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Review

Effect of Nature of Substituents on Coordination Properties of Mono- and Disubstituted Derivatives of Boron Cluster Anions $[B_nH_n]^{2-}$ (n = 10, 12) and Carboranes with exo-Polyhedral B–X Bonds (X = N, O, S, Hal)

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Abstract: This review systematizes data on the coordination ability of mono- and disubstituted derivatives of boron cluster anions and carboranes in complexation with transition metals. Boron clusters anions $[B_nH_n]^{2-}$, monocarborane anions $[CB_nH_{n-1}]^-$, and dicarboranes $[C_2B_nH_{n-2}]$ (with non-functionalized carbon atoms) (n = 10, 12) containing the B–X exo-polyhedral bonds (X = N, O, S, Hal) are discussed. Synthesis and structural features of complexes known to date are described. The effect of complexing metal and substituent attached to the boron cage on the composition and structures of the final complexes is analyzed. It has been established that substituted derivatives of boron cluster anions and carboranes can act as both ligands and counterions. A complexing agent can coordinate substituted derivatives of the boron cluster anions due to three-center two-electron 3c2e MHB bonds, by the substituent functional groups, or a mixed type of coordination can be realized, through the BH groups of the boron cage and the substituent. As for B-substituted carboranes, complexes with coordinated substituents or salts with non-coordinated carborane derivatives have been isolated; compounds with MHB bonding are not characteristic of carboranes.

Keywords: decahydro-*closo*-decaborate anion; dodecahydro-*closo*-dodecaborate anion; complexation

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1. Introduction

Boron has a particularly rich chemistry; various structures can be found for elemental boron [1–3], boric acids and borates [4–6], metal and non-metal borides [7–9], boranes and carboranes [10–18]. In the number of hydrides that it forms, boron is second only to carbon. Boron cluster anions $[B_nH_n]^{2-}$ (n = 10, 12) and carboranes (Figure 1) are fascinating objects with versatile chemistry. Owing to their tendency to participate in reactions of substitution of exo-polyhedral hydrogen atoms, they allow one to design new cage systems differing in geometry and electronic structure.

The application fields of boron clusters are traditionally explained by their high energy intensity [19]. Moreover, it was proposed to use them in boron neutron capture therapy of tumor tissues because of the high neutron absorption capacity of boron atoms [20–22]. Boron clusters can be used to manufacture heat-resistant polymers and materials with neutron-protective properties [23–26], and contrast agents for MRI diagnostics [27]. Metal complexes with boron clusters are applied as heavy metal extractants, as coordination polymers, etc. [28–32]. Recently, complexes containing boron clusters have been proposed to prepare metal borides [33–36]. The physiological properties of boron clusters and their applications in medicine are discussed in recent reviews [37–41].

