Review

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

Marina Yu. Stogniy * and Igor B. Sivaev †

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-undecaborane anion [7,8-C$_2$B$_9$H$_{12}$]$^-$ (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-C$_2$B$_9$H$_{11}$]$^{2-}$, 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 asymetrically substituted derivatives [9-X-7,8-C$_2$B$_9$H$_{11}$]$^-$ [41–49].

Several approaches to the synthesis of symmetrically substituted derivatives of nido-carborane [10-X-7,8-C$_2$B$_9$H$_{11}$]$^-$ 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-decarborate 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 FeCl₃ in a mixture of benzene and tetrahydrofuran. The reaction gave a mixture of asymmetric 9-(CH₂)₄O-7,8-C₂B₉H₁₁ and symmetric 10-(CH₂)₄O-7,8-C₂B₉H₁₁ 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-(CH₂)₄O-7,8-C₂B₉H₁₁ and 10-(CH₂)₄O-7,8-C₂B₉H₁₁ by the reaction of nido-carborane with FeCl₃ 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 HgCl₂ in tetrahydrofuran leads to the selective formation of the symmetrically substituted product 10-(CH₂)₄O-7,8-C₂B₉H₁₁ [60,61]. In a similar way, the derivatives with 1,4-dioxane 10-O(CH₂CH₂)₂O-7,8-C₂B₉H₁₁ [60] and tetrahydropyran 10-(CH₂)₅O-7,8-C₂B₉H₁₁ [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 η¹-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-C₂B₉H₁₃, 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-(CH₂)₄O-7,8-C₂B₉H₁₁ can be obtained by the reaction of tetramethylammonium salt of nido-carborane with AlCl₃ 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].
methods of synthesis of symmetrically substituted oxonium derivatives of nido-carborane are summarized in Scheme 2.

Reagents and conditions:

X = - : HgCl₂, THF, benzene, reflux [60,61];
AlCl₃, acetone, THF, reflux [69];
HC(O)H or MeC(O)H, HCl, THF, toluene, r.t. [70]

X=O: HgCl₂, 1,4-dioxane, benzene, reflux [60];
H₂SO₄, toluene, r.t.; 1,4-dioxane, reflux [68];
HC(O)H, HCl, 1,4-dioxane, toluene, r.t. [70]

X=CH₂: HgCl₂, THP, benzene, reflux [62,63]

Scheme 2. The different synthetic pathways to the 10-(CH₂)₄O-7,8-C₂B₉H₁₁, 10-O(CH₂CH₂)₂O-7,8-C₂B₉H₁₁ and 10-(CH₂)₅O-7,8-C₂B₉H₁₁.

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(CH₂CH₂)₂O-7,8-C₂B₉H₁₁.

It should be noted that, in addition to cyclic oxonium derivatives of nido-carborane, some acyclic oxonium derivatives such as the dimethyloxonium 9-Me₂O-7,8-C₂B₉H₁₁ and 10-Me₂O-7,8-C₂B₉H₁₁ [72] and the diethyloxonium 9-Et₂O-7,8-C₂B₉H₁₁ [73] and 10-Et₂O-7,8-C₂B₉H₁₁ [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-MeOCH₂CH₂(Me)O-7,8-C₂B₉H₁₁ and 10-MeOCH₂CH₂(Me)O-7,8-C₂B₉H₁₁ was also reported, however they have low stability and easily lose the methyl group, giving the corresponding alkoxy derivatives [75].

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.](image)

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[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$_{11}$] [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-OOCC$_6$H$_4$O)-C$_4$H$_8$O-7,8-C$_2$B$_9$H$_{11}$], K[10-(4-OOCC$_6$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-methoxyphenol 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).
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$_2$H$_4$OC$_2$H$_4$O-7,8-C$_2$B$_9$H$_{11}$)$_2$C$_6$H$_4$], whereas the reaction with hydroquinone leads to two products K$_2$[1,4-(10-OC$_2$H$_4$OC$_2$H$_4$O-7,8-C$_2$B$_9$H$_{11}$)$_2$C$_6$H$_4$] and K[10-(4'-KOC$_6$H$_4$O)-CH$_2$CH$_2$OCH$_2$CH$_2$O-7,8-C$_2$B$_9$H$_{11}$] [78] (Scheme 8).

