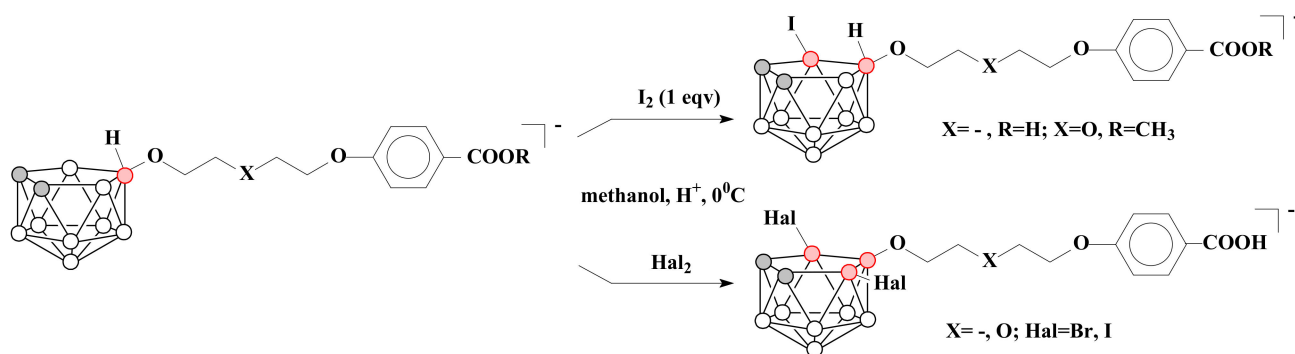
Scheme 4. The halogenation of K[10-(4-HOOCC$_6$H$_4$O)-C$_4$H$_8$O-7,8-C$_2$B$_9$H$_{11}$], K[10-(4-HOOCC$_6$H$_4$O)-CH$_2$CH$_2$OCH$_2$CH$_2$O-7,8-C$_2$B$_9$H$_{11}$] and K[10-(4-CH$_3$OOCC$_6$H$_4$O)-CH$_2$CH$_2$OCH$_2$CH$_2$O-7,8-C$_2$B$_9$H$_{11}$].

The ring-opening reaction of 1,4-dioxane derivative of *nido*-carborane with 2-methoxy phenol in the presence of K$_2$CO$_3$ resulted in the compound with a terminal guaiacol group K[10-(2-CH$_3$OC$_6$H$_4$O)-CH$_2$CH$_2$OCH$_2$CH$_2$O-7,8-C$_2$B$_9$H$_{11}$] [71] (Scheme 5). The boron-containing calixarene [4-*t*-Bu-calix[4]arene-1,3-(10-CH$_2$CH$_2$OCH$_2$CH$_2$O-7,8-C$_2$B$_9$H$_{11}$)$_2$]$^{2-}$ was prepared in similar conditions by the treatment of 1,4-dioxane derivative of *nido*-carborane with 4-*t*-Bu-calix[4]arene [71].
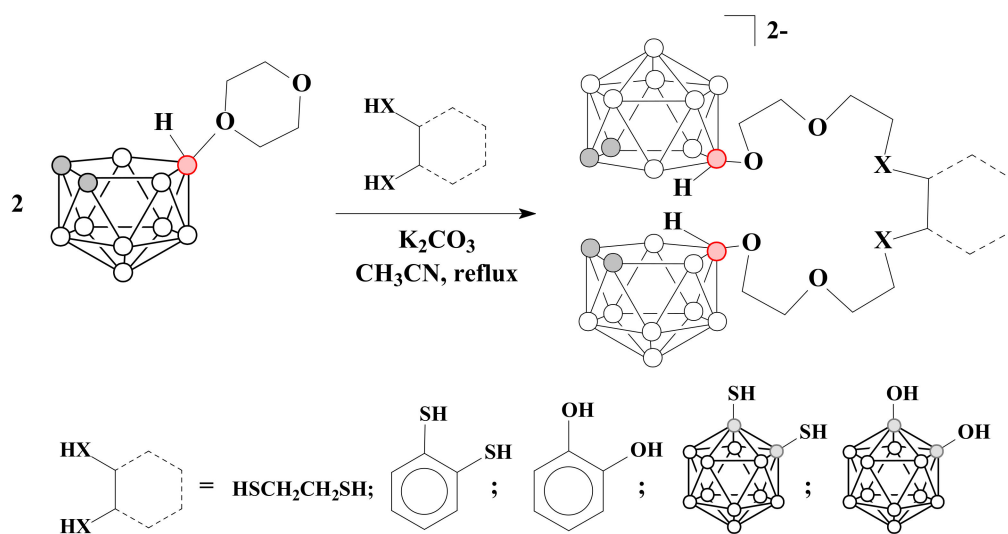

Scheme 5. The synthesis of the *nido*-carborane derivative with the terminal guaiacol group.

The ring-opening reactions of 1,4-dioxane and tetrahydropyran derivatives of *nido*-carborane with 7-diethyl-4-hydroxycoumarin led to the water-soluble conjugates of the *nido*-carborane cluster with coumarin [77] (Scheme 6). The measurement of the distribution coefficients (log D$_{7,4}$) of the obtained compounds showed their appropriate lipophilicity for medicinal applications [77].
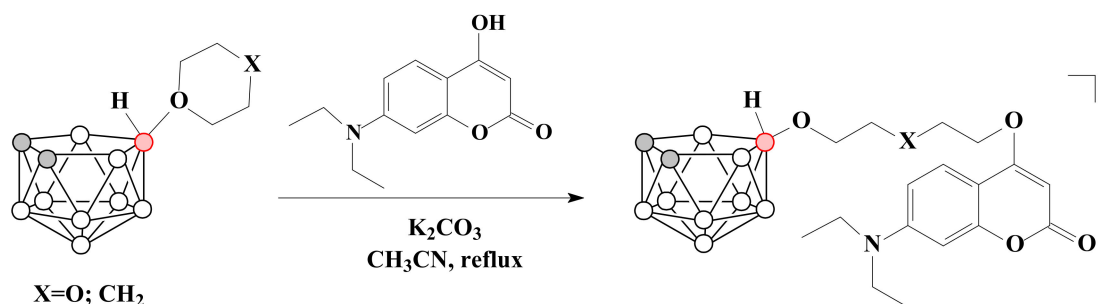

Scheme 6. The synthesis of *nido*-carborane conjugates with coumarin.

The reactions of two equivalents of 1,4-dioxane derivative of *nido*-carborane with 1,2-*O,O'*- and 1,2-*S,S'*-dinucleophiles (1,2-dihydroxybenzene [78], 1,2-dimercaptoethane, 1,2-dimercaptobenzene [79], 1,2-dihydroxy-*closo*-carborane, 1,2-dimercapto-*closo*-carborane[79]) in the presence of K$_2$CO$_3$ in acetonitrile makes it possible to obtain *nido*-carborane-based podands related to acyclic crown ether 18-crown-6 [78,79] (Scheme 7).

Scheme 7. The synthesis of *nido*-carborane-based podands.

The reaction of two equivalents of 1,4-dioxane derivative of *nido*-carborane with resorcinol proceeds in a similar way, resulting in $K_2[1,3-(10-OC_2H_4OC_2H_4O-7,8-C_2B_9H_{11})_2C_6H_4]$, whereas the reaction with hydroquinone leads to two products $K_2[1,4-(10-OC_2H_4OC_2H_4O-7,8-C_2B_9H_{11})_2C_6H_4]$ and $K[10-(4'-KOC_6H_4O)-CH_2CH_2OCH_2CH_2O-7,8-C_2B_9H_{11}]$ [78] (Scheme 8).
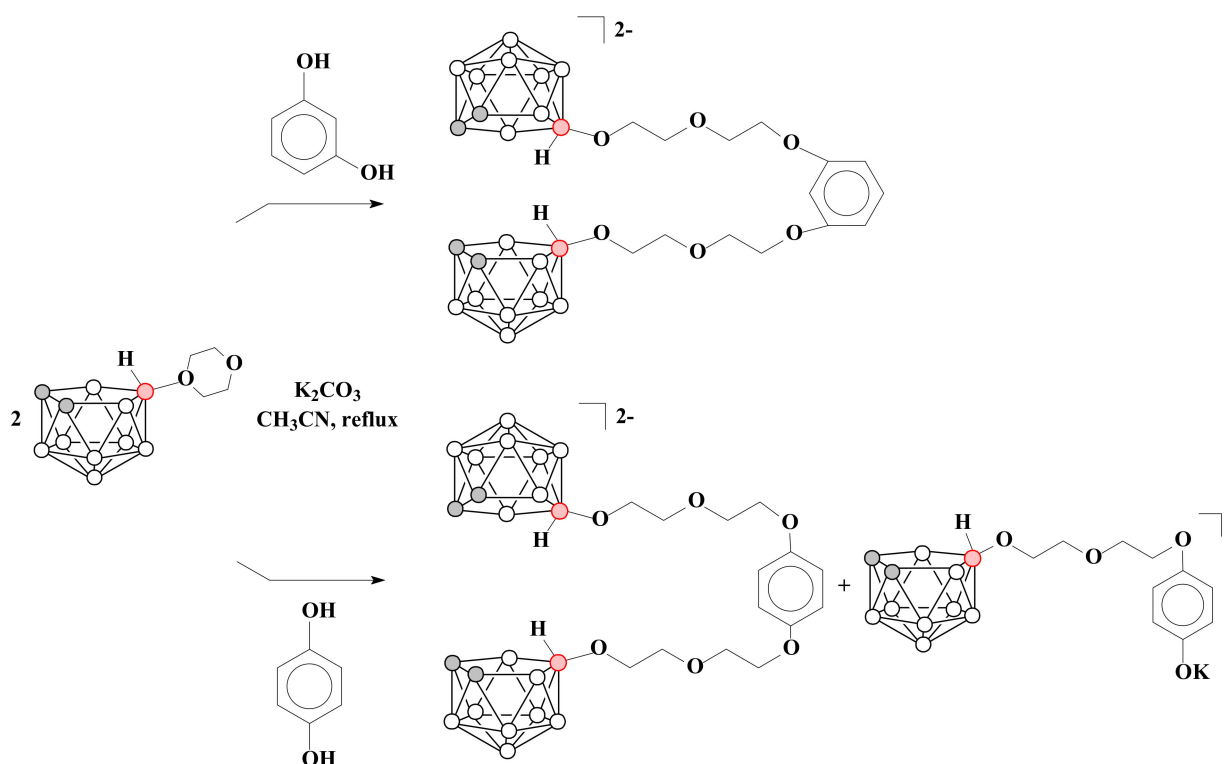
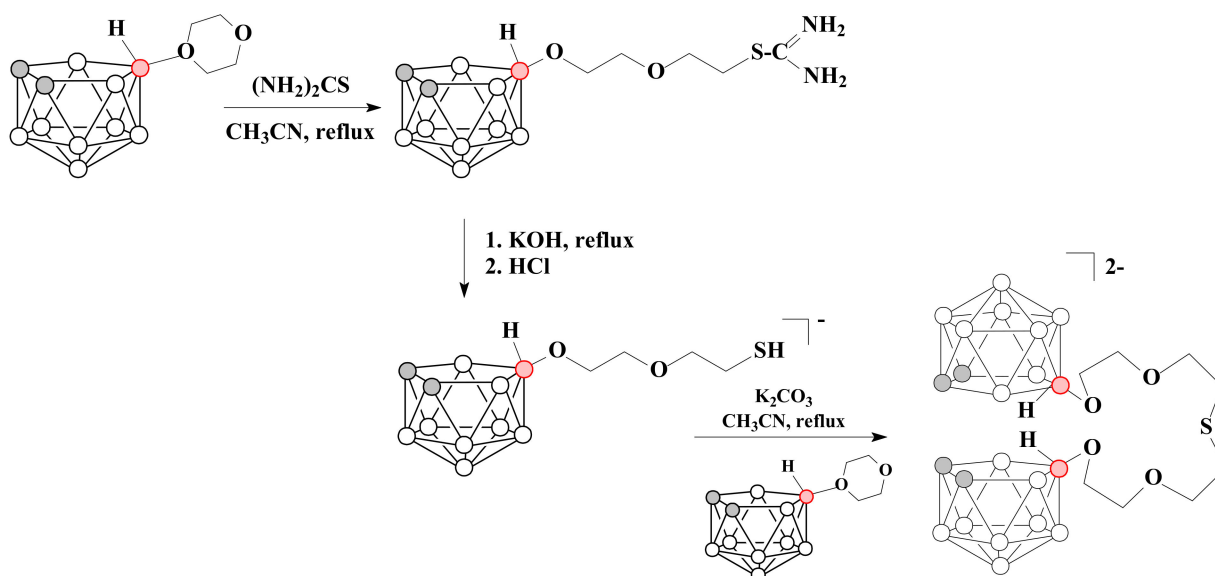**Scheme 8.** The reactions of the 1,4-dioxane derivative of *nido*-carborane with resorcinol and hydroquinone.

