Charge-Compensated Derivatives of Nido-Carborane

Subjects: Chemistry, Organic

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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.

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 ^{[Z][8]}. 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 ^{[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]} and other ^{[28][29][30][31][32][33][34][35][36]}[37][38][39][40] applications.



Figure 1. The idealized structure and atom numbering of nido-carborane $[7,8-C_2B_9H_{12}]^-$.

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 [41][42][43][44][45][46][47][48][49][50].

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**) ^[51], the structure of which was later supported via a single-crystal X-ray diffraction study (**Figure 2**) ^[52]. 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 ^[52]. The reaction with 7,8-dimethyl-nido-carborane proceeds in a similar way, giving 9-Py-7,8-Me₂-7,8-C₂B₉H₉ ^[51]. 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)CC₅H₃N)-7,8-C₂B₉H₁₁ ^[53].



Scheme 1. The synthetic process to obtain 9-Py-7,8-C₂B₉H₁₁.



Figure 2. Crystal molecular structures of 9-Py-7,8-C₂B₉H₁₁ (**left**) and 10-Py-7,8-C₂B₉H₁₁ (**right**). Hydrogen atoms of organic substituents are omitted for clarity.

The reaction of *nido*-carborane with pyridine in the presence of $HgCl_2$ in refluxing benzene gives a mixture of the symmetrically and asymmetrically substituted pyridinium derivatives 10-Py-7,8-C₂B₉H₁₁ and 9-Py-7,8-C₂B₉H₁₁ in a ratio of 2:1 (**Scheme 2**) ^{[50][54]}. The reaction of 7,8-dimethyl-*nido*-carborane [7,8-Me₂-7,8-C₂B₉H₁₀]⁻ with pyridine proceeds in a similar way ^[54].



Scheme 2. Synthesis of 10-Py-7,8-C₂B₉H₁₁ and 9-Py-7,8-C₂B₉H₁₁ via the reaction of *nido*-carborane with pyridine in the presence of HgCl₂.

The asymmetrically substituted 9-pyridinium derivative of *nido*-carborane was also prepared via the reaction of the parent *ortho*-carborane with pyridine in the presence of copper acetate and water. Similar reactions with *C*-monosubstituted *ortho*-carboranes give a mixture of the corresponding isomeric pyridinium derivatives 9-Py-7-R-7,8-C₂B₉H₁₀ and 11-Py-7-R-7,8-C₂B₉H₁₀ (R = Me, Ph). In the case of 1-XCH₂ derivatives of *ortho*-carborane (X = Cl, Br, OH), in addition to a mixture of the corresponding 9- and 11-pyridinium derivatives of *nido*-carborane, the reaction gives the pyridinium methyl derivative 7-PyCH₂-7,8-C₂B₉H₁₁ [55].

3. Charge-Compensated Derivatives of *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-C₂B₉H₁₂] with Ph₂PCI 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**) ^{[56][57]}.



Scheme 3. The synthesis of $9-Ph_2PH-7$, $8-C_2B_9H_{11}$ and its alkylation.



Figure 3. Crystal molecular structures of $9-MePh_2P-7, 8-C_2B_9H_{11}$ (left) and $10-MePh_2P-7, 8-C_2B_9H_{11}$ (right). Hydrogen atoms of phenyl and methyl groups are omitted for clarity.

The symmetrically substituted phosphonium derivatives $10-Ph_2PH-7,8-C_2B_9H_{11}$ and $10-MePh_2P-7,8-C_2B_9H_{11}$ (**Figure 4**) were prepared in a similar way using the disodium dicarbollide salt Na₂[7,8-C₂B₉H₁₁] as a starting material (**Scheme 4**) ^[57].



Scheme 4. The synthesis of 10-Ph₂PH-7,8-C₂B₉H₁₁ and its alkylation.



Figure 4. Crystal molecular structures of $9-MePh_2P-7, 8-C_2B_9H_{11}$ (left) and $10-MePh_2P-7, 8-C_2B_9H_{11}$ (right). Hydrogen atoms of phenyl and methyl groups are omitted for clarity.

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 $K[7,8-C_2B_9H_{12}]$ with PPh₃ in the presence FeCl₃ in benzene at 80 °C leads to a mixture of triphenylphosphonium 9-Ph₃P-7,8-C₂B₉H₁₁ and 10-Ph₃P-7,8-C₂B₉H₁₁, which were separated using column chromatography on silica (**Scheme 5**) ^{[56][57]}.



Scheme 5. Reaction of *nido*-carborane with triphenylphosphine in the presence of FeCl₃.