The reaction of two equivalents of 10-O(CH$_2$CH$_2$)$_2$O-7,8-C$_2$B$_9$H$_{11}$ with ethylene glycol in the presence of K$_2$CO$_3$ leads to the formation of carboranyl triethylene glycol ether...
[10-HO(CH_2CH_2O)_3-7,8-C_2B_9H_11]^- along with a certain amount of carboranyl diethylene glycol formate [10-HC(O)O(CH_2CH_2O)_2-7,8-C_2B_9H_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)_2CSCH_2CH_2OCH_2CH_2O-7,8-C_2B_9H_11, the subsequent hydrolysis of which gives the corresponding thiol [10-HSCH_2CH_2OCH_2CH_2O-7,8-C_2B_9H_11]^- . The formed thiol was reacted with one equivalent of 1,4-dioxane derivative of nido-carborane to give a podand [(10-CH_2CH_2OCH_2CH_2O-7,8-C_2B_9H_11)_2S]^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_2CH_2OCH_2CH_2O-7,8-C_2B_9H_11]^- can also be obtained directly by the reaction of 10-O(CH_2CH_2)_2O-7,8-C_2B_9H_11 with excess of aqueous sodium hydrosulfide in tetrahydrofuran. The by-product of this reaction is a thioether [(10-CH_2CH_2OCH_2CH_2O-7,8-C_2B_9H_11)_2S]^2- [71].

Two nido-carborane-based podands [(10-CH_2CH_2OCH_2CH_2O-7,8-C_2B_9H_11)_2S]^2- and [1,2-(10-SCH_2CH_2OCH_2CH_2O-7,8-C_2B_9H_11)_2C_6H_4]^2- were used for the synthesis of crown ethers with the cobalt bis(dicarbollide) fragment incorporated in heteromacrocyle [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′-(OCH₂CH₂OCH₂CH₂S)₂-o-C₆H₄-3,3′-Co(1,2-C₂B₉H₉)₂]⁻, which was obtained during the drying of the solution of parent potassium salt in diethyl ether over Na₂SO₄, was determined by X-ray analysis [79] (Figure 3).

Figure 3. The molecular structure of Na[8,8′-(OCH₂CH₂OCH₂CH₂S)₂-o-C₆H₄-3,3′-Co(1,2-C₂B₉H₉)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-N$_3$CH$_2$CH$_2$OCH$_2$CH$_2$O-7,8-C$_2$B$_9$H$_{11}$ 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$_3$N 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-NH₃CH₂CH₂OCH₂CH₂O-7,8-C₂B₉H₁₁ was determined by single crystal X-ray diffraction [71] (Figure 4).

![Figure 4. The molecular structure of 10-NH₃CH₂CH₂OCH₂CH₂O-7,8-C₂B₉H₁₁.](image)

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.](image)

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-C₆H₄)-NH₂CH₂CH₂OCH₂CH₂O-7,8-C₂B₉H₁₁, whereas the treatment of 10-O(CH₂CH₂)₂O-7,8-C₂B₉H₁₁ with 2-amino-1,3-propanediol resulted in a mixture of 10-(HOC₆H₄)₂CHNH₂CH₂CH₂OCH₂CH₂O-7,8-C₂B₉H₁₁ and [(HOC₆H₄)₂CHNH-N,N-(10,10′-CH₂CH₂OCH₂CH₂O-7,8-C₂B₉H₁₁)₂]⁻ [71]. At the same time the reaction with n-butylamine led only to [n-C₄H₉NH-(10-CH₂CH₂OCH₂CH₂O-7,8-C₂B₉H₁₁)]⁻ [68] (Scheme 16).

The treatment of 1,4-dioxane derivative of nido-carborane with 4-aminophenol in the presence of K₂CO₃ in acetonitrile under reflux conditions gave the product of ring-opening both by amino and hydroxyl groups [7,8-C₂B₉H₁₁-10-CH₂CH₂OCH₂CH₂O-H₂N-C₆H₄-O-10′-CH₂CH₂OCH₂CH₂O-7,8-C₂B₉H₁₁]⁻ [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$_2$CO$_3$.

The reactions of 1,4-dioxane derivative of nido-carborane with halide ions from tetrabutylammonium salts Bu$_4$NX 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$_2$CH$_2$OCH$_2$CH$_2$O-7,8-C$_2$B$_9$H$_{11}$]$^-$ (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$_2$CH$_2$OCH$_2$CH$_2$O-7,8-C$_2$B$_9$H$_{11}$]$^-$, whereas the heating of 10-O(CH$_2$CH$_2$)$_2$O-7,8-C$_2$B$_9$H$_{11}$ 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$_2$B$_9$H$_{11}$]$^-$ [71] (Scheme 19).