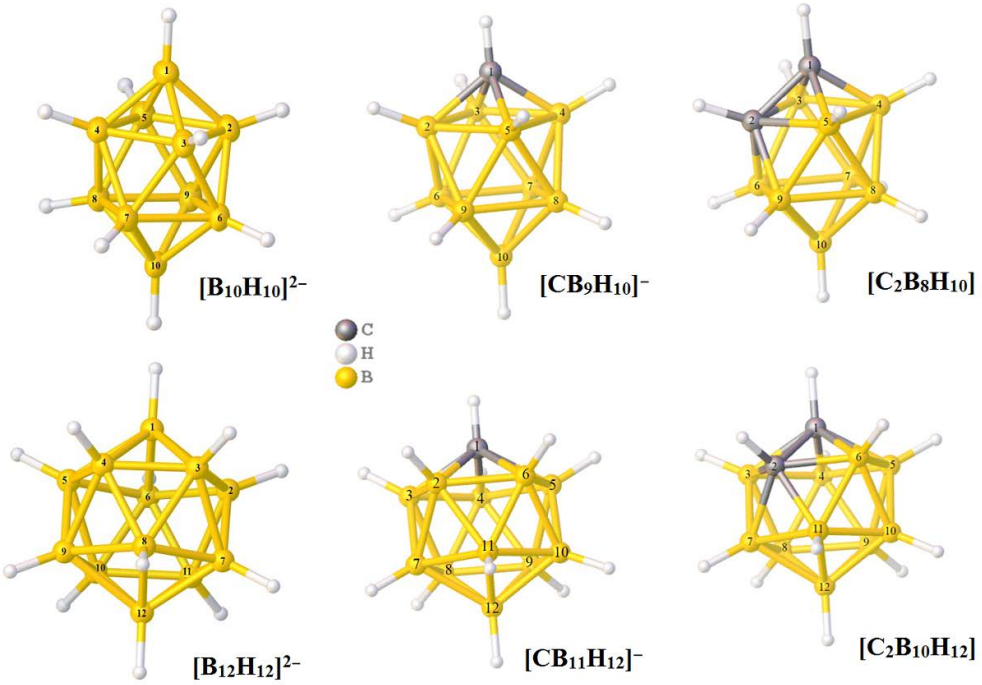


Figure 1. Structures of *closo*-decaborates anions, 1-carba-*closo*-borates anions and 1,2-dicarba-*closo*-boranes.

To date, the coordination ability of boron clusters $[B_nH_n]^{2-}$ (n = 10, 12), perchlorinated clusters $[B_{10}Cl_{10}]^{2-}$, and dimeric clusters $[B_{20}H_{18}]^{2-}$ has been studied in sufficient detail and analyzed in recent reviews [42–51]. It is concluded that boron cluster anions are soft bases according to Pearson; therefore, their participation in complexation reactions as ligands is observed in complexation with metals that act as Pearson's soft acids (Cu(I), Ag(I), and Pb(II)). In this case, boron cluster anions allow synthesizing of a great number of mononuclear, binuclear, polymeric complexes with boron polyhedra coordinated by the metal atom via vertices (BH group), edges (HBBH group) or faces (BBB) of the boron cage. When interacting with metals which act as hard acids (Fe(III), Co(III)), boron cluster anions act as reducing agents and reduce the oxidation state of metals to M(II) or M(0). Classical 3*d* metals in the 2+ oxidation state are acids of the intermediate group (Zn(II), Ni(II), Cu(II), etc.) and usually afford salts consisting of cationic metal complexes $[ML_x]^{2+}$ with neutral ligands L (organic, inorganic or solvent molecules) and boron cluster anions as counterions. In this case, numerous non-covalent interactions can be found in the structures of compounds, including hydrogen and dihydrogen bonds between BH groups of the boron clusters and organic cations, ligand molecules or solvents.

Boron cluster anions tend to participate in reactions of substitution of exo-polyhedral hydrogen atoms to form substituted derivatives with various functional groups [52–56]. The resulting substituted boron clusters can also participate in complexation as ligands. However, the currently known complexes are scarcely studied, prepared in different systems, in the presence of various metals and ligands, which makes it difficult to analyze and compare the reactivity of substituted derivatives of boron cluster anions as ligands.

Carboranes differ from the boron clusters in their charge: monocarboranes $[CB_9H_{10}]^-$ and $[CB_{11}H_{12}]^-$ are monoanions, whereas dicarboranes $[C_2B_8H_{10}]$ and $[C_2B_{10}H_{12}]$ are neutral compounds. The boron atoms in carboranes have a lower negative charge as compared to boron clusters; therefore, their ability to act as a donor of electronic density reduces. In this case, there are the following ways to form complexes with carboranes: (i) the formation of a B–Hg bond during electrophilic mercurization, which proceeds to the position furthest from the carbon atoms (actually, formation of a C–Hg bond is also possible) (see review [57] and references thereof); (ii) B–H activation with the formation of a B–M bond in the presence of a substituent with a donor atom in the *ortho* position acting

as a ligand (the substituent is usually attached to the carbon atom); therefore, activation of neighboring positions is observed (see reviews [58,59] and recent articles [60,61]); (iii) coordination by a substituent, as a rule, attached to the carbon atom of carborane cage (see, for example, review [62]).

The chemistry of carboranes is realized as a rule via carbon atoms of the carborane cage which provides wide opportunities to vary functional groups and metal atoms bonded to them. Here, we wanted to compare the coordination ability of the boron cage in substituted boron clusters and B-substituted carboranes without C-functionalization.

In this work, we have systematized the data on complexes of mono- and disubstituted derivatives of boron cluster anions $[B_nH_n]^{2-}$, monocarborane anions $[CB_nH_{n-1}]^-$, and dicarboranes $[C_2B_nH_{n-2}]$ (with non-functionalized carbon atoms) (n = 10, 12) containing exo-polyhedral B–X bonds (X = N, O, S, Hal) in order to compare the coordination ability of substituted boron cages and determine directions for further systematic research.