The reaction of two equivalents of $10-O(CH_2CH_2)_2O-7,8-C_2B_9H_{11}$ with ethylene glycol in the presence of K_2CO_3 leads to the formation of carboranyl triethylene glycol ether

[10-HO(CH$_2$CH$_2$O)$_3$-7,8-C$_2$B$_9$H$_{11}$]$^-$ along with a certain amount of carboranyl diethylene glycol formate [10-HC(O)O(CH$_2$CH$_2$O)$_2$-7,8-C$_2$B$_9$H$_{11}$]$^-$ [78] (Scheme 9).
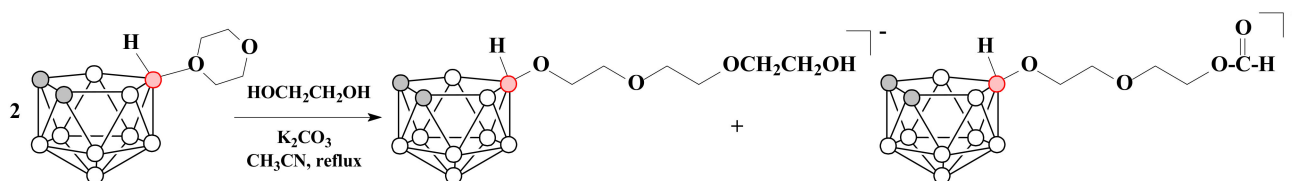
**Scheme 9.** The reaction of 1,4-dioxane derivative of *nido*-carborane with ethylene glycol.

The reaction of a 1,4-dioxane derivative of *nido*-carborane with thiourea leads to the formation of a thiouronium salt 10-(NH$_2$)$_2$CSCH$_2$CH$_2$OCH$_2$CH$_2$O-7,8-C$_2$B$_9$H$_{11}$, the subsequent hydrolysis of which gives the corresponding thiol [10-HSCH$_2$CH$_2$OCH$_2$CH$_2$O-7,8-C$_2$B$_9$H$_{11}$]$^-$. The formed thiol was reacted with one equivalent of 1,4-dioxane derivative of *nido*-carborane to give a podand [(10-CH$_2$CH$_2$OCH$_2$CH$_2$O-7,8-C$_2$B$_9$H$_{11}$)$_2$S]$^{2-}$ related to acyclic crown ether 15-crown-5 [79] (Scheme 10).

Scheme 10. The reaction of 1,4-dioxane derivative of *nido*-carborane with thiourea.

The *nido*-carborane thiol [10-HSCH$_2$CH$_2$OCH$_2$CH$_2$O-7,8-C$_2$B$_9$H$_{11}$]$^-$ can also be obtained directly by the reaction of 10-O(CH$_2$CH$_2$)$_2$O-7,8-C$_2$B$_9$H$_{11}$ with excess of aqueous sodium hydrosulfide in tetrahydrofuran. The by-product of this reaction is a thioether [(10-CH$_2$CH$_2$OCH$_2$CH$_2$O-7,8-C$_2$B$_9$H$_{11}$)$_2$S]$^{2-}$ [71].

Two *nido*-carborane-based podands [(10-CH$_2$CH$_2$OCH$_2$CH$_2$O-7,8-C$_2$B$_9$H$_{11}$)$_2$S]$^{2-}$ and [1,2-(10-SCH$_2$CH$_2$OCH$_2$CH$_2$O-7,8-C$_2$B$_9$H$_{11}$)$_2$C$_6$H$_4$]$^{2-}$ were used for the synthesis of crown ethers with the cobalt bis(dicarbollide) fragment incorporated in heteromacrocycle [79] (Scheme 11).
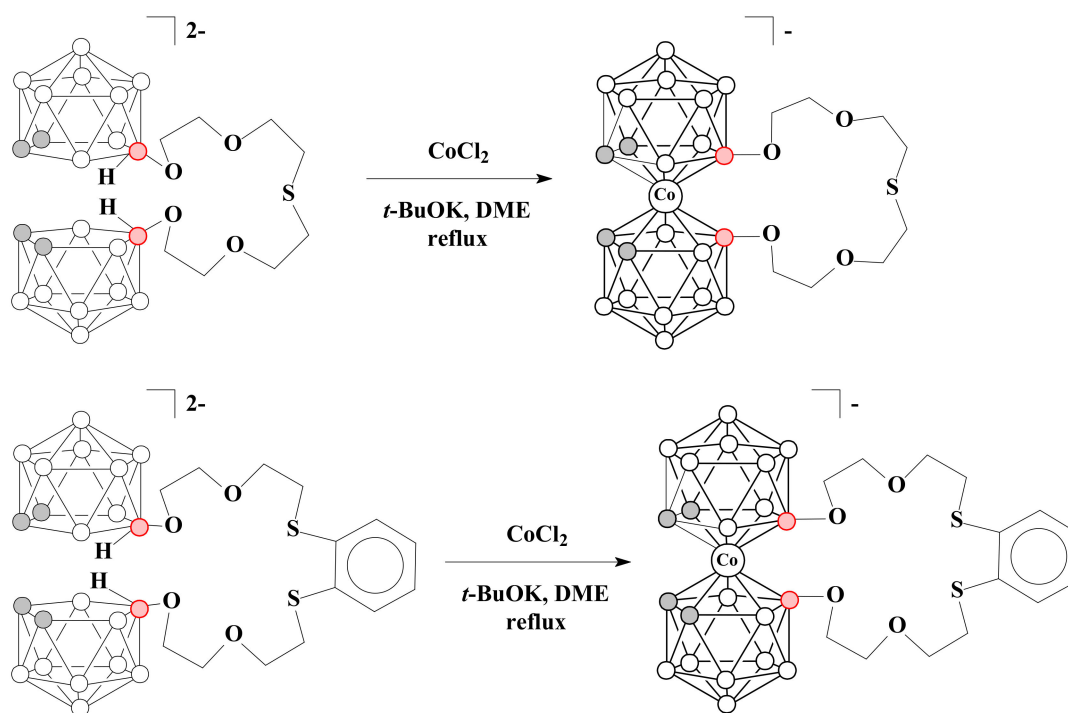
Scheme 11. Synthesis of crown ethers with the incorporated cobalt bis(dicarbollide) fragment.

The crystal structure of sodium salt of [8,8′-(OCH$_2$CH$_2$OCH$_2$CH$_2$S)$_2$-*o*-C$_6$H$_4$-3,3′-Co(1,2-C$_2$B$_9$H$_9$)$_2$]$^-$, which was obtained during the drying of the solution of parent potassium salt in diethyl ether over Na$_2$SO$_4$, was determined by X-ray analysis [79] (Figure 3).
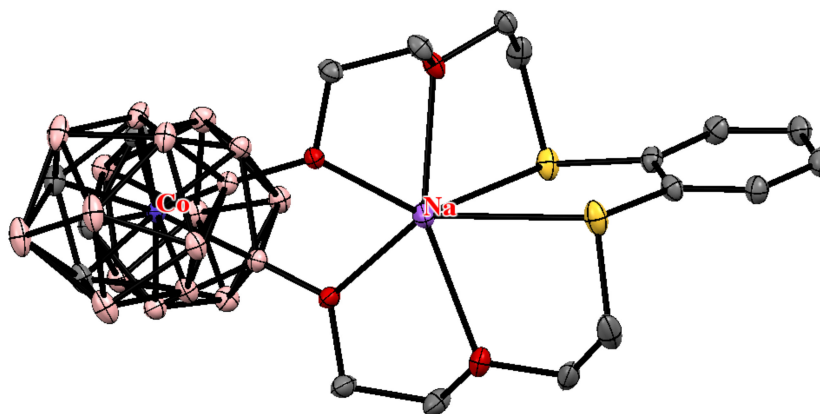
Figure 3. The molecular structure of Na[8,8′-(OCH$_2$CH$_2$OCH$_2$CH$_2$S)$_2$-*o*-C$_6$H$_4$-3,3′-Co(1,2-C$_2$B$_9$H$_9$)$_2$].

By the ring-opening reactions of tetrahydrofuran and 1,4-dioxane derivatives of *nido*-carborane with sodium azide a series of *nido*-carborane-based azides with different spacer lengths between the *nido*-carborane cage and functional group was synthesized [60,80,81] (Scheme 12).
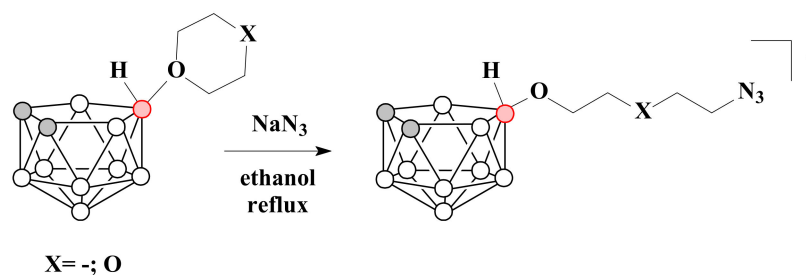
Scheme 12. The synthesis of *nido*-carborane derivatives with terminal azido group.