The asymmetrical triphenylphosphonium derivative $9-Ph_3P-7, 8-C_2B_9H_{11}$ was also obtained via the reaction of triphenylphosphine with the dithallium dicarbollide salt $Tl_2[7, 8-C_2B_9H_{11}]$ in dichloromethane and in the presence of AgBr at ambient temperature (**Scheme 6**) ^[58].



Scheme 6. Synthesis of $9-Ph_3P-7, 8-C_2B_9H_{11}$.

Similar to the pyridinium derivatives, a series of asymmetrically substituted phosphonium derivatives $9-R'R_2P-7,8-P_2-7,8-C_2B_9H_9$ was prepared via electrocatalyzed B-P oxidative couplings of 7,8-diphenyl-*nido*-carborane with various phosphines and phosphites (**Scheme 7**, **Figure 5**) ^[59].



 $R = R' = Me, Bu, C_{6}H_{5}, C_{6}H_{4}-p-Me, C_{6}H_{4}-m-Me, C_{6}H_{4}-p-F, C_{6}H_{4}-m-F, C_{6}H_{4}-m-Cl, 2-C_{4}H_{3}O, 2-C_{4}H_{3}S, OEt, OBu, OCH_{2}CH_{2}Cl, OCH_{2}CH=CH_{2}; R = Me, R' = Ph; R = Ph, R' = Me, CH_{2}CH=CH$

Scheme 7. The electrocatalyzed B-P oxidative coupling of triarylphosphines, diarylalkylphosphines, and trialkylphosphines with 7,8-diphenyl-*nido*-carborane.



Figure 5. Crystal molecular structure of 9-Ph₃P-7,8-Ph₂-7,8-C₂B₉H₉. Hydrogen atoms of phenyl rings are omitted for clarity.

4. Charge-Compensated Derivatives of *Nido*-Carborane with Boron–Arsenic and Boron–Antimony Bonds

The charge-compensated derivatives of *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 tetraphenylstilbonium derivatives $9-Ph_3X-7, 8-Ph_2-7, 8-C_2B_9H_9$ (X = As, Sb) were prepared via electrocatalyzed oxidative couplings of 7,8-diphenyl-*nido*-carborane with Ph₃As and Ph₃Sb, respectively (Scheme 8, Figure 6) ^[59].



Scheme 8. Synthesis of 9-Ph₃As-7,8-Ph₂-7,8-C₂B₉H₉ and 9-Ph₃As-7,8-Ph₂-7,8-C₂B₉H₉.



Figure 6. Crystal molecular structure of $9-Ph_3As-7, 8-Ph_2-7, 8-C_2B_9H_9$. Hydrogen atoms of phenyl groups are omitted for clarity.

The reaction of 2-pyridyl-substituted *nido*-carborane $[7-(2'-Py)-7,8-C_2B_9H_{11}]^-$ 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**) ^[60].



Scheme 9. Synthesis of 11-Ph₃As-7-(2'-Py)-7,8-C₂B₉H₁₀.

5. Charge-Compensated Derivatives of *Nido*-Carborane with Boron–Oxygen Bond

Alkyloxonium 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 ^[61], is capable of stabilizing their oxonium derivatives ^{[62][63]}. 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**) ^[51].



Scheme 10. Synthesis of $9-(CH_2)_4O-7, 8-C_2B_9H_{11}$ and $10-(CH_2)_4O-7, 8-C_2B_9H_{11}$ via the reaction of *nido*-carborane with FeCl₃ in THF–benzene mixture.

It was later found that the replacement of $FeCl_3$ with $HgCl_2$ in this reaction leads to the selective formation of the symmetrically substituted tetrahydrofuran derivative $10-(CH_2)_4O-7,8-C_2B_9H_{11}$ ^{[54][64]}. 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. 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 $10-O(CH_2CH_2)_2O-7,8-C_2B_9H_{11}$ 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 ^[66]. 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 ^[67] (**Scheme 12**). The molecular structure of the 1,4-dioxane derivative of *nido*-carborane was determined using single-crystal X-ray diffraction (**Figure 7**) ^[68].



Scheme 12. Different pathways for synthesis of 10-O(CH₂CH₂)₂O-7,8-C₂B₉H₁₁.



Figure 7. Crystal molecular structure of $10-O(CH_2CH_2)_2O-7, 8-C_2B_9H_{11}$. 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 $10-(CH_2)_5O-7,8-C_2B_9H_{11}$ (**Scheme 13**) ^{[69][70]}.



Scheme 13. Different pathways for synthesis of 10-(CH₂)₅O-7,8-C₂B₉H₁₁.