2. Metal Complexes with Substituted Derivatives of Boron Cluster Anions

It is known that unsubstituted boron clusters make it possible to prepare complexes of soft acids with coordinated boron hydride ligands [42,43] (first of all, copper(I), silver(I), lead(II)). Heteroleptic silver(I) complexes with inner-sphere boron cluster anions are the most studied group of complexes. This is probably due to the correspondence between the softness of silver(I) acid and softness of the boron cluster bases, as compared to other metals.

The introduction of a substituent containing electron-donor groups makes it possible to obtain complexes in which the coordination of the boron cage is realized via the functional groups of the substituent; thus, those metals that are too hard to coordinate boron clusters are able to coordinate substituted derivatives through a substituent being introduced. Moreover, the substituent can decrease the total charge of the boron cluster, thus decreasing its coordination ability in complexation.

2.1. Halogen Atoms

In the literature, there are a great number of complexes containing perhalogenated *closo*-borate anions $[B_nHal_n]^{2-}$ (n = 10, 12; Hal = F, Cl, Br, I). These anions are interesting because they are weak coordinating ligands; they form various complexes with silver atoms as complexing agents. Complexes with these anions are discussed in detail in a number of reviews [45–47] and are beyond this work. Here, we would discuss only mono- and disubstituted derivatives containing halogen atoms.

When the *closo*-dodecaborate anion was allowed to react with hydrogen halides (HCl, HBr or HI) in dichloroethane, **monochloro- and dichlorosubstituted *closo*-dodecaborate derivatives** were isolated [63]. The source of the chlorine atoms is the solvent used, whereas halohydrogens act as electrophilic initiators. The structure of Bipy-containing tris-chelate **nickel(II)** complex $[Ni(Bipy)_3][B_{12}H_{10.668}Cl_{1.332}]$ was determined by single-crystal X-ray diffraction. It was found that the compound consists of tris-chelate cationic complex $[Ni(Bipy)_3]^{2+}$, chlorine-substituted anions $[B_{12}H_{11}Cl]^{2-}$ or $[B_{12}H_{10}Cl_2]^{2-}$, and crystallization solvent molecules. In the crystal, mono- and disubstituted derivatives present a ratio of 2:1. Thus, it is clear that Cl has no effect on the coordination ability of the boron cage.

Silver(I) complex $[Ag(CH_3CN)_3]_2[Ag_2[2\text{-}B_{10}H_9F]_2]$ [64] with the **monofluoro-substituted derivative of the *closo*-decaborate anion** was isolated by the reaction between tetraphenylphosphonium 2-fluoro-*closo*-decaborate $[2\text{-}B_{10}H_9F]^{2-}$ and silver trifluoroacetate. The structure of this complex (Figure 2) is built of anions $[Ag_2[2\text{-}B_{10}H_9F]_2]^{2-}$ (Ag–H 2.02(5)–2.36(5) Å) linked by cations $[Ag(CH_3CN)_3]^+$ (Ag . . . H 2.36 Å) forming double chains.

Silver(I) complex $[Ag_2(Ph_3P)_4[B_{12}H_{11}Cl]]$ [65] with triphenylphosphine Ph_3P was also obtained for the **monochloro-substituted derivative of the *closo*-dodecaborate anion**. The binuclear complex was isolated when the $[B_{10}H_{11}Cl]^{2-}$ anions reacted with $[Ag(Ph_3P)_3NO_3]$ in CH_3CN or DMF. The compound is a centrosymmetric complex in which the silver atoms

coordinate the *closo*-dodecaborate anion along opposite edges (Ag–B 2.779 and 2.790 Å) that are as far as possible from the chlorine atom introduced (Figure 3).

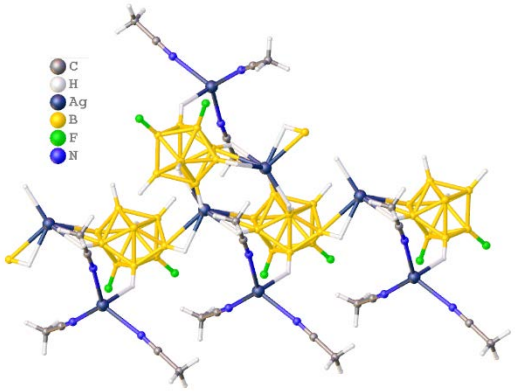


Figure 2. Structure of polymeric silver(I) complex $[Ag(CH_3CN)_3]_2(Ag_2[2\text{-}B_{10}H_9F]_2]_n$ (F is disordered into two positions).