The obtained azides can be used for medical application due to the possibility of their conjugation with biomolecules by standard methods of bioorganic chemistry such as, for example, Cu(I)-catalyzed reaction of 1,3-dipolar [3 + 2] -cycloaddition of terminal azido group with alkynes ("click" reaction) [44,82–86]. Thus, several conjugates with nucleosides were prepared by Cu(I)-catalyzed click reaction of $10\text{-}N_3CH_2CH_2OCH_2CH_2O\text{-}7,8\text{-}C_2B_9H_{11}$ with modified derivatives of 2′-deoxyadenosine [80], uridine and thymidine [81], containing terminal alkyne group (Scheme 13).
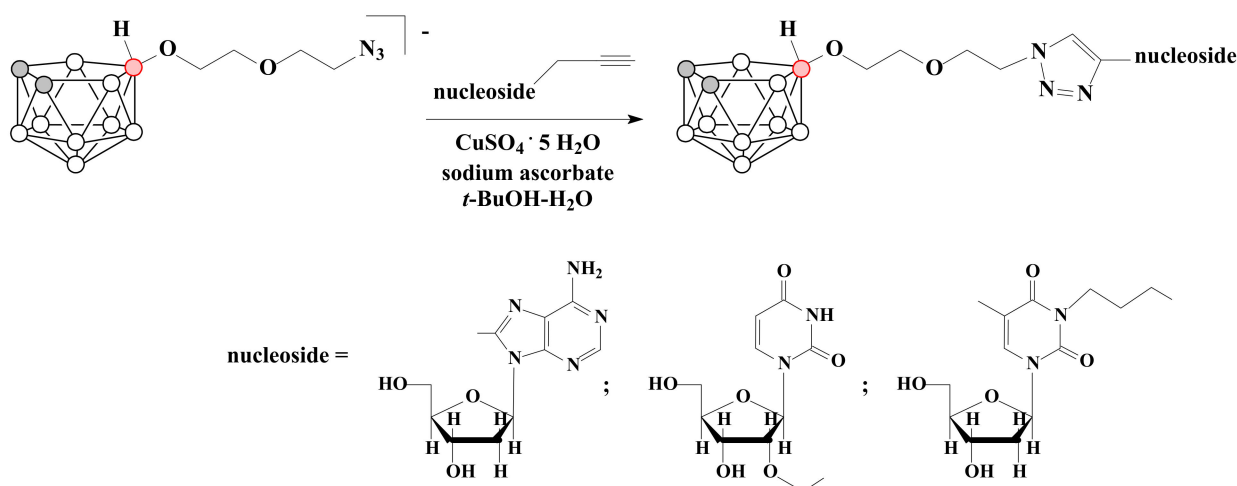
Scheme 13. The synthesis of *nido*-carborane-based conjugates with nucleosides.

The reactions of 1,4-dioxane [63,71] and tetrahydropyran [63] derivatives of *nido*-carborane with ammonia in tetrahydrofuran led to the corresponding ammonium derivatives of *nido*-carborane. The obtained compounds were used for the conjugation with 3-nitro-1,8-naphthalic anhydride in the presence of Et_3N to give water-soluble boron containing 3-nitro-1,8-naphthalimides, which are potential interesting agents for boron neutron capture therapy [63] (Scheme 14).
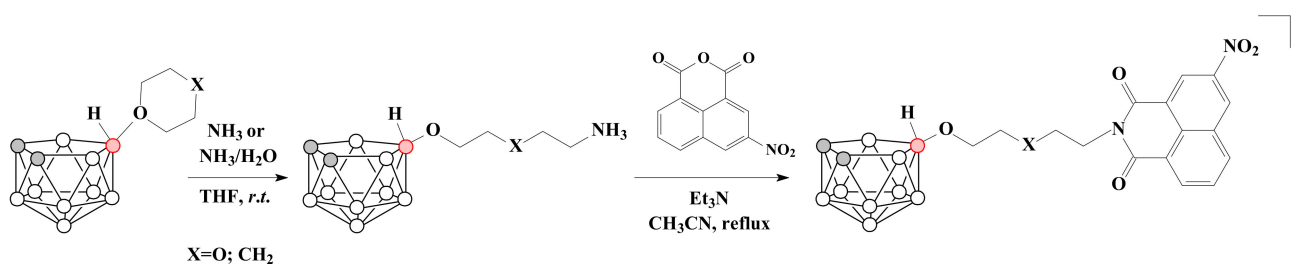
Scheme 14. The synthesis of ammonium derivatives of *nido*-carborane and their conjugates with 3-nitro-1,8-naphthalic anhydride.

The molecular structure of 10-NH$_3$CH$_2$CH$_2$OCH$_2$CH$_2$O-7,8-C$_2$B$_9$H$_{11}$ was determined by single crystal X-ray diffraction [71] (Figure 4).
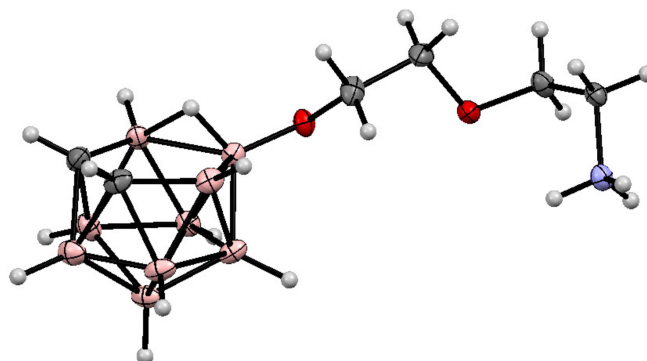
**Figure 4.** The molecular structure of 10-NH$_3$CH$_2$CH$_2$OCH$_2$CH$_2$O-7,8-C$_2$B$_9$H$_{11}$.

The charge-compensated *nido*-carborane-based conjugates with mitonafide were prepared in mild conditions by the ring-opening reactions of 1,4-dioxane and tetrahydropyran derivatives of *nido*-carborane with dimethylamino group of mitonafide [63] (Scheme 15).
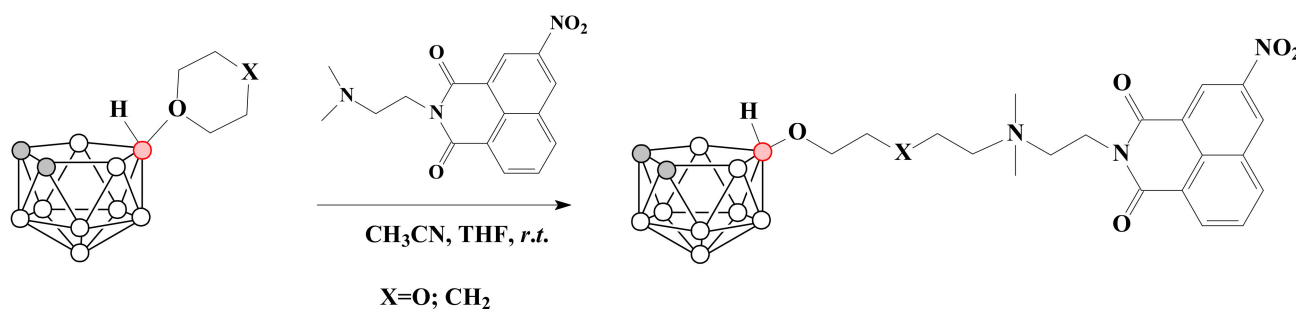

Scheme 15. The synthesis of *nido*-carborane-based conjugates with mitonafide.

The reactions of 1,4-dioxane derivative of *nido*-carborane with 4-aminophenol in tetrahydrofuran in mild conditions led to the formation of the corresponding ammonium derivative 10-(4-OH-C$_6$H$_4$)-NH$_2$CH$_2$CH$_2$OCH$_2$CH$_2$O-7,8-C$_2$B$_9$H$_{11}$, whereas the treatment of 10-O(CH$_2$CH$_2$)$_2$O-7,8-C$_2$B$_9$H$_{11}$ with 2-amino-1,3-propanediol resulted in a mixture of 10-(HOCH$_2$)$_2$CHNH$_2$CH$_2$CH$_2$OCH$_2$CH$_2$O-7,8-C$_2$B$_9$H$_{11}$ and [(HOCH$_2$)$_2$CHNH-*N,N*-(10,10′-CH$_2$CH$_2$OCH$_2$CH$_2$O-7,8-C$_2$B$_9$H$_{11}$)$_2$]$^-$ [71]. At the same time the reaction with *n*-butylamine led only to [*n*-C$_4$H$_9$NH-(10-CH$_2$CH$_2$OCH$_2$CH$_2$O-7,8-C$_2$B$_9$H$_{11}$)$_2$]$^-$ [68] (Scheme 16).

The treatment of 1,4-dioxane derivative of *nido*-carborane with 4-aminophenol in the presence of K$_2$CO$_3$ in acetonitrile under reflux conditions gave the product of ring-opening both by amino and hydroxyl groups [7,8-C$_2$B$_9$H$_{11}$-10-CH$_2$CH$_2$OCH$_2$CH$_2$O-H$_2$N-C$_6$H$_4$-O-10′-CH$_2$CH$_2$OCH$_2$CH$_2$O-7,8-C$_2$B$_9$H$_{11}$]$^-$ [71] (Scheme 17).
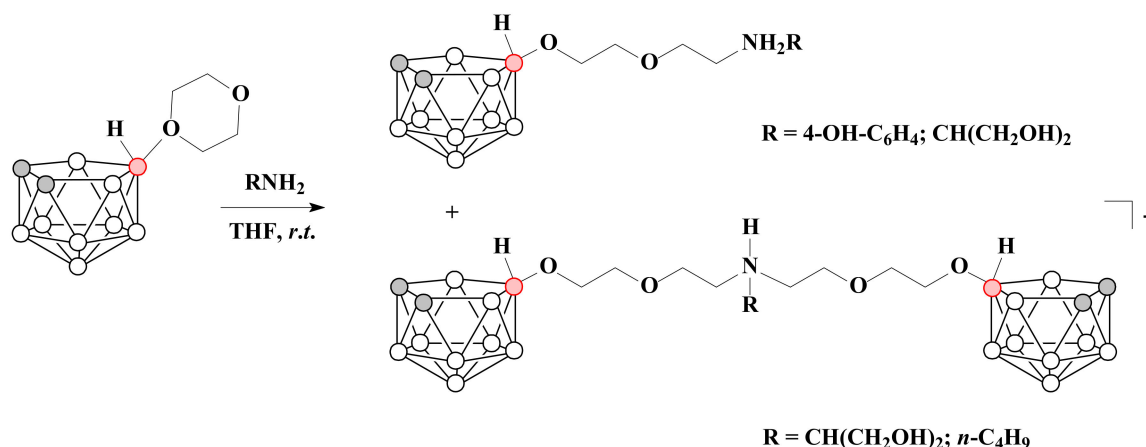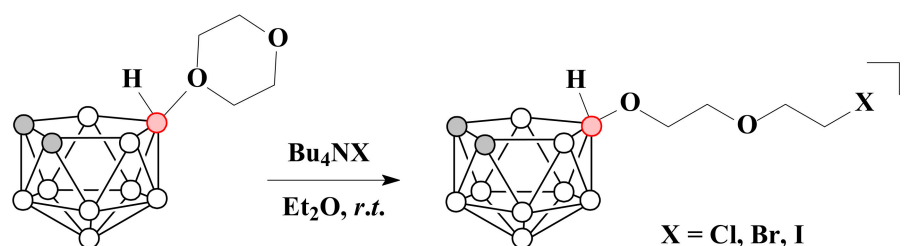
Scheme 16. The ring-open reactions of 1,4-dioxane derivative of *nido*-carborane with primary amines.
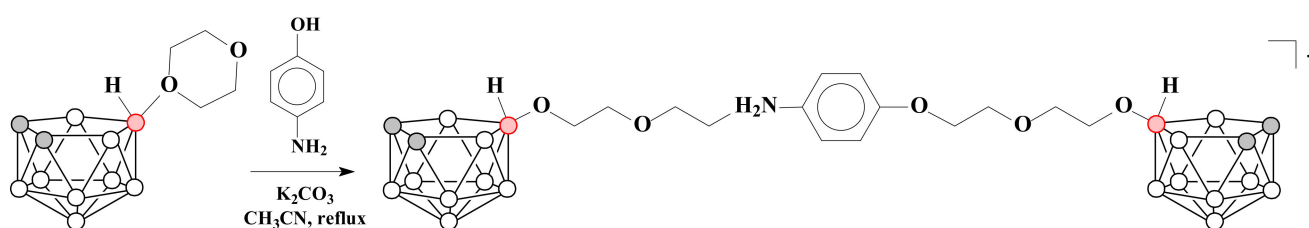
Scheme 17. The reaction of 1,4-dioxane derivative of *nido*-carborane with 4-aminophenol in the presence of K_2CO_3.

