Charge-Compensated Derivatives of Nido-Carborane

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Compared with organic analogs, onium derivatives of nido-carborane have increased stability due to the stabilizing electron-donor action of the boron cage. Charge-compensated derivatives are considered according to the type of heteroatom bonded to a boron atom.

Keywords: nido-carborane ; charge compensation ; onium derivatives

1. Introduction

The synthesis of the first polyhedral boranes, carboranes, and metallacarboranes in the early 1960s was one of the major highlights in the development of inorganic chemistry over the last century [1]. The first reports on the synthesis of icosahedral carboranes appeared almost sixty years ago, at the end of 1963 when both the United States and the Soviet Union almost simultaneously declassified documents about their boron fuel projects [2][3][4][5]. A few months later, the nucleophile-promoted removal of one boron atom from the icosahedral ortho-carborane cage to form the 11-vertex nido-carborane cage species (Figure 1) was reported [6]. It was one of the most significant findings in the early years of the development of carborane chemistry, and now, more than five decades later, it remains indispensable for the synthesis of numerous metallacarboranes [7][8][9][10][11][12][13][14][15][16][17] and hydrophilic functionalized carboranes for medical [18][19][20][21][22][23][24][25][26][27][28][29][30][31][32][33][34][35][36][37][38][39][40] applications.
Metallacarboranes based on the dicarbollide ligand \([7,8-C_2B_9H_{11}]^{2-}\), which is formed upon the deprotonation of nido-carborane with strong bases, resemble the well-known transition metal cyclopentadienyl complexes. However, the dicarbollide ligand differs from the cyclopentadienyl ligand in a number of ways. In addition to its 3D character, the dicarbollide ligand is a significantly stronger donor than the cyclopentadienyl one and has a double charge. The donor nature of the dicarbollide ligand can be largely tuned via the introduction of substituents of various natures. At the same time, the charge of the ligand can be partially compensated by introducing into the dicarbollide ligand the so-called charge-compensating substituents of an onium nature (ammonium, phosphonium, sulfonium, etc.). This significantly brings the properties of the dicarbollide and cyclopentadienyl complexes closer together and causes a high interest in metallacarboranes based on charge-compensated dicarbollide ligands.

2. Charge-Compensated Derivatives of Nido-Carborane with Boron–Nitrogen Bond

Due to the great diversity of nitrogen chemistry, the charge-compensated derivatives of nido-carborane with the B-N bond are characterized by the greatest variety of forms. The first example of the synthesis of charge-compensated derivatives of nido-carborane with a B-N bond was the reaction of the parent nido-carborane with pyridine in benzene in the presence of anhydrous FeCl₃, leading to the asymmetrically substituted pyridinium derivative 9-Py-7,8-C₂B₉H₁₁ (Scheme 1) \([41]\), the structure of which was later supported via a single-crystal X-ray diffraction study (Figure 2) \([42]\). When FeCl₃·6H₂O was used instead of anhydrous FeCl₃, the by-product of the reaction was the disubstituted pyridinium derivative 9,11-Py₂-7,8-C₂B₉H₉ \([43]\). The reaction with 7,8-dimethyl-nido-carborane proceeds in a similar way, giving 9-Py-7,8-Me₂-7,8-C₂B₉H₉ \([44]\). In a similar way, the reaction of nido-carborane with methyl isonicotinate in the presence of FeCl₃ in refluxing benzene results in 9-(4'-MeO(O)CC₆H₅)₇,8-C₂B₉H₁₁ \([45]\).
Scheme 1. The synthetic process to obtain 9-Py-7,8-C\textsubscript{2}B\textsubscript{9}H\textsubscript{11}.

Figure 2. Crystal molecular structures of 9-Py-7,8-C\textsubscript{2}B\textsubscript{9}H\textsubscript{11} (left) and 10-Py-7,8-C\textsubscript{2}B\textsubscript{9}H\textsubscript{11} (right). Hydrogen atoms of organic substituents are omitted for clarity.