6. Charge-Compensated Derivatives of *Nido*-Carborane with Boron–Sulfur Bond

Compared with the oxonium derivatives, the sulfonium derivatives of *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 *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 *nido*-carborane are usually obtained in different ways, which excludes the formation of mixtures of their isomers. The asymmetrically substituted 9-dimethylsulfonium derivative of *nido*-carborane 9-Me₂S-7,8-C₂B₉H₁₁ was prepared via the reaction of the parent *nido*-carborane with dimethylsulfoxide in the presence of sulfuric acid at 80°C ^{[52][72]}. The reactions of the *C*,*C*'-substituted derivatives of *nido*-carborane proceed in a similar way, leading to the corresponding dimethylsulfonium derivatives 9-Me₂S-7,8-R₂-7,8-C₂B₉H₉ (R = Me, Ph) ^{[52][74]} (Scheme 54). These conditions are similar to those used for the synthesis of the dimethylsulfonium derivatives of the *closo*-decaborate ^[75] and *closo*-dodecaborate ^[76] anions. The *C*,*C*'-substituted derivatives 9-Me₂S-7,8-Me₂-7,8-Me₂-7,8-C₂B₉H₉ and 9-Me₂S-7,8- μ (1',2'-C₆H₄(CH₂)₂)-7,8-C₂B₉H₉ were prepared via the reactions of the corresponding *nido*-carboranes with dimethylsulfoxide in the presence of triflic acid in 1,2-dichloroethane ^[77] (Scheme 14). The structures of 9-Me₂S-7,8-R₂-7,8-C₂B₉H₉(R = H, Ph) were determined using single-crystal X-ray diffraction (Figure 8) ^{[78][79]}.



Scheme 14. Synthesis of the asymmetrically substituted dimethylsulfonium derivatives of *nido*-carborane 9-Me₂S-7,8-R₂-7,8-C₂B₉H₉ (R = H, Me, Ph; RR = μ -1',2'-C₆H₄(CH₂)₂).



Figure 8. Crystal molecular structures of $9-Me_2S-7, 8-C_2B_9H_{11}$ (**top**), $11-Me_2S-7-Ph-7, 8-R_2-7, 8-C_2B_9H_{10}$ (**bottom left**), and $9-Me_2S-7, 8-Ph_2-7, 8-C_2B_9H_9$ (**bottom right**). Hydrogen atoms of organic substituent are omitted for clarity.

The asymmetrically substituted dimethylsulfonium derivatives $9-Me_2S-7, 8-Me_2-7, 8-C_2B_9H_9$ and $9-Me_2S-7, 8-\mu$ -(CH₂OCH₂)-7, $8-C_2B_9H_9$ were prepared via the reactions of the corresponding *nido*-carboranes with dimethylsulfide in the presence of Fe(NO₃)₃ in aqueous ethanol ^[49].

In the case of *C*-substituted *nido*-carboranes, such as K[7-Ph-7,8-C₂B₉H₁₁], the introduction of a Me₂S group results in a mixture of 9-Me₂S-7-Ph-7,8-C₂B₉H₁₀ and 11-Me₂S-7-Ph-7,8-C₂B₉H₁₀ isomers, which can be separated using column chromatography ^[73]. The molecular structure of 11-Me₂S-7-Ph-7,8-C₂B₉H₁₀ was determined using single-crystal X-ray diffraction (**Figure 8**) ^[74].

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 triakyl(aryl)selenium and triaryltellurium derivatives $9-RR'X-7,8-Ph_2-7,8-C_2B_9H_9$ (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- Ph_2 -7,8- $C_2B_9H_9$.



Figure 9. Crystal molecular structure of 9-Ph₂Te-7,8-Ph₂-7,8-C₂B₉H₉. Hydrogen atoms of phenyl groups are omitted for clarity.

8. Some Other Charge-Compensated Derivatives of *Nido*-Carborane

The asymmetrically substituted 9-carbonyl derivative of *nido*-carborane $9-O=C-7,8-C_2B_9H_{11}$ and the $3,3,8-(CO)_3-3,1,2-CoC_2B_9H_{10}$ cobaltacarborane based on its symmetrically substituted analog as a ligand were isolated as minor products of the reaction of the parent *nido*-carborane with $[Co_2(CO)_8]^{[80]}$.

The symmetrically substituted cobaltacenium derivative of *nido*-carborane $10-\{CpCo(C_5H_4)\}-7,8-Me_2-7,8-C_2B_9H_9$ (**Figure 10**) was prepared along with the 3-Cp-1,2-Me_2-3,1,2-CoC_2B_9H_9 cobaltacarborane in the reaction of the dithallium dicarbollide salt $TI_2[7,8-Me_2-7,8-C_2B_9H_9]$ with CpCo(CO)I₂ in acetonitrile [81].



Figure 10. Crystal molecular structure of $10-\{CpCo(C_5H_4)\}-7,8-Me_2-7,8-C_2B_9H_9$. Hydrogen atoms of methyl groups are omitted for clarity.

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