Scheme 19. The 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.
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 = SM$_2$$_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\(_2\)B\(_9\)H\(_{13}\) with [(CO)\(_3\)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\(_{10}\))].](image)

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).

![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\(_{10}\))].](image)
It was shown that the reaction of tetrahydrofuran derivative of the tricarbonyl manganese complex $[3,3,3-(\text{CO})_3-3\text{-Mn}(8-(\text{CH}_2)_4\text{O}-1,2-C_2B_9H_{10})]^{-}$ with $\text{NEt}_4\text{I}$ in THF under reflux conditions resulted in the opening of the tetrahydrofuran cycle with the formation of $[3,3,3-(\text{CO})_3-3\text{-Mn}(8-I\text{-CH}_2(\text{CH}_2)_3\text{O}-1,2-C_2B_9H_{10})]^{-}$ [89] (Scheme 23).

The treatment of $[3,3,3-(\text{CO})_3-3\text{-Mn}(8-(\text{CH}_2)_4\text{O}-1,2-C_2B_9H_{10})]$ with donor molecules such as $\text{PPh}_3$, $\text{NEt}_3$ and 4-methylpyridine in THF at room temperature gave the corresponding charge-compensated complexes $[3,3,3-(\text{CO})_3-3\text{-Mn}(8-L\text{-CH}_2(\text{CH}_2)_3\text{O}-1,2-C_2B_9H_{10})]^{-}$ (L = $\text{PPh}_3$, $\text{NEt}_3$, 4-Me-$\text{C}_5\text{H}_4\text{N}$) [89] (Scheme 24).

The ruthenium(II) complex $[3\text{-Cp}^*\text{-3-Ru}(8-(\text{CH}_2)_4\text{O}-1,2-C_2B_9H_{10})]$ was prepared by the reaction of thallium salt of parent $[3\text{-Cp}^*\text{-3-Ru}(1,2-\mu-O(\text{CH}_2)_2\text{-1,2-C}_2\text{B}_9\text{H}_9)]^{-}$ with $[\text{Cp}^*\text{RuCl}]_4$ in tetrahydrofuran [91] (Scheme 25). It should be noted that, in the absence of the $\text{CH}_2\text{OCH}_2$ bridge between carbon atoms, this reaction leads to the 13-vertex dimetallacarborane $[\text{Cp}^*\text{Ru}(\text{C}_2\text{B}_9\text{H}_{11})\text{RuCp}^*]$ [91].
Scheme 25. The synthetic route to \([3\text{-Cp}^*\text{-3-Ru}(8-(\text{CH}_2)_4\text{O}-1,2-\mu\text{-O}(\text{CH}_2)_2-1,2-\text{C}_2\text{B}_9\text{H}_8)]\).

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

Scheme 26. The synthetic route to \([3-(\eta^3\text{-C}_3\text{H}_5)-3-(\text{CO})_2-3-\text{Mo}(8-(\text{CH}_2)_4\text{O}-1,2-\text{Me}_2-1,2-\text{C}_2\text{B}_9\text{H}_8)]\).

In similar conditions, but in the presence of Et_2O, the acyclic oxonium complexes of molybdenum and tungsten were prepared [92] (Scheme 27).

Scheme 27. The synthetic route to acyclic diethyloxonium \(\text{nido}\)-carborane-based complexes with molybdenum and tungsten.

The molecular structure of \([3-(\eta^3\text{-C}_3\text{H}_5)-3-(\text{CO})_2-3-\text{Mo}(8-\text{Et}_2\text{O}-1,2-\text{Me}_2-1,2-\text{C}_2\text{B}_9\text{H}_8)]\) was determined by X-ray diffraction [92] (Figure 7).
The reaction of a tetrahydrofuran derivative of the allyl dicarbonyl molybdenum complex \([3-(\eta^3-C_3H_5)-3-(CO)_2-3-Mo(8-\text{Et}_2\text{O}-1,2-Me_2-1,2-C_2\text{B}_9\text{H}_8)]\) with NEt$_4$F or NBu$_4$F in THF at room temperature led to the corresponding ammonium salts of \([3-(\eta^3-C_3H_5)-3-(CO)_2-3-Mo(8-\text{F-CH}_2(\text{CH}_2)_3\text{O}-1,2-Me_2-1,2-C_2\text{B}_9\text{H}_8)]^-\). 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 \([3-(CO)_4-3-Mo(8-\text{F-CH}_2(\text{CH}_2)_3\text{O}-1,2-Me_2-1,2-C_2\text{B}_9\text{H}_8)]\) [92] (Scheme 28).

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.


Reactions 2022, 3


87. Shmaľ’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]