The reaction of \textit{nido}-carborane with pyridine in the presence of HgCl\textsubscript{2} in refluxing benzene gives a mixture of the symmetrically and asymmetrically substituted pyridinium derivatives 10-Py-7,8-C\textsubscript{2}B\textsubscript{9}H\textsubscript{11} and 9-Py-7,8-C\textsubscript{2}B\textsubscript{9}H\textsubscript{11} in a ratio of 2:1 (Scheme 2)\textsuperscript{50,54}. The reaction of 7,8-dimethyl-\textit{nido}-carborane [7,8-Me\textsubscript{2}-7,8-C\textsubscript{2}B\textsubscript{9}H\textsubscript{11}]\textsuperscript{−} with pyridine proceeds in a similar way\textsuperscript{54}.

Scheme 2. Synthesis of 10-Py-7,8-C\textsubscript{2}B\textsubscript{9}H\textsubscript{11} and 9-Py-7,8-C\textsubscript{2}B\textsubscript{9}H\textsubscript{11} via the reaction of \textit{nido}-carborane with pyridine in the presence of HgCl\textsubscript{2}.

The asymmetrically substituted 9-pyridinium derivative of \textit{nido}-carborane was also prepared via the reaction of the parent \textit{ortho}-carborane with pyridine in the presence of copper acetate and water. Similar reactions with C-monosubstituted \textit{ortho}-carboranes give a mixture of the corresponding isomeric pyridinium derivatives 9-Py-7-R-7,8-C\textsubscript{2}B\textsubscript{9}H\textsubscript{10} and 11-Py-7-R-7,8-C\textsubscript{2}B\textsubscript{9}H\textsubscript{10} (R = Me, Ph). In the case of 1-XCH\textsubscript{2} derivatives of \textit{ortho}-carborane (X = Cl, Br, OH), in addition to a mixture of the corresponding 9- and 11-pyridinium derivatives of \textit{nido}-carborane, the reaction gives the pyridinium methyl derivative 7-PyCH\textsubscript{2}-7,8-C\textsubscript{2}B\textsubscript{9}H\textsubscript{11}\textsuperscript{58}.

3. Charge-Compensated Derivatives of \textit{Nido}-Carborane with Boron–
Phosphorus Bond

Unlike derivatives with a boron–nitrogen bond, derivatives of nido-carboranes with a boron–phosphorus bond can be prepared using electrophilic substitution reactions. Heating the potassium salt of nido-carborane K[7,8-C₂B₉H₁₁] with Ph₂PCl in tetrahydrofuran at reflux leads to the P-protonated diphenylphosphonium derivative 9-Ph₂PH-7,8-C₂B₉H₁₁, which can be alkylated with MeI under reflux in ethanol in the presence of EtONa as a base to give the methyldiphenylphosphonium derivative 9-MePh₂P-7,8-C₂B₉H₁₁ (Scheme 3, Figure 3).

Scheme 3. The synthesis of 9-Ph₂PH-7,8-C₂B₉H₁₁ and its alkylation.

Figure 3. Crystal molecular structures of 9-MePh₂P-7,8-C₂B₉H₁₁ (left) and 10-MePh₂P-7,8-C₂B₉H₁₁ (right). Hydrogen atoms of phenyl and methyl groups are omitted for clarity.

The symmetrically substituted phosphonium derivatives 10-Ph₂PH-7,8-C₂B₉H₁₁ and 10-MePh₂P-7,8-C₂B₉H₁₁ (Figure 4) were prepared in a similar way using the disodium dicarbollide salt Na₂[7,8-C₂B₉H₁₁] as a starting material (Scheme 4).

Scheme 4. The synthesis of 10-Ph₂PH-7,8-C₂B₉H₁₁ and its alkylation.
Phosphonium derivatives of nido-carborane also can be prepared via Lewis-acid-mediated nucleophilic substitution reactions. The reaction of the potassium salt of nido-carborane K[7,8-C\(_2\)B\(_9\)H\(_{12}\)] with PPh\(_3\) in the presence FeCl\(_3\) in benzene at 80 °C leads to a mixture of triphenylphosphonium 9-Ph\(_3\)P-7,8-C\(_2\)B\(_9\)H\(_{11}\) and 10-Ph\(_3\)P-7,8-C\(_2\)B\(_9\)H\(_{11}\), which were separated using column chromatography on silica (Scheme 5)\(^{56,57}\).