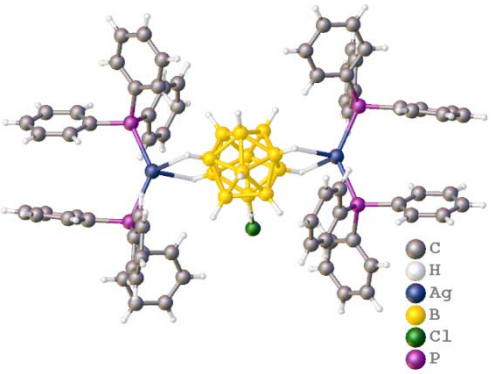
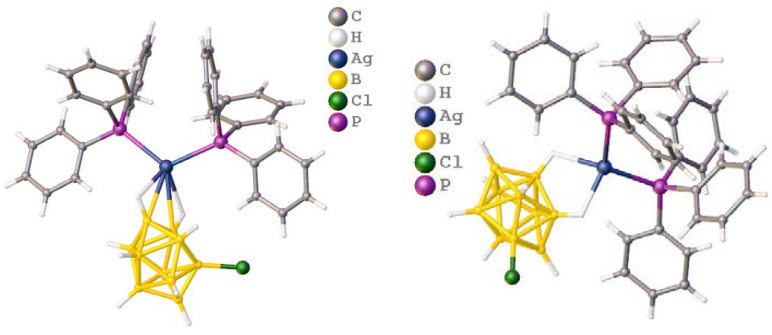


Figure 3. Structure of binuclear silver(I) complex $[Ag_2(Ph_3P)_4[B_{12}H_{11}Cl]]$.

Two positional isomers of the monoanions $[Ag[B_{10}H_{10}](PPh_3)_2]^-$ (with unsubstituted *closo*-decaborate anion) and $[Ag[B_{10}H_9Cl](PPh_3)_2]^-$ (**with monochlorosubstituted *closo*-decaborate anion**) were found co-crystallized in complexes $[Ag(PPh_3)_4][Ag[B_{10}H_{9.14}Cl_{0.86}](PPh_3)_2]$ and $[Ag(PPh_3)_4][(PPh_3)_2Ag[B_{10}H_{9.5}Cl_{0.5}]]$ [66] with equatorial and apical coordination of the boron cage, which were obtained from DMF and acetonitrile, respectively (Figure 4). It should be noted that in both compounds, monochlorosubstituted derivatives are coordinated by edges opposite to the chlorine atom introduced.



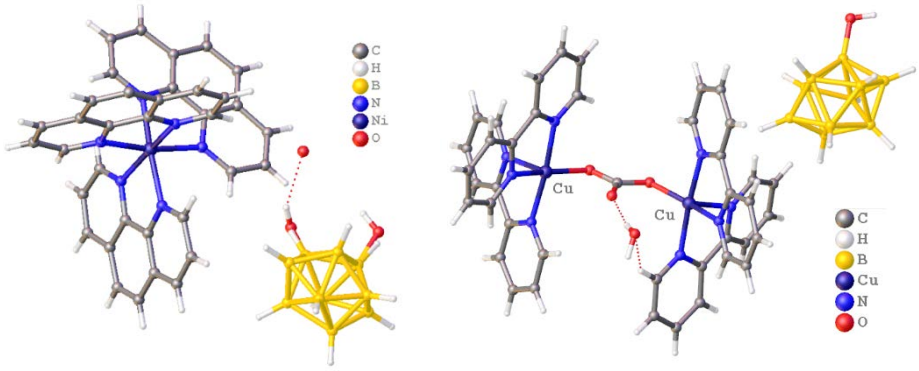
(**a**) (**b**)

Figure 4. Structures of isomers of mononuclear complex $[Ag[2\text{-}B_{10}H_9Cl](PPh_3)_2]^-$ with (**a**) apical and (**b**) equatorial coordination of the boron cluster.

The data present show that one (or two) halogen atoms have no effect on the coordination ability of the boron cage. For both the $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ anions, nickel(II) resulted in complex salts, whereas silver(I) afforded complexes with boron clusters coordinated by edges located as far as possible from the substituent introduced.