The reactions of 1,4-dioxane derivative of *nido*-carborane with halide ions from tetrabutylammonium salts Bu_4NX in diethyl ether at room temperature led to the ring-opening of the cycle with the formation of the corresponding halogen derivatives [10-X-$CH_2CH_2OCH_2CH_2O$-7,8-$C_2B_9H_{11}$]$^-$ (X = Cl, Br, I) [71] (Scheme 18).

Scheme 18. The reactions of 1,4-dioxane derivative of *nido*-carborane with halide ions.

The ring-opening reaction of 1,4-dioxane derivative of *nido*-carborane with KOH under mild conditions in biphasic system of diethyl ether and 2,5M aqueous KOH proceeded with the formation of [10-HO-$CH_2CH_2OCH_2CH_2O$-7,8-$C_2B_9H_{11}$]$^-$, whereas the heating of 10-$O(CH_2CH_2)_2O$-7,8-$C_2B_9H_{11}$ in 2,5M aqueous KOH through deprotonation of bridge hydrogen led to the substitution of the ether by hydroxyl group [10-HO-7,8-$C_2B_9H_{11}$]$^-$ [71] (Scheme 19).
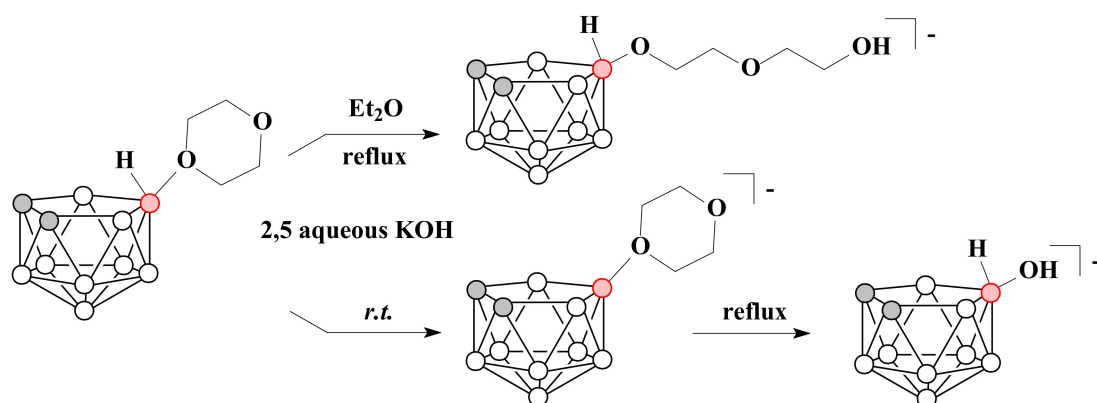
Scheme 19. The reactions of 1,4-dioxane derivative of *nido*-carborane with KOH.

The ring-opening reactions of 1,4-dioxane derivative of *nido*-carborane with dimethyl sulfide or triphenylphosphine gave the corresponding sulfonium and phosphonium derivatives 10-L-CH$_2$CH$_2$OCH$_2$CH$_2$O-7,8-C$_2$B$_9$H$_{11}$ (L = SMe$_2$, PPh$_3$). Subsequent treatment of these compounds with a base such as potassium *tert*-butoxide in both cases led to a side chain shortening product [10-HOCH$_2$CH$_2$O-7,8-C$_2$B$_9$H$_{11}$]$^-$ [87] (Scheme 20).
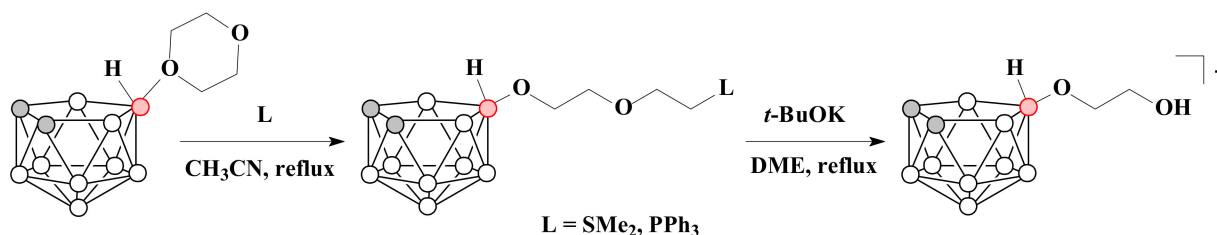
Scheme 20. The synthetic route to [10-HOCH$_2$CH$_2$O-7,8-C$_2$B$_9$H$_{11}$]$^-$ through the contraction of disclosed 1,4-dioxane ring.

The molecular structure of 10-Me$_2$SCH$_2$CH$_2$OCH$_2$CH$_2$O-7,8-C$_2$B$_9$H$_{11}$ was determined by single crystal X-ray diffraction [88] (Figure 5).
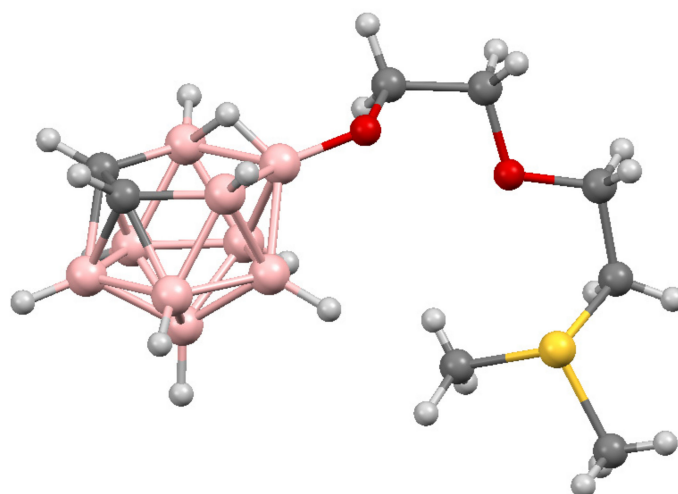
Figure 5. The molecular structure of 10-Me$_2$SCH$_2$CH$_2$OCH$_2$CH$_2$O-7,8-C$_2$B$_9$H$_{11}$.

The dimethyl- and diethyloxonium derivatives of *nido*-carborane are also easily reacted with nucleophiles with the loss of the methyl or ethyl group, respectively, and can be used as alkylating agents [72,73].

4. Synthesis and Properties of Oxonium Derivatives of *nido*-carborane-Based Half-Sandwich Complexes

At the moment, for *nido*-carborane-based half-sandwich complexes only derivatives with tetrahydrofuran are known. With rare exceptions, they were obtained randomly, due to the fact that reactions involving metallacarboranes are most often carried out in dry tetrahydrofuran.

Thus, the reaction of protonated *nido*-carborane 7,8-*nido*-$C_2B_9H_{13}$ with [(CO)$_5$MnX] (X = Me, Et or BF$_4$) in tetrahydrofuran results in [3,3,3-(CO)$_3$-3-Mn(8-(CH$_2$)$_4$O-1,2-C$_2$B$_9$H$_{10}$)] [89] (Scheme 21). The molecular structure of this complex was determined by X-ray diffraction [89] (Figure 6).
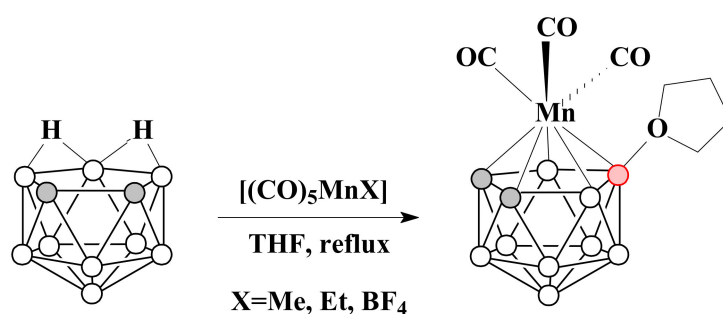
Scheme 21. The synthesis of [3,3,3-(CO)$_3$-3-Mn(8-(CH$_2$)$_4$O-1,2-C$_2$B$_9$H$_{10}$)].
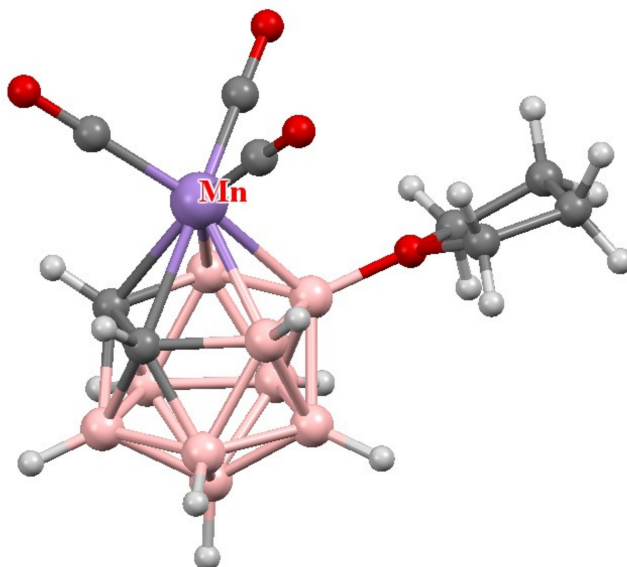
Figure 6. The molecular structure of [3,3,3-(CO)$_3$-3-Mn(8-(CH$_2$)$_4$O-1,2-C$_2$B$_9$H$_{10}$)].

The THF derivatives of the same tricarbonyl manganese(I) complex [3,3,3-(CO)$_3$-3-Mn(8-(CH$_2$)$_4$O-1,2-C$_2$B$_9$H$_{10}$)], as well as its C,C′-dimethyl derivative [3,3,3-(CO)$_3$-3-Mn(8-(CH$_2$)$_4$O-1,2-Me$_2$-1,2-C$_2$B$_9$H$_8$)], can also be prepared directly from the parent metallacarboranes with tetrahydrofuran in the presence of methyl triflate [90] (Scheme 22).
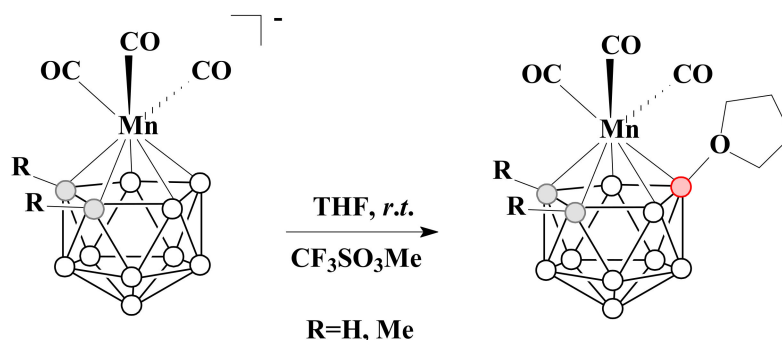
Scheme 22. The synthetic route to [3,3,3-(CO)$_3$-3-Mn(8-(CH$_2$)$_4$O-1,2-C$_2$B$_9$H$_{10}$)] and [3,3,3-(CO)$_3$-3-Mn(8-(CH$_2$)$_4$O-1,2-Me$_2$-1,2-C$_2$B$_9$H$_8$)].