![Scheme 5](image)

**Scheme 5.** Reaction of nido-carborane with triphenylphosphine in the presence of FeCl\(_3\).

The asymmetrical triphenylphosphonium derivative 9-Ph\(_3\)P-7,8-C\(_2\)B\(_9\)H\(_{11}\) was also obtained via the reaction of triphenylphosphine with the dithallium dicarbollide salt Tl\(_2\)[7,8-C\(_2\)B\(_9\)H\(_{11}\)] in dichloromethane and in the presence of AgBr at ambient temperature (Scheme 6)\(^{58}\).

![Scheme 6](image)

**Scheme 6.** Synthesis of 9-Ph\(_3\)P-7,8-C\(_2\)B\(_9\)H\(_{11}\).

Similar to the pyridinium derivatives, a series of asymmetrically substituted phosphonium derivatives 9-R'R\(_2\)P-7,8-Ph\(_2\)-7,8-C\(_2\)B\(_9\)H\(_3\) was prepared via electrocatalyzed B-P oxidative couplings of 7,8-diphenyl-nido-carborane with various phosphines and phosphites (Scheme 7, Figure 5)\(^{59}\).

Figure 4. Crystal molecular structures of 9-MePh\(_2\)P-7,8-C\(_2\)B\(_9\)H\(_{11}\) (left) and 10-MePh\(_2\)P-7,8-C\(_2\)B\(_9\)H\(_{11}\) (right). Hydrogen atoms of phenyl and methyl groups are omitted for clarity.
Scheme 7. The electrocatalyzed B-P oxidative coupling of triarylphosphines, diarylalkylphosphines, and trialkylphosphines with 7,8-diphenyl-\textit{nido}-carborane.

\[ R = R' = \text{Me, Bu, } C_6H_5, \ C_6H_4-p\text{-Me}, \ C_6H_4-m\text{-Me}, \ C_6H_4-p\text{-F}, \ C_6H_4-m\text{-F}, \ C_6H_4-m\text{-Cl}, \ 2-C_4H_3O, \ 2-C_4H_3S, \ OEt, \ OBu, \ OCH_2CH_2Cl, \ OCH_2CH=CH_2; \]
\[ R = \text{Me}, \ R' = \text{Ph}; \ R = \text{Ph}, \ R' = \text{Me}, \ CH_2CH=CH \]

Figure 5. Crystal molecular structure of 9-Ph\textsubscript{3}P-7,8-Ph\textsubscript{2}-7,8-C\textsubscript{2}B\textsubscript{9}H\textsubscript{9}. Hydrogen atoms of phenyl rings are omitted for clarity.

4. Charge-Compensated Derivatives of \textit{Nido}-Carborane with Boron–Arsenic and Boron–Antimony Bonds

The charge-compensated derivatives of \textit{nido}-carborane with boron–arsenic and boron–antimony bonds are rare and are limited to a few examples. Similar to the triphenylphosphonium derivative, the asymmetrically substituted triphenylarsonium and tetraphenylstiboniun derivatives 9-Ph\textsubscript{3}X-7,8-Ph\textsubscript{2}-7,8-C\textsubscript{2}B\textsubscript{9}H\textsubscript{9} (X = As, Sb) were prepared via electrocatalyzed oxidative couplings of 7,8-diphenyl-\textit{nido}-carborane with Ph\textsubscript{3}As and Ph\textsubscript{3}Sb, respectively (Scheme 8, Figure 6).
Scheme 8. Synthesis of 9-Ph₃As-7,8-Ph₂-7,8-C₂B₉H₁₀ and 9-Ph₃As-7,8-Ph₂-7,8-C₂B₉H₉.

Figure 6. Crystal molecular structure of 9-Ph₃As-7,8-Ph₂-7,8-C₂B₉H₁₀. Hydrogen atoms of phenyl groups are omitted for clarity.

The reaction of 2-pyridyl-substituted nido-carborane [7-(2’-Py)-7,8-C₂B₉H₁₁]⁻ with triphenylarsine in the presence of catalytic amounts of PdCl₂ in a mixture of toluene, water, and acetonitrile at 120°C results in the corresponding triphenylarsonium derivative 11-Ph₃As-7-(2’-Py)-7,8-C₂B₉H₁₀ (Scheme 9).