2.2. Hydroxy Substituent

When the *closo*-decaborate anion reacts with sulfolane in the presence of *p*-toluenesulfonic acid followed by alkaline hydrolysis of the resulting product, salts of the **2-hydroxy-*closo*-decaborate anion $[2\text{-}B_{10}H_9OH]^{2-}$** are isolated [56]. The formation of tris-chelate **nickel(II)** complex $[NiL_3][B_{10}H_9OH]$ (L = 2,2′-bipyridyl (Bipy), 1,10-phenanthroline (Phen), 2,2′-bipyridylamine (BPA), 1,2-diaminobenzene (DAB)) [67] with the $[2\text{-}B_{10}H_9OH]^{2-}$ anion as a counterion were observed in the nickel(II) complexation reactions in the presence of organic ligands L. Structures of solvates $[Ni(Phen)_3][B_{10}H_9OH]\cdot 0.75CH_3CN\cdot 0.5H_2O$ (Figure 5a) and $[Ni(Phen)_3][B_{10}H_9OH]\cdot 2CH_3CN\cdot 0.67DMF$ were isolated and studied by X-ray diffraction.



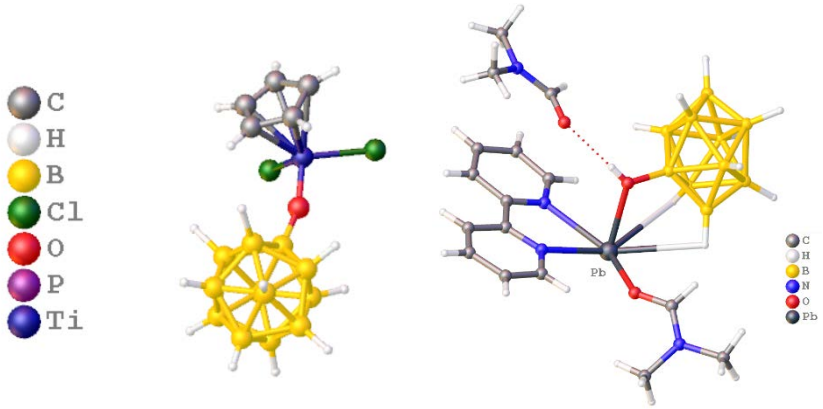
(**a**) (**b**)

Figure 5. Structures of (**a**) $[Ni(Phen)_3][B_{10}H_9OH]\cdot 0.75CH_3CN\cdot 0.5H_2O$ and (**b**) $[Cu_2(bipy)_4(\mu\text{-}CO_3)][2\text{-}B_{10}H_9OH]\cdot 2DMSO\cdot H_2O$.

The synthesis and structure of **copper(II)** complex with the $[2\text{-}B_{10}H_9OH]^{2-}$ anion was reported [68]. It was found that the $[2\text{-}B_{10}H_9OH]^{2-}$ anion can be prepared in situ, starting from an unsubstituted $[B_{10}H_{10}]^{2-}$ boron cluster. Long-term heating of copper(II) complex $[Cu_2(bipy)_4(\mu\text{-}CO_3)][B_{10}H_{10}]$ in DMSO led to partial substitution of one hydrogen atom by the OH group to form copper(II) complex $[Cu_2(bipy)_4(\mu\text{-}CO_3)][2\text{-}B_{10}H_{9.83}OH_{0.17}]\cdot 2DMSO\cdot H_2O$ (Figure 5b). In this compound, the cationic part is the same as in the starting copper(II) complex, while the anionic part contains the unsubstituted *closo*-decaborate anion and its monohydroxy-substituted derivative cocrystallized in one crystal in the ratio 0.17:0.83.

Titanium complex with **the monohydroxy-substituted *closo*-dodecaborate anion $[B_{12}H_{11}OH]^{2-}$** and the cyclopentadienyl ligand was prepared and characterized [69] (Figure 6a). The complex was isolated when $[TiCpCl_2]$ was allowed to react with $(Ph_3MeP)_2[B_{12}H_{11}OH]$. As it was found, titanium coordinates the oxygen atom of the 2-hydroxy-*closo*-decaborate anion; the distances Ti–O and B–O are 1.711(9) Å and 1.45(2) Å, respectively.

In **lead(II) complex** with the monohydroxy-substituted *closo*-decaborate derivative $[Pb(Bipy)(DMF)[2\text{-}B_{10}H_9OH]]\cdot DMF$ [70] (Figure 6b), Pb(II) coordinates one Bipy molecule (Pb–N 2.520(6), 2.583(7) Å), the hydroxyl substituent (Pb–O 2.285(6) Å), and one DMF molecule (Pb–O 2.504(7) Å). The coordination environment of lead(II) is completed by two BH groups (Pb–H 2.944, 3.286 Å); the corresponding distances allow one to conclude that the boron polyhedron participates in coordination.



(**a**) (**b**)

Figure 6. Structure of (**a**) titanium complex $[Ph_3(CH_3)P)]_2[CpTiCl_2[B_{12}H_{11}OH]$ and (**b**) lead(II) complex [Pb(Bipy)(DMF)[2-$B_{10}H_9OH$]]·DMF.

For the OH substituent, it can be concluded that copper(II) and nickel(II) are able to coordinate a boron cluster neither by the BH group nor by the substituent. At the same time, titanium(II) coordinates the functional group in the corresponding complexes, whereas lead(II) exhibits combination coordination via the OH substituent and BH groups of the boron cage.

2.3. Ammonium Substituents

As a rule, the presence of substituents reduces the coordination ability of the boron ligand. This is especially true for substituents that decrease the total charge of the boron cluster. Thus, the reaction of salts of the *closo*-decaborate anion with hydroxylamine sulfonic acid leads to the formation of **the ammonium-substituted derivative [2-$B_{10}H_9NH_3$]$^-$ [70]**. Silver(I) complexation with triphenylphosphine and the substituted anion afforded solvate $[Ag(PPh_3)_4][B_{10}H_9NH_3]$·2DMF with the $[B_{10}H_9NH_3]^-$ derivative acting as a counterion [71]. According to the single-crystal X-ray diffraction data, the compound consists of silver(I) cationic complexes $[Ag(PPh_3)_4]^+$ and the ammonium-substituted anions as counterions.

Lead(II) complexes with **the [2-$B_{12}H_{11}NEt_3$]$^-$ anion** and ligands Bipy, BPA were described [72]. Complexes {PbL_2[2-$B_{12}H_{11}NEt_3]_2$} were obtained in lead(II) complexation in the presence of ligands L. The complexes were characterized by IR spectroscopy as well as elemental analysis. The authors concluded that lead(II) coordinates the boron cage via the 3c2e PBHB bonds.

When $[NHEt_3]_2[B_{12}H_{12}]$ was allowed to react with $[RuCl_2(PPh_3)_3]$, **ruthenium(II)** complex $[(PPh_3)_2ClRu[B_{12}H_{11}(NEt_3)]$ with **the singly charged [$B_{12}H_{11}NEt_3$]$^-$** was isolated [73] as solvate $[(PPh_3)_2ClRu[B_{12}H_{11}(NEt_3)]\cdot CH_2Cl_2$. The boron cage anion demonstrates facial coordination (Ru–B 2.268–2.485 Å) (Figure 7), whereas the substituent remains non-coordinated.

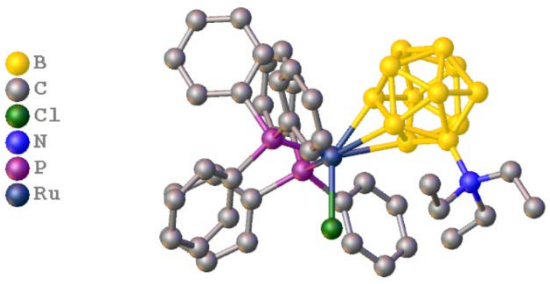


Figure 7. Structure of ruthenium(II) complex $[(PPh_3)_2ClRu[B_{12}H_{11}(NEt_3)]\cdot CH_2Cl_2$ (solvent molecules are omitted).

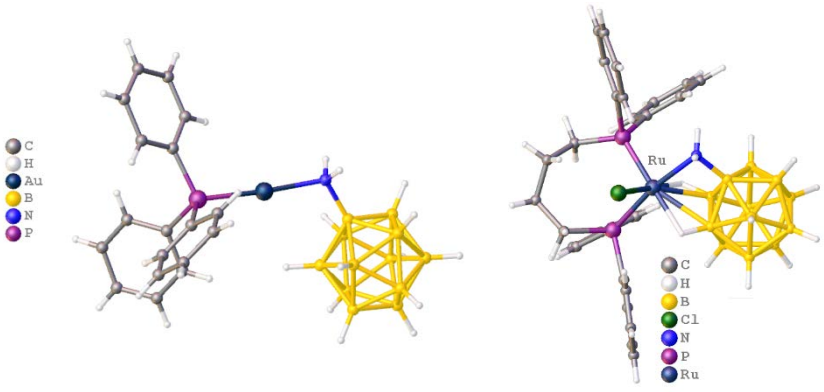
We can conclude that this ruthenium(II) complex is the first example of complexes where the metal atom is able to coordinate singly charged anion $[2\text{-}B_{12}H_{11}NEt_3]^-$ with lower coordination ability as compared to unsubstituted boron clusters. Lead(II) can be expected to coordinate the boron cage (the conclusions are based on IR spectral data), whereas silver(I) affords complexes with an inner-sphere position of the mono-charged substituted derivatives.

2.4. Amino Group

Salt **$Na_2[B_{12}H_{11}NH_2]$** salt can be obtained by the reaction of $(Bu_3NH)_2[B_{12}H_{11}NH_3]$ with sodium hydride in THF [74]. When the **amino-*closo*-dodecaborate ion** reacted with **nickel(II)** complex $[Ni(THF)_2Br_2]$, compound $[Na_6(THF)_{15}][Ni[B_{12}H_{11}NH_2]]_4 \cdot THF$ was isolated. Nickel coordinates four N atoms from the substituents and is in a square planar environment (Ni–N 1.924(4), 1.931(4) Å).

When $Na_2[B_{12}H_{11}NH_2]$ was allowed to react with $[Au(Ph_3P)Cl]$, neutral **gold(I)** complex bis((triphenylphosphine)-(1-amino-*closo*-dodecaborate(11))-gold) $[Au(PPh_3)[NH_2–B_{12}H_{11}]]$ [74] was isolated. The Au–N bonds are 2.076(8) and 2.067(9) Å.

An effective method for preparation of complexes starting from the singly charged **ammonio-substituted derivative $[B_{12}H_{11}NH_3]^-$** is the deprotonation of the monoanion with a strong base to form the **amino-substituted dianion $[B_{12}H_{11}NH_2]^{2-}$**, which can participate in complexation reactions. Thus, **ruthenium(II)** complexes $Bu_3MeN[Ru(PPh_3)_2Cl[B_{12}H_{11}NH_2]] \cdot CH_2Cl_2$ and $Bu_4N[Ru(dppb)Cl[B_{12}H_{11}NH_2]] \cdot CH_2Cl_2$ (dppb = bis(diphenylphosphine)butane) (Figure 8b) [75] were isolated when the $[B_{12}H_{11}NH_2]^{2-}$ reacted with $[Ru(Ph_3P)_3Cl_2]$ or $[Ru(dppb)(Ph_3P)Cl_2]$, respectively. In both complexes, the complexing agent coordinates the boron cage by the N atom of the substituent and two BH groups (Ru–B 2.323(3), 2.591(3) Å in the first one and 2.350(2), 2.490(3) Å in the second; Ru–N 2.186(2) and 2.2177(19) Å, respectively).



(**a**) (**b**)

Figure 8. Structures of (**a**) $[Au(PPh_3)[NH_2–B_{12}H_{11}]]$ and (**b**) $Bu_4N[Ru(dppb)Cl[B_{12}H_{11}NH_2]] \cdot CH_2Cl_2$ (solvent molecules and cation are omitted).

In addition, it was found [75] that sodium salt $Na[Ru(PPh_3)_2Cl[B_{12}H_{11}NH_2]]$ reacts with carbon monoxide affording ruthenium(II) complex $[Ru(PPh_3)_2CO[B_{12}H_{11}NH_2]]$. In this compound, the metal atom coordinates the substituted derivative of the boron cluster by the nitrogen atom of the substituent and two BH groups (Ru–N, 2.211(4) Å, Ru–B 2.418(5), 2.442(5) Å).

Rhodium(I) complex $MePPh_3[Rh(PPh_3)_2[B_{12}H_{11}NH_2]]$ with **the amino-substituted derivative $[B_{12}H_{11}NH_2]^{2-}$** is known [74], which was isolated when $(MePPh_3)Na[B_{12}H_{11}NH_2]$ was allowed to react with $[Rh(PPh_3)_3Cl]$. The boron cage is coordinated by the rhodium atom through the N atom of the substituent and the BH group (Rh–N 2.146(6) Å, Rh–B 2.592(8) Å, Rh–H 1.919 Å).

Thus, ruthenium(II) and rhodium(I) are metals that could form a combined coordination mode of NH_2-substituted derivatives: via 3c2e MHB bonds with the boron cage and functional groups of the substituent.

2.5. Sulfonium Group

The reaction of the *closo*-decaborate anion with DMSO in the presence of HCl leads to the formation of the singly charged **dimethylsulfonium derivative [1-$B_{10}H_9SMe_2$]$^-$** [76]. **Lead(II)** complexes [PbL_2[1-$B_{10}H_9SMe_2$]$_2$] (L = Bipy, BPA) [72] were obtained when aqueous solutions of salts with [1-$B_{10}H_9SMe_2$]$^-$ were allowed to react with $Pb(NO_3)_2$ and organic ligand L. It was determined by X-ray diffraction that in complex [$Pb(Bipy)_2$[1-$B_{10}H_9SMe_2$]$_2$] (Figure 9) lead(II) coordinates two Bipy and two boron cages by the equatorial and apical faces, both anions being coordinated by edges connecting two equatorial belts of the B_{10} polyhedron (Pb–B 3.24–3.55 Å).

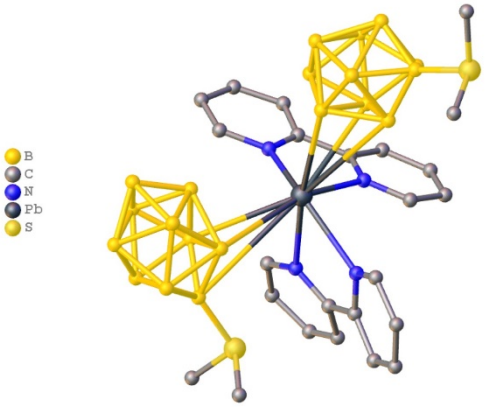


Figure 9. Structure of lead(II) complex [$Pb(Bipy)_2$[1-$B_{10}H_9SMe_2$]$_2$]. Hydrogen atoms are omitted.

The interaction of the 2-sulfanyl derivative of the *closo*-decaborate anion $(Bu_4N)_2$[2-$B_{10}H_9SH$] with phthalimide in the presence of cesium carbonate leads to **the sulfonium derivative of the *closo*-decaborate anion [2-$B_{10}H_9S(CH_2N(CO)_2C_6H_4)_2$]$^-$**. The introduction of this compound into the **silver(I)** complexation makes it possible to obtain a complex with 2-[bis(N-phthalimidomethyl)sulfonio]-*closo*-decaborate as a counterion [$Ag(PPh_3)_4$][2-$B_{10}H_9S(CH_2N(CO)_2C_6H_4)_2$] [77]. According to the single-crystal X-ray diffraction data, the compound contains cationic complexes $[Ag(PPh_3)_4]^+$ and the derivative of the boron cluster as counterions.

Lead(II) and silver(I) complexes with **[2-$B_{10}H_9S(CH_2C(O)NH_2)_2$]$^-$** were briefly discussed [78]. The compounds were identified by IR spectroscopy and elemental analysis. It was concluded that silver(I) compound [$Ag_2(bipy)_2$[2-$B_{10}H_9S(CH_2C(O)NH_2]NO_3$ contains boron clusters coordinated by complexing agents via the AgHB bonds, whereas in [$Pb(bipy)_2$[2-$B_{10}H_9S(CH_2C(O)NH_2]_2$] there are no 3c2e PbHB bonds in the IR spectrum, indicating that the complexing agent coordinates the boron cage via the substituent.

Thus, lead(II) is the second metal (after ruthenium(II)) that is able to coordinate singly-charged substituted derivatives of the boron clusters. Silver(I) seems to be harder than lead(II) and ruthenium(II) because it gives complexes with an inner-sphere position of the monocharged derivatives.

2.6. Sulfanyl Group

A number of **lead(II) and silver(I)** complexes with **sulfanyl-substituted *closo*-decaborate derivative [2-$B_{10}H_9SH$]$^{2-}$** were reported [78]. Based on the data of IR spectroscopy and elemental analysis, it was concluded that [$Ag_2(bipy)_2$[2-$B_{10}H_9SH$]] contains boron clusters coordinated by complexing agents via the AgHB bonds; the [2-$B_{10}H_9SH]^{2-}$ anion is involved in coordination by lead(II) in complexes [Pb[2-$B_{10}H_9SH$]] and [$Pb(bipy)_2$[2-$B_{10}H_9SH$]] via 3c2e PbHB bonds and the substituent.

The thiol derivative $[B_{12}H_{11}SH]^{2-}$ is formed by the interaction of the $[B_{12}H_{12}]^{2-}$ anion with