It was shown that the reaction of tetrahydrofuran derivative of the tricarbonyl manganese complex [3,3,3-(CO)$_3$-3-Mn(8-(CH$_2$)$_4$O-1,2-C$_2$B$_9$H$_{10}$)] with NEt$_4$I in THF under reflux conditions resulted in the opening of the tetrahydrofuran cycle with the formation of [3,3,3-(CO)$_3$-3-Mn(8-I-CH$_2$(CH$_2$)$_3$O-1,2-C$_2$B$_9$H$_{10}$)]$^-$ [89] (Scheme 23).
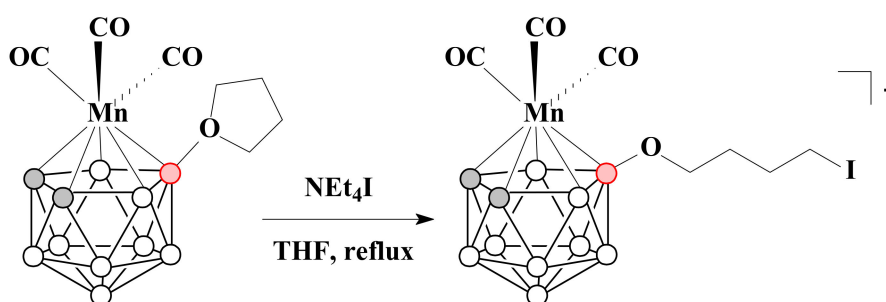
Scheme 23. The reaction of [3,3,3-(CO)$_3$-3-Mn(8-(CH$_2$)$_4$O-1,2-C$_2$B$_9$H$_{10}$)] with NEt$_4$I.

The treatment of [3,3,3-(CO)$_3$-3-Mn(8-(CH$_2$)$_4$O-1,2-C$_2$B$_9$H$_{10}$)] with donor molecules such as PPh$_3$, NEt$_3$ and 4-methylpyridine in THF at room temperature gave the corresponding charge-compensated complexes [3,3,3-(CO)$_3$-3-Mn(8-L-CH$_2$(CH$_2$)$_3$O-1,2-C$_2$B$_9$H$_{10}$)] (L = PPh$_3$, NEt$_3$, 4-Me-C$_5$H$_4$N) [89] (Scheme 24).
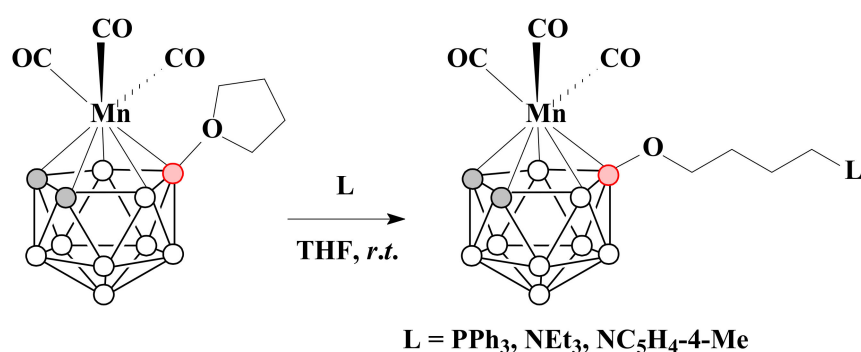
Scheme 24. The reaction of [3,3,3-(CO)$_3$-3-Mn(8-(CH$_2$)$_4$O-1,2-C$_2$B$_9$H$_{10}$)] with PPh$_3$, NEt$_3$ and 4-methylpyridine.

The ruthenium(II) complex [3-Cp*-3-Ru(8-(CH$_2$)$_4$O-1,2-μ-O(CH$_2$)$_2$-1,2-C$_2$B$_9$H$_8$)] was prepared by the reaction of thallium salt of parent [3-Cp*-3-Ru(1,2-μ-O(CH$_2$)$_2$-1,2-C$_2$B$_9$H$_9$)]$^-$ with [Cp*RuCl]$_4$ in tetrahydrofuran [91] (Scheme 25). It should be noted that, in the absence of the CH$_2$OCH$_2$ bridge between carbon atoms, this reaction leads to the 13-vertex dimetallacarborane [Cp*Ru(C$_2$B$_9$H$_{11}$)RuCp*] [91].
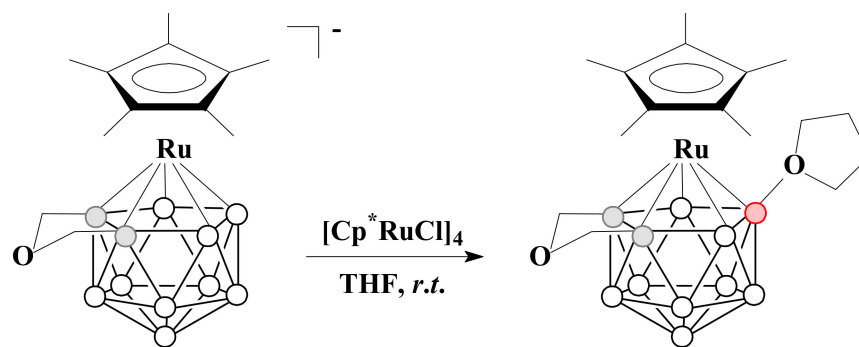
Scheme 25. The synthetic route to [3-Cp*-3-Ru(8-(CH$_2$)$_4$O-1,2-μ-O(CH$_2$)$_2$-1,2-C$_2$B$_9$H$_8$)].

The allyl dicarbonyl molybdenum complex with THF [3-(η^3-C$_3$H$_5$)-3-(CO)$_2$-3-Mo(8-(CH$_2$)$_4$O-1,2-Me$_2$-1,2-C$_2$B$_9$H$_8$)] can be synthesized by the reaction of parent metallacarborane with tetrahydrofuran in the presence of [Ph$_3$C][BF$_4$] [92] (Scheme 26).
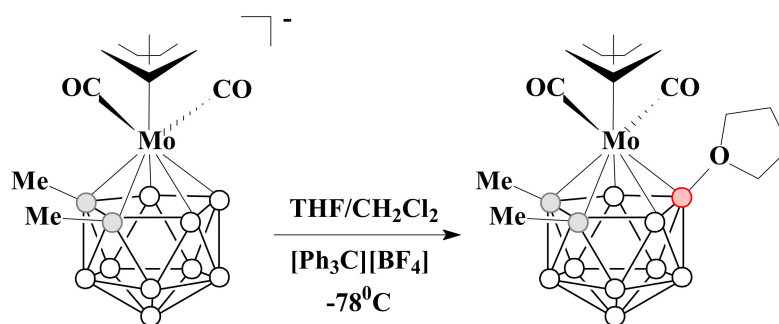
Scheme 26. The synthetic route to [3-(η^3-C$_3$H$_5$)-3-(CO)$_2$-3-Mo(8-(CH$_2$)$_4$O-1,2-Me$_2$-1,2-C$_2$B$_9$H$_8$)].

In similar conditions, but in the presence of Et$_2$O, the acyclic oxonium complexes of molybdenum and tungsten were prepared [92] (Scheme 27).
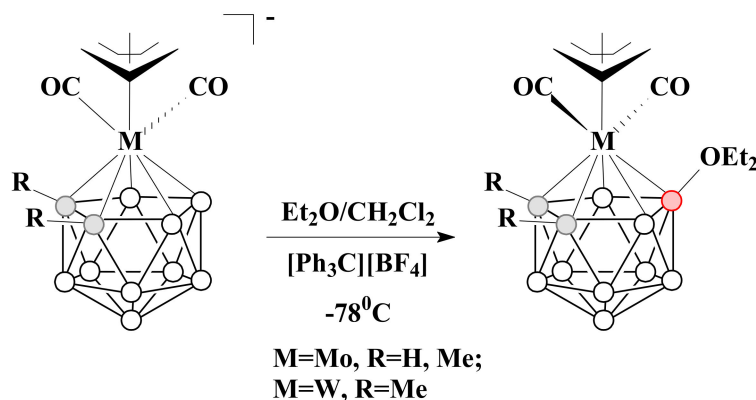
Scheme 27. The synthetic route to acyclic diethyloxonium *nido*-carborane-based complexes with molybdenum and tungsten.

The molecular structure of [3-(η^3-C$_3$H$_5$)-3-(CO)$_2$-3-Mo(8-Et$_2$O-1,2-Me$_2$-1,2-C$_2$B$_9$H$_8$)] was determined by X-ray diffraction [92] (Figure 7).
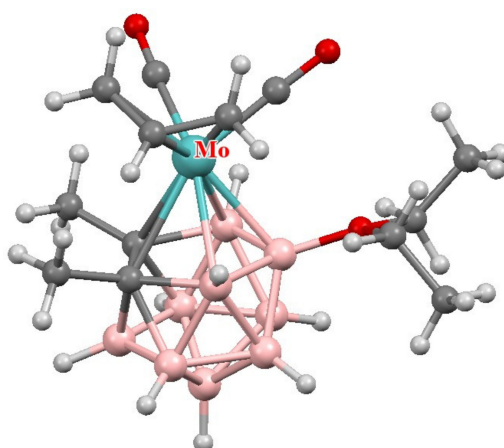
Figure 7. The molecular structure of [3-(η^3-C$_3$H$_5$)-3-(CO)$_2$-3-Mo(8-Et$_2$O-1,2-Me$_2$-1,2-C$_2$B$_9$H$_8$)].

The reaction of a tetrahydrofuran derivative of the allyl dicarbonyl molybdenum complex [3-(η^3-C$_3$H$_5$)-3-(CO)$_2$-3-Mo(8-(CH$_2$)$_4$O-1,2-Me$_2$-1,2-C$_2$B$_9$H$_8$)] with NEt$_4$F or NBu$_4$F in THF at room temperature led to the corresponding ammonium salts of [3-(η^3-C$_3$H$_5$)-3-(CO)$_2$-3-Mo(8-F-CH$_2$(CH$_2$)$_3$O-1,2-Me$_2$-1,2-C$_2$B$_9$H$_8$)]$^-$. The treatment of tetraethylammonium salt of the obtained complex with HBF$_4$.OEt$_2$ under an atmosphere of CO gave the charge-compensated tetracarbonyl molybdenum complex [3-(CO)$_4$-3-Mo(8-F-CH$_2$(CH$_2$)$_3$O-1,2-Me$_2$-1,2-C$_2$B$_9$H$_8$)] [92] (Scheme 28).
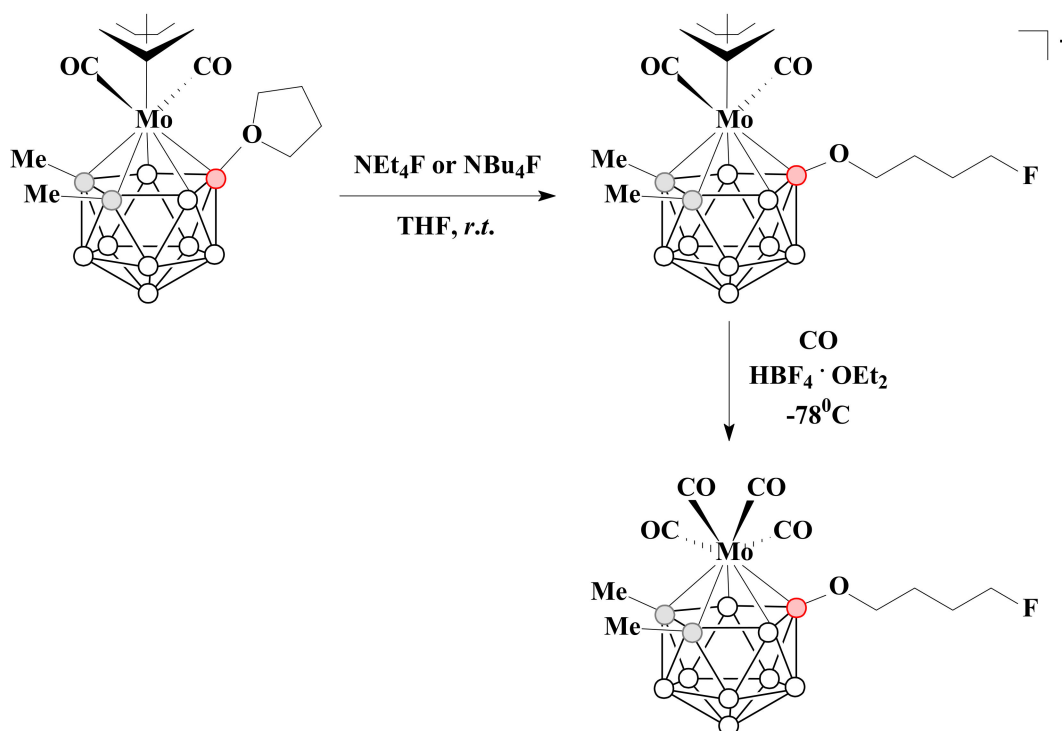
Scheme 28. The synthetic route to [3-(η^3-C$_3$H$_5$)-3-(CO)$_2$-3-Mo(8-F-CH$_2$(CH$_2$)$_3$O-1,2-Me$_2$-1,2-C$_2$B$_9$H$_8$)]$^-$ and [3-(CO)$_4$-3-Mo(8-F-CH$_2$(CH$_2$)$_3$O-1,2-Me$_2$-1,2-C$_2$B$_9$H$_8$)].

In summary, the oxonium derivatives of *nido*-carborane offer a convenient and simple method for modifying the *nido*-carborane cluster, which allows both the introduction of necessary functional groups into the side substituent and the direct preparation of conjugates with the required molecules. The resulting products of their ring-opening reactions are symmetric derivatives free from enantiomeric and diasteriomeric mixtures.

References

1. McCleverty, J.A. Highlights in inorganic chemistry over the last 100 years. *Annu. Rep. Prog. Chem. Sect. A* **2004**, *100*, 3–13. [CrossRef]
2. Wiesboeck, R.A.; Hawthorne, M.F. Dicarbaundecaborane(13) and Derivatives. *J. Am. Chem. Soc.* **1964**, *86*, 1642–1643. [CrossRef]
3. Hawthorne, M.F.; Young, D.C.; Garrett, P.M.; Owen, D.A.; Schwerin, S.G.; Tebbe, F.N.; Wegner, P.A. Preparation and characterization of the (3)-1,2- and (3)-1,7-dicarbadodecahydroundecarborate(-1) ions. *J. Am. Chem. Soc.* **1968**, *90*, 862–868. [CrossRef]
4. Zakharkin, L.I.; Kalinin, V.I. On the reaction of amines with barenes. *Tetrahedron Lett.* **1965**, *7*, 407–409. [CrossRef]
5. Hawthorne, M.F.; Wegner, P.A.; Stafford, R.C. Comments on the reaction of amines with 1,2-dicarbaclovododecaborane(12). *Inorg. Chem.* **1965**, *4*, 1675. [CrossRef]
6. Davidson, M.G.; Fox, M.A.; Hibbert, T.G.; Howard, J.A.K.; Mackinnon, A.; Neretin, I.S.; Wade, K. Deboronation of *ortho*-carborane by an iminophosphorane: Crystal structures of the novel carborane adduct *nido*-$C_2B_{10}H_{12}$·$HNP(NMe_2)_3$ and the borenium salt $[(Me_2N)_3PNHBNP(NMe_2)_3]_2O^{2+}(C_2B_9H_{12}^{-})_2$. *Chem. Commun.* **1999**, 1649–1650. [CrossRef]
7. Wise, S.D.; Au, W.; Getman, T.D. The effect of varying the solvent system on the rate of the deboration of *o*-carborane by *n*-butyl amine. *Main Group Met. Chem.* **2002**, *25*, 411–413. [CrossRef]
8. Tomita, H.; Luu, H.; Onak, T. Cage opening of parent *closo* cage carboranes with fluoride ion: Formation of 5-fluoro-hexahydro-*nido*-2,4-dicarbahexaborate(1-) ([5-F-*nido*-2,4-$C_2B_4H_6$]$^{-}$). *Inorg. Chem.* **1991**, *30*, 812–815. [CrossRef]
9. Fox, M.A.; Gill, W.R.; Herbertson, P.L.; MacBride, J.A.H.; Wade, K.; Colquhoun, H.M. Deboronation of *C*-substituted *ortho*- and *meta-closo*-carboranes using "wet" fluoride ion solutions. *Polyhedron* **1996**, *15*, 565–571. [CrossRef]
10. Getman, T.D. Investigation of potassium fluoride supported on alumina in the deboronation of *o*-carborane. *Inorg. Chem.* **1998**, *37*, 3422–3423. [CrossRef]
11. Yoo, J.; Hwang, J.-W.; Do, Y. Facile and mild deboronation of *o*-carboranes using cesium fluoride. *Inorg. Chem.* **2001**, *40*, 568–570. [CrossRef] [PubMed]
12. Hawthorne, M.F.; Young, D.C.; Andrews, T.D.; Howe, D.V.; Pilling, R.L.; Pitts, A.D.; Reintjer, M.; Warren, L.F.; Wegner, P.A. π-Dicarbollyl derivatives of the transition metals. Metallocene analogs. *J. Am. Chem. Soc.* **1968**, *90*, 879–896. [CrossRef]
13. Grimes, R.N. Transitional metal metallacarbaboranes. In *Comprehensive Organometallic Chemistry II*; Elsevier: Oxford, UK, 1995; Volume 1, pp. 373–430.
14. Grimes, R.N. Metallacarboranes in the new millennium. *Co-ord. Chem. Rev.* **2000**, *200*, 773–811. [CrossRef]
15. Hosmane, N.S.; Maguire, J.A. Metallacarboranes of d- and f-block metals. In *Comprehensive Organometallic Chemistry III*; Elsevier: Oxford, UK, 2007; Volume 3, pp. 175–264.
16. Gozzi, M.; Schwarze, B.; Hey-Hawkins, E. Half- and mixed-sandwich metallacarboranes in catalysis. In *Handbook of Boron Chemistry with Applications in Organometallics, Catalysis, Materials and Medicine. Boron in Catalysis*; Hosmane, N.S., Eagling, R., Eds.; World Scientific Publishing Europe Ltd.: London, UK, 2019; Volume 2, pp. 27–80. [CrossRef]
17. Zhu, Y.; Hosmane, N.S. Carborane-based catalysts for polymerization of olefins. In *Handbook of Boron Chemistry with Applications in Organometallics, Catalysis, Materials and Medicine. Boron in Catalysis*; Hosmane, N.S., Eagling, R., Eds.; World Scientific Publishing Europe Ltd.: London, UK, 2019; Volume 2, pp. 117–134. [CrossRef]
18. Hawthorne, M.F. The role of chemistry in the development of boron neutron capture therapy of cancer. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 950–984. [CrossRef]
19. Soloway, A.H.; Tjarks, W.; Barnum, B.A.; Rong, F.-G.; Barth, R.F.; Codogni, I.M.; Wilson, J.G. The chemistry of neutron capture therapy. *Chem. Rev.* **1998**, *98*, 1515–1562. [CrossRef] [PubMed]
20. Valliant, J.F.; Guenther, K.J.; King, A.S.; Morel, P.; Schaffer, P.; Sogbein, O.O.; Stephenson, K.A. The medicinal chemistry of carboranes. *Co-ord. Chem. Rev.* **2002**, *232*, 173–230. [CrossRef]
21. Armstrong, A.F.; Valliant, J.F. The bioinorganic and medicinal chemistry of carboranes: From new drug discovery to molecular imaging and therapy. *Dalton Trans.* **2007**, 4240–4251. [CrossRef]
22. Lee, W.; Sarkar, S.; Ahn, H.; Kim, J.Y.; Lee, Y.J.; Chang, Y.; Yoo, J. PEGylated liposome encapsulating *nido*-carborane showed significant tumor suppression in boron neutron capture therapy (BNCT). *Biochem. Biophys. Res. Commun.* **2020**, *522*, 669–675. [CrossRef]

23. Varaksin, M.V.; Smyshliaeva, L.A.; Rusinov, V.L.; Makeev, O.G.; Melekhin, V.V.; Baldanshirieva, A.D.; Gubina, O.G.; Charushin, V.N.; Chupakhin, O.N. Synthesis, characterization, and in vitro assessment of cytotoxicity for novel azaheterocyclic *nido*-carboranes—Candidates in agents for boron neutron capture therapy (BNCT) of cancer. *Tetrahedron* **2021**, *102*, 132525. [CrossRef]

24. Tolmachev, V.V.; Sjöberg, S. Polyhedral boron compounds as potential linkers for attachment of radiohalogens to targeting proteins and peptides. A review. *Collect. Czech. Chem. Commun.* **2002**, *67*, 913–935. [CrossRef]

25. Wilbur, D.S.; Chyan, M.-C.; Hamlin, D.K.; Vessella, R.L.; Wedge, T.J.; Hawthorne, M.F. Reagents for astatination of biomolecules. 2. Conjugation of anionic boron cage pendant groups to a protein provides a method for direct labeling that is stable to in vivo deastatination. *Bioconjugate Chem.* **2007**, *18*, 1226–1240. [CrossRef]

26. Green, A.E.C.; Harrington, L.E.; Valliant, J.F. Carborane-carbohydrate derivatives—Versatile platforms for developing targeted radiopharmaceuticals. *Can. J. Chem.* **2008**, *86*, 1063–1069. [CrossRef]

27. Armstrong, A.F.; Lebert, J.M.; Brennan, J.D.; Valliant, J.F. Functionalized carborane complexes of the $[M(CO)_2(NO)]^{2+}$ core (M = ^{99m}Tc, Re): A new class of organometallic probes for correlated in vitro and in vivo imaging. *Organometallics* **2009**, *28*, 2986–2992. [CrossRef]

28. El-Zaria, M.E.; Janzen, N.; Valliant, J.F. Room-temperature synthesis of Re(I) and Tc(I) metallocarboranes. *Organometallics* **2012**, *31*, 5940–5949. [CrossRef]

29. Visbal, R.; Ospino, I.; López-de-Luzuriaga, J.M.; Laguna, A.; Gimeno, M.C. *N*-Heterocyclic carbene ligands as modulators of luminescence in three-coordinate gold(I) complexes with spectacular quantum yields. *J. Am. Chem. Soc.* **2013**, *135*, 4712–4715. [CrossRef] [PubMed]

30. Axtell, J.C.; Kirlikovali, K.O.; Djurovich, P.I.; Jung, D.; Nguyen, V.T.; Munekiyo, B.; Royappa, A.T.; Rheingold, A.L.; Spokoyny, A.M. Blue phosphorescent zwitterionic iridium(III) complexes featuring weakly coordinating *nido*-carborane-based ligands. *J. Am. Chem. Soc.* **2016**, *138*, 15758–15765. [CrossRef]

31. Shafikov, M.Z.; Suleymanova, A.F.; Czerwieniec, R.; Yersin, H. Design strategy for Ag(I)-based thermally activated delayed fluorescence reaching an efficiency breakthrough. *Chem. Mater.* **2017**, *29*, 1708–1715. [CrossRef]

32. Nghia, N.V.; Jana, S.; Sujith, S.; Ryu, J.Y.; Lee, J.; Lee, S.U.; Lee, M.H. *nido*-Carboranes: Donors for thermally activated delayed fluorescence. *Angew. Chem. Int. Ed.* **2018**, *57*, 12483–12488. [CrossRef]

33. Nghia, N.V.; Oh, J.; Sujith, S.; Jung, J.; Lee, M.H. Tuning the photophysical properties of carboranyl luminophores by *closo*- to *nido*-carborane conversion and application to OFF–ON fluoride sensing. *Dalton Trans.* **2018**, *47*, 17441–17449. [CrossRef]

34. He, T.-F.; Ren, A.-M.; Chen, Y.-N.; Hao, X.-L.; Shen, L.; Zhang, B.-H.; Wu, T.-S.; Zhang, H.-X.; Zou, L.-Y. Molecular-level insight of Cu(I) complexes with the 7,8-bis(diphenylphosphino)-7,8-dicarba-*nido*-undecaborate ligand as a thermally activated delayed fluorescence emitter: Luminescent mechanism and design strategy. *Inorg. Chem.* **2021**, *59*, 12039–12053. [CrossRef]

35. Li, Q.; Shi, C.; Huang, M.; Zhang, X.; Sun, F.; Zheng, Y.; Yan, H.; Yang, C.; Yuan, A. Three types of charged ligand-based neutral phosphorescent iridium(III) complexes featuring *nido*-carborane: Synthesis, structures, and solution processed organic light-emitting diode applications. *Dalton Trans.* **2021**, *50*, 16304–16310. [CrossRef]

36. Alconchel, A.A.; Crespo, O.; García-Orduña, P.; Gimeno, M.C. *closo*- or *nido*-Carborane diphosphane as responsible for strong thermochromism or time activated delayed fluorescence (TADF) in $[Cu(N\hat{}N)(P\hat{}P)]^0$. *Inorg. Chem.* **2021**, *60*, 18521–18528. [CrossRef] [PubMed]

37. Lerouge, F.; Ferrer-Ugalde, A.; Viñas, C.; Teixidor, F.; Sillanpää, R.; Abreu, A.; Xochitiotzi, E.; Farfán, N.; Santillan, R.; Núñez, R. Synthesis and fluorescence emission of neutral and anionic di- and tetra-carboranyl compounds. *Dalton Trans.* **2011**, *40*, 7541–7550. [CrossRef] [PubMed]

38. Zhu, Y.; Hosmane, N.S. Ionic liquids: Recent advances and applications in boron chemistry. *Eur. J. Inorg. Chem.* **2017**, *38-39*, 4369–4377. [CrossRef]

39. Sivaev, I.B. Nitrogen heterocyclic salts of polyhedral borane anions: From ionic liquids to energetic materials. *Chem. Heterocycl. Compd.* **2017**, *53*, 638–658. [CrossRef]

40. Grimes, R.N. *Carboranes*, 3rd ed.; Academic Press: London, UK, 2016; pp. 179–257. [CrossRef]

41. Zakharova, M.V.; Sivaev, I.B.; Anufriev, S.A.; Timofeev, S.V.; Suponitsky, K.Y.; Godovikov, I.A.; Bregadze, V.I. A new approach to the synthesis of functional derivatives of *nido*-carborane: Alkylation of [9-MeS-*nido*-7,8-$C_2B_9H_{11}]^-$. *Dalton Trans.* **2014**, *43*, 5044–5053. [CrossRef]

42. Anufriev, S.A.; Zakharova, M.V.; Sivaev, I.B.; Bregadze, V.I. New carborane-containing acids and amines. *Russ. Chem. Bull.* **2017**, *66*, 1643–1649. [CrossRef]

43. Timofeev, S.V.; Zhidkova, O.B.; Prikaznova, E.A.; Sivaev, I.B.; Semioshkin, A.; Godovikov, I.A.; Starikova, Z.A.; Bregadze, V.I. Direct synthesis of *nido*-carborane derivatives with pendant functional groups by copper-promoted reactions with dimethylalkylamines. *J. Organomet. Chem.* **2014**, *757*, 21–27. [CrossRef]

44. Druzina, A.A.; Zhidkova, O.B.; Dudarova, N.V.; Kosenko, I.D.; Ananyev, I.V.; Timofeev, S.V.; Bregadze, V.I. Synthesis and structure of *nido*-carboranyl azide and its "click" reactions. *Molecules* **2021**, *26*, 530. [CrossRef]

45. Druzina, A.A.; Zhidkova, O.B.; Dudarova, N.V.; Nekrasova, N.A.; Suponitsky, K.Y.; Timofeev, S.V.; Bregadze, V.I. Synthesis of zwitter-ionic conjugate of *nido*-carborane with cholesterol. *Molecules* **2021**, *26*, 6687. [CrossRef]

46. Yang, Z.; Zhao, W.; Liu, W.; Wei, X.; Chen, M.; Zhang, X.; Zhang, X.; Liang, Y.; Lu, C.; Yan, H. Metal-free oxidative B-N coupling of *nido*-carborane with N-heterocycles. *Angew. Chem. Int. Ed.* **2019**, *58*, 11886–11892. [CrossRef] [PubMed]

47. Yang, L.; Jei, B.B.; Scheremetjew, A.; Kuniyil, R.; Ackermann, L. Electrochemical B-H nitrogenation: Access to amino acids and BODIPY-labeled *nido*-carboranes. *Angew. Chem. Int. Ed.* **2021**, *60*, 1482–1487. [CrossRef]

48. Chen, M.; Zhao, D.; Xu, J.; Li, C.; Lu, C.; Yan, H. Electrooxidative B-H functionalization of *nido*-carboranes. *Angew. Chem. Int. Ed.* **2021**, *60*, 7838–7844. [CrossRef] [PubMed]

49. Huang, R.; Zhao, W.; Xu, S.; Xu, J.; Li, C.; Lu, C.; Yan, H. Photoredox B-H functionalization to selective B-N(sp^3) coupling of *nido*-carborane with primary and secondary amines. *Chem. Commun.* **2021**, *57*, 8580–8583. [CrossRef] [PubMed]

50. Anufriev, S.A.; Sivaev, I.B.; Suponitsky, K.Y.; Godovikov, I.A.; Bregadze, V.I. Synthesis of 10-methylsulfide and 10-alkylmethylsulfonium *nido*-carborane derivatives: B–H π interactions between the B–H–B hydrogen atom and alkyne group in 10-RC≡CCH$_2$S(Me)-7,8-C$_2$B$_9$H$_{11}$. *Eur. J. Inorg. Chem.* **2017**, *2017*, 4436–4443. [CrossRef]

51. Erokhina, S.A.; Stogniy, M.Y.; Suponitsky, K.Y.; Kosenko, I.D.; Sivaev, I.B.; Bregadze, V.I. Synthesis of new *nido*-carborane based carboxylic acids and amines. *Polyhedron* **2018**, *153*, 145–151. [CrossRef]

52. Stogniy, M.Y.; Erokhina, S.A.; Suponitsky, K.Y.; Anisimov, A.A.; Sivaev, I.B.; Bregadze, V.I. Nucleophilic addition reactions to the ethylnitrilium derivative of nido-carborane 10-EtC≡N-7,8-C$_2$B$_9$H$_{11}$. *New J. Chem.* **2018**, *42*, 17958–17967. [CrossRef]

53. Stogniy, M.Y.; Erokhina, S.A.; Anisimov, A.A.; Suponitsky, K.Y.; Sivaev, I.B.; Bregadze, V.I. 10-NCCH$_2$CH$_2$OCH$_2$CH$_2$C≡N-7,8-C$_2$B$_9$H$_{11}$: Synthesis and reactions with various nucleophiles. *Polyhedron* **2019**, *174*, 114170. [CrossRef]

54. Stogniy, M.Y.; Erokhina, S.A.; Suponitsky, K.Y.; Anisimov, A.A.; Godovikov, I.A.; Sivaev, I.B.; Bregadze, V.I. Synthesis of novel carboranyl amidines. *J. Organomet. Chem.* **2020**, *909*, 121111. [CrossRef]

55. Stogniy, M.Y.; Erokhina, S.A.; Suponitsky, K.Y.; Markov, V.Y.; Sivaev, I.B. Synthesis and crystal structures of nickel(II) and palladium(II) complexes with *o*-carboranyl amidine ligands. *Dalton Trans.* **2021**, *50*, 4967–4975. [CrossRef]

56. Semioshkin, A.A.; Sivaev, I.B.; Bregadze, V.I. Cyclic oxonium derivatives of polyhedral boron hydrides and their synthetic applications. *Dalton Trans.* **2008**, 977–992. [CrossRef]

57. Sivaev, I.B.; Bregadze, V.I. Cyclic oxonium derivatives as an efficient synthetic tool for the modification of polyhedral boron hydrides. In *Boron Science: New Technologies and Applications*; Hosmane, N.S., Ed.; CRC Press: Boca Raton, FL, USA, 2012; pp. 623–637.

58. Druzina, A.A.; Shmalko, A.V.; Sivaev, I.B.; Bregadze, V.I. Cyclic oxonium derivatives of cobalt and iron bis(dicarbollide)s and their use in organic synthesis. *Russ. Chem. Rev.* **2021**, *90*, 785–830. [CrossRef]

59. Young, D.C.; Howe, D.V.; Hawthorne, M.F. Ligand derivatives of (3)-1,2-dicarbadodecahydroundecaborate(-1). *J. Am. Chem. Soc.* **1969**, *91*, 859–862. [CrossRef]

60. Stogniy, M.Y.; Abramova, E.N.; Lobanova, I.A.; Sivaev, I.B.; Bragin, V.I.; Petrovskii, P.V.; Tsupreva, V.N.; Sorokina, O.V.; Bregadze, V.I. Synthesis of functional derivatives of 7,8-dicarba-*nido*-undecaborate anion by ring-opening of its cyclic oxonium derivatives. *Collect. Czech. Chem. Commun.* **2007**, *72*, 1676–1688. [CrossRef]

61. Zakharkin, L.I.; Kalinin, V.N.; Zhigareva, G.G. Oxidation of dicarbadodecahydronidoundecaborate anions by mercury chloride in tetrahydrofuran and pyridine. *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1979**, *28*, 2198–2199. [CrossRef]

62. Stogniy, M.Y.; Sivaev, I.B.; Malysheva, Y.B.; Bregadze, V.I. Synthesis of tetrahydropyran oxonium derivative of 7,8-dicarba-*nido*-undecaborane anion [10-(CH$_2$)$_5$O-7,8-C$_2$B$_9$H$_{11}$]. *Vestnik N. I. Lobachevskiy Nizhegorod Univ.* **2013**, *4*, 115–117. Available online: http://www.unn.ru/pages/e-library/vestnik/99999999_West_2013_4(1)/19.pdf (accessed on 30 December 2021).

63. Laskova, J.; Kosenko, I.; Serdyukov, A.; Sivaev, I.; Bregadze, V.I. Synthesis of naphthalimide derivatives of *closo*-dodecaborate and *nido*-carborane. *J. Organomet. Chem.* **2022**, *959*, 122186. [CrossRef]

64. Sivaev, I.B.; Stogniy, M.Y. Mercury derivatives of polyhedral boranes, carboranes, and metallacarboranes. *Russ. Chem. Bull.* **2019**, *68*, 217–253. [CrossRef]

65. Colquhoun, H.M.; Greenhough, T.J.; Wallbridge, M.G.H. Carbaborane derivatives of the late- and post-transition elements. Part 2. Dicarbaundecaboranyl compounds of copper(I), gold(I), and mercury(II); the crystal and molecular structure of 3-triphenylphosphine-3-mercura-1,2-dicarbadodecaborane(II), a pseudo-σ-bonded metallacarbaborane. *J. Chem. Soc. Dalton Trans.* **1979**, 619–628. [CrossRef]

66. Teixidor, F.; Ayllon, J.A.; Viñas, C.; Kivekäs, R.; Sillanpää, R.; Casabo, J. Mercury coordination to Exo-dithio-7,8-dicarba-*nido*-undecaborate derivatives. *J. Organomet. Chem.* **1994**, *483*, 153–157. [CrossRef]

67. Shaw, K.F.; Reid, B.D.; Welch, A.J. Synthesis and characterisation of metal complexes of ether carboranes. Molecular structures of d^6 ML$_3$, d^8 ML$_2$ and d^{10} ML complexes of mono- and di-ether C$_2$B$_9$ carborane ligands, showing the progressive importance of secondary M . . . O bonding. *J. Organomet. Chem.* **1994**, *482*, 207–220. [CrossRef]

68. Řezácová, P.; Pokorná, J.; Brynda, J.; Kožíšek, M.; Cígler, P.; Lepšík, M.; Fanfrlík, J.; Řezáč, J.; Šašková, K.G.; Sieglová, I.; et al. Design of HIV protease inhibitors based on inorganic polyhedral metallacarboranes. *J. Med. Chem.* **2009**, *52*, 7132–7141. [CrossRef]

69. Frank, R.; Auer, H.; Hey-Hawkins, E. Functionalization of the *nido*-dicarbaborate anion *nido*-7,8-C$_2$B$_9$H$_{12}$$^-$ by hydride abstraction. *J. Organomet. Chem.* **2013**, *747*, 217–224. [CrossRef]

70. Plešek, J.; Jelínek, T.; Mareš, F.; Heřmánek, S. Unique dialkylsulfoniomethylation of the 7,8-C$_2$B$_9$H$_{12}$$^-$ ion to the 9-R$_2$S-CH$_2$-7,8-C$_2$B$_9$H$_{11}$ zwitterions by formaldehyde and dialkyl sulfides. General synthesis of the compounds 10-R$_2$E-7,8-C$_2$B$_9$H$_{11}$ (E = O, S). *Collect. Czech. Chem. Commun.* **1993**, *58*, 1534–1547. [CrossRef]

71. Bakardjiev, M.; El Anwar, S.; Bavol, D.; Růžičková, Z.; Grüner, B. Focus on chemistry of the 10-dioxane-*nido*-7,8-dicarba-undecahydrido undecaborate zwitterion; exceptionally easy abstraction of hydrogen bridge and double-action pathways observed in ring cleavage reactions with OH$^-$ as nucleophile. *Molecules* **2020**, *25*, 814. [CrossRef] [PubMed]

72. Stogniy, M.Y.; Erokhina, S.A.; Kosenko, I.D.; Semioshkin, A.A.; Sivaev, I.B. Dimethyloxonium and methoxy derivatives of *nido*-carborane and metal complexes thereof. *Inorganics* **2019**, *7*, 46. [CrossRef]

73. Shmal'ko, A.V.; Anufriev, S.A.; Anisimov, A.A.; Stogniy, M.Y.; Sivaev, I.B.; Bregadze, V.I. Synthesis of cobalt and nickel 6,6′-diphenylbis(dicarbollides). *Russ. Chem. Bull.* **2019**, *68*, 1239–1247. [CrossRef]

74. Stogniy, M.Y.; Anufriev, S.A.; Bogdanova, E.V.; Sivaev, I.B.; Bregadze, V.I. Mercury(II) chloride in the synthesis of *nido*-carborane derivatives with B-N, B-O and B-S bonds. *Russ. Chem. Bull.* **2022**, *71*, 91–101.

75. Stogniy, M.Y.; Anufriev, S.A.; Shmal'ko, A.V.; Antropov, S.M.; Anisimov, A.A.; Suponitsky, K.Y.; Filippov, O.A.; Sivaev, I.B. The un-expected reactivity of 9-iodo-*nido*-carborane: From nucleophilic substitution reactions to the synthesis of tricobalt tris(dicarbollide) Na[4,4′,4′′-(MeOCH$_2$CH$_2$O)$_3$-3,3′,3′′-Co$_3$(μ^3-O)(μ^3-S)(1,2-C$_2$B$_9$H$_{10}$)$_3$]. *Dalton Trans.* **2021**, *50*, 2671–2688. [CrossRef]

76. Stogniy, M.Y.; Sivaev, I.B.; Petrovskii, P.V.; Bregadze, V.I. Halogenation of the 7,8-dicarba-*nido*-undecaborate anion derivatives [10-RO-7,8-C$_2$B$_9$H$_{11}$]$^-$. *Russ. Chem. Bull.* **2012**, *82*, 91–94. [CrossRef]

77. Serdyukov, A.; Kosenko, I.; Druzina, A.; Grin, M.; Mironov, A.F.; Bregadze, V.I.; Laskova, J. Anionic polyhedral boron clusters conjugates with 7-diethylamino-4-hydroxycoumarin. Synthesis and lipophilicity determination. *J. Organomet. Chem.* **2021**, *946–947*, 121905. [CrossRef]

78. Stogniy, M.Y.; Kazakov, G.S.; Sivaev, I.B.; Bregadze, V.I. Synthesis of podands with *nido*-carboranyl groups as a basis for construction of crown ethers with an incorporated metallacarborane moiety. *Russ. Chem. Bull.* **2013**, *3*, 699–704. [CrossRef]

79. Kazakov, G.S.; Stogniy, M.Y.; Sivaev, I.B.; Suponitsky, K.Y.; Godovikov, I.A.; Kirilin, A.D.; Bregadze, V.I. Synthesis of crown ethers with the incorporated cobalt bis(dicarbollide) fragment. *J. Organomet. Chem.* **2015**, *798*, 196–203. [CrossRef]

80. Olejniczak, A.; Wojtczak, B.; Lesnikowski, Z.J. 2′-Deoxyadenosine bearing hydrophobic carborane pharmacophore nucleosides. *Nucleotides Nucleic Acids* **2007**, *26*, 1611–1613. [CrossRef] [PubMed]

81. Wojtczak, B.A.; Andrysiak, A.; Grüner, B.; Lesnikowski, Z.J. "Chemical ligation": A versatile method for nucleoside modification with boron clusters. *Chem. Eur. J.* **2008**, *14*, 10675–10682. [CrossRef] [PubMed]

82. Stanislav, I.; Presolski, V.; Hong, P.; Finn, M.G. Copper-catalyzed azide-alkyne click chemistry for bioconjugation. *Curr. Protoc. Chem. Biol.* **2011**, *3*, 153–162. [CrossRef]

83. Liang, L.; Astruc, D. The copper(I)-catalyzed alkyne-azide cycloaddition (CuAAC) "click" reaction and its applications. An overview. *Coord. Chem. Rev.* **2011**, *255*, 2933–2945. [CrossRef]

84. Jiang, Z.; He, H.; Liu, H.; Thayumanavan, S. Azide-terminated RAFT polymers for biological applications. *Curr. Protoc. Chem. Biol.* **2020**, *12*, e85. [CrossRef]

85. Tiwari, V.K.; Mishra, B.B.; Mishra, K.B.; Mishra, N.; Singh, A.S.; Chen, X. Cu-catalyzed click reaction in carbohydrate chemistry. *Chem. Rev.* **2016**, *116*, 3086–3240. [CrossRef]

86. Druzina, A.A.; Stogniy, M.Y. Synthesis of cholesterol derivatives based on *closo*- and *nido*-carboranes. *Russ. Chem. Bull.* **2021**, *70*, 527–532. [CrossRef]

87. Shmal'ko, A.V.; Stogniy, M.Y.; Kazakov, G.S.; Anufriev, S.A.; Sivaev, I.B.; Kovalenko, L.V.; Bregadze, V.I. Cyanide free contraction of disclosed 1,4-dioxane ring as a route to cobalt bis(dicarbollide) derivatives with short spacer between the boron cage and terminal functional group. *Dalton Trans.* **2015**, *44*, 9860–9878. [CrossRef] [PubMed]

88. Šubrtová, V.; Petříček, V.; Hummel, L. Structure of the zwitterionic 10-[2-(dimethylsulfonioethoxy)ethoxy]undecahydro-7,8-dicarba-*nido*-undecaborate(1-). *Acta Crystallogr. Sect. C Cryst. Struct. Commun.* **1989**, *45*, 1964–1966. [CrossRef]

89. Gómez-Saso, M.; Mullica, D.F.; Sappenfield, E.; Stone, F.G.A. Reaction of *nido*-7,8-C$_2$B$_9$H$_{13}$ with pentacarbonyl(methyl)manganese: Crystal structure of the charge-compensated complex [Mn(CO)3{η^5-7,8-C$_2$B$_9$H$_{10}$-10-O(CH$_2$)$_4$}]. *Polyhedron* **1996**, *15*, 793–801. [CrossRef]

90. Hata, M.; Kautz, J.A.; Lu, X.L.; McGrath, T.D.; Stone, F.G.A. Revisiting [Mn(CO)$_3$(η^5-*nido*-7,8-C$_2$B$_9$H$_{11}$)]$^-$, the dicarbollide analogue of [(η^5-C$_5$H$_5$)Mn(CO)$_3$]: Reactivity studies leading to boron atom functionalization. *Organometallics* **2004**, *23*, 3590–3602. [CrossRef]

91. Perekalin, D.S.; Lyssenko, K.A.; Kudinov, A.R.; Corsini, M.; Fabrizi de Biani, F. Synthesis of 13-vertex dimetallacarboranes by electrophilic insertion into 12-vertex ruthenacarboranes. *Dalton Trans.* **2017**, *46*, 15710–15718. [CrossRef] [PubMed]

92. Mullica, D.F.; Sappenfield, E.L.; Stone, F.G.A.; Woollam, S.F. Allyl carborane complexes of molybdenum and tungsten: Cage-hydride abstraction reactions in the presence of donor molecules. *Organometallics* **1994**, *13*, 157–166. [CrossRef]