Scheme 9. Synthesis of 11-Ph₃As-7-(2’-Py)-7,8-C₂B₉H₁₀.
5. Charge-Compensated Derivatives of Nido-Carborane with Boron–Oxygen Bond

Alkyl oxonium salts are much less stable than ammonium and phosphonium salts, and some of them are used in organic chemistry as strong alkylating agents. Nevertheless, strong electron-withdrawing of polyhedral boron hydride clusters substituted at boron atoms and, in particular, nido-carborane,[6] is capable of stabilizing their oxonium derivatives.[6–8] The first example of such a derivative was obtained very soon after the discovery of nido-carborane via the reaction of the potassium salt of nido-carborane with tetrahydrofuran in the presence of FeCl₃ in benzene. As a result, a mixture of two isomeric tetrahydrofuran derivatives of nido-carborane was obtained. The reaction with the C,C′-dimethyl derivative of nido-carborane proceeds in a similar way (Scheme 10).[53].

![Scheme 10](image)

Scheme 10. Synthesis of 9-(CH₂)₃O-7,8-C₂B₉H₁₁ and 10-(CH₂)₄O-7,8-C₂B₉H₁₁ via the reaction of nido-carborane with FeCl₃ in THF–benzene mixture.

It was later found that the replacement of FeCl₃ with HgCl₂ in this reaction leads to the selective formation of the symmetrically substituted tetrahydrofuran derivative 10-(CH₂)₄O-7,8-C₂B₉H₁₁.[43,44] The symmetrically substituted derivative was also obtained via the reaction of the tetramethylammonium salt of nido-carborane with AlCl₃ in a mixture of tetrahydrofuran and acetone[65] and by the treatment of the potassium salt of nido-carborane with tetrahydrofuran in the presence of acetaldehyde or formaldehyde and hydrochloric acid in a mixture of water and toluene[66] (Scheme 11).

![Scheme 11](image)

Scheme 11. Different pathways for synthesis of 10-(CH₂)₄O-7,8-C₂B₉H₁₁.

Oxonium derivatives of nido-carborane with other cyclic ethers were synthesized as well. The symmetrically substituted 1,4-dioxane derivative 10-O(CH₂CH₂)₂O-7,8-C₂B₉H₁₁ can be prepared via the reaction of the potassium salt of nido-carborane with 1,4-dioxane in the presence of HgCl₂ in benzene[64] or in the presence of acetaldehyde and hydrochloric acid in a water–toluene mixture[67]. The 1,4-dioxane derivative can also be synthesized via the heating of the protonated form of nido-carborane 7,8-C₂B₉H₁₃ with 1,4-dioxane[68] (Scheme 12). The molecular structure of the 1,4-dioxane derivative of nido-carborane was determined using single-crystal X-ray diffraction (Figure 7)[69].
Scheme 12. Different pathways for synthesis of 10-O(CH₂CH₂)₂O-7,8-C₂B₉H₁₁.

Figure 7. Crystal molecular structure of 10-O(CH₂CH₂)₂O-7,8-C₂B₉H₁₁. Hydrogen atoms of organic substituent are omitted for clarity.

The reaction of the potassium salt of nido-carborane with tetrahydropyran in the presence of mercury(II) chloride in benzene results in the tetrahydropyran derivative 10-(CH₂)₂O-7,8-C₂B₉H₁₁ (Scheme 13) [88P720].

Scheme 13. Different pathways for synthesis of 10-(CH₂)₂O-7,8-C₂B₉H₁₁.
Compared with the oxonium derivatives, the sulfonium derivatives of \textit{nido}-carborane are represented by a wider variety of derivatives and synthetic methods for their preparation. However, the most studied of them are the dimethylsulfonium derivatives of \textit{nido}-carborane, which are widely used for the synthesis of metallacarboranes.\[^{[41][50][71]}\]

It should be noted that symmetrically and asymmetrically substituted dimethylsulfonium derivatives of \textit{nido}-carborane are usually obtained in different ways, which excludes the formation of mixtures of their isomers. The asymmetrically substituted 9-dimethylsulfonium derivative of \textit{nido}-carborane 9-Me$_2$S-7,8-C$_2$B$_9$H$_{11}$ was prepared via the reaction of the parent \textit{nido}-carborane with dimethylsulfoxide in the presence of sulfuric acid at 80°C.\[^{[52][72]}\] The reactions of the C,C'-substituted derivatives of \textit{nido}-carborane proceed in a similar way, leading to the corresponding dimethylsulfonium derivatives 9-Me$_2$S-7,8-R$_2$-7,8-C$_2$B$_9$H$_9$ (R = Me, Ph)\[^{[50][74]}\] (Scheme 54). These conditions are similar to those used for the synthesis of the dimethylsulfonium derivatives of the \textit{closo}-decaborate\[^{[42]}\] and \textit{closo}-dodecaborate\[^{[42]}\] anions. The C,C'-substituted derivatives 9-Me$_2$S-7,8-Me$_2$-7,8-C$_2$B$_9$H$_9$ and 9-Me$_2$S-7,8-μ-(1',2'-C$_6$H$_4$(CH$_2$)$_2$)-7,8-C$_2$B$_9$H$_9$ were prepared via the reactions of the corresponding \textit{nido}-carboranes with dimethylsulfoxide in the presence of triflic acid in 1,2-dichloroethane\[^{[74]}\] (Scheme 14). The structures of 9-Me$_2$S-7,8-R$_2$-7,8-C$_2$B$_9$H$_9$ (R = H, Ph) were determined using single-crystal X-ray diffraction (Figure 8)\[^{[70][72]}\].

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\textbf{Scheme 14.} Synthesis of the asymmetrically substituted dimethylsulfonium derivatives of \textit{nido}-carborane 9-Me$_2$S-7,8-R$_2$-7,8-C$_2$B$_9$H$_9$ (R = H, Me, Ph; RR = μ-1',2'-C$_6$H$_4$(CH$_2$)$_2$).}
\end{tikzpicture}
\end{center}
The asymmetrically substituted dimethylsulfonium derivatives 9-MeS-7,8-Me2-CB11H6 and 9-MeS-7,8-µ-(CH2OCH2)-7,8-C8B13H6 were prepared via the reactions of the corresponding nido-carboranes with dimethylsulfide in the presence of Fe(NO3)3 in aqueous ethanol [58].

In the case of C-substituted nido-carboranes, such as K[7-Ph-7,8-C8B23H11], the introduction of a Me2S group results in a mixture of 9-MeS-7-Ph-7,8-C8B3H10 and 11-MeS-7-Ph-7,8-C8B3H10 isomers, which can be separated using column chromatography [23]. The molecular structure of 11-MeS-7-Ph-7,8-C8B3H10 was determined using single-crystal X-ray diffraction (Figure 8) [24].

### 7. Charge-Compensated Derivatives of Nido-Carborane with Boron–Selenium and Boron–Tellurium Bonds

The charge-compensated derivatives of nido-carborane with boron–selenium and boron–tellurium bonds are rather rare. Similar to the dialkyl- and diarylsulfonium derivatives, a series of asymmetrically substituted trialkyl(aryl)selenium and triaryltellurium derivatives 9-RR′X-7,8-Ph2-7,8-C8B9H9 (X = Se, Te) were prepared via electrocatalyzed oxidative couplings of 7,8-diphenyl-nido-carborane with RR′Se and R2Te, respectively (Scheme 15, Figure 9) [59].

**Scheme 15.** Synthesis of 9-dialkyl(aryl)selenium and 9-diaryltellurium derivatives of nido-carborane 9-RR′X-7,8-Ph2-7,8-C8B9H9.
8. Some Other Charge-Compensated Derivatives of Nido-Carborane

The asymmetrically substituted 9-carbonyl derivative of nido-carborane 9-O≡C-7,8-C₃B₆H₁₄ and the 3,3,8-(CO)₂-3,1,2-CoC₂B₆H₁₀ cobaltacarborane based on its symmetrically substituted analog as a ligand were isolated as minor products of the reaction of the parent nido-carborane with [Co₂(CO)₆]²⁺.

The symmetrically substituted cobaltacenium derivative of nido-carborane 10-{CpCo(C₅H₅)}-7,8-Me₂-7,8-C₃B₆H₁₄ (Figure 10) was prepared along with the 3-Cp-1,2-Me₂-3,1,2-CoC₂B₆H₉ cobaltacarborane in the reaction of the dithallium dicarbollide salt Tl₂[7,8-Me₂-7,8-C₃B₆H₉] with CpCo(CO)₂ in acetonitrile [81].
Figure 10. Crystal molecular structure of 10-{CpCo(C₂H₅)}-7,8-Me₂-7,8-C₂B₉H₅. Hydrogen atoms of methyl groups are omitted for clarity.

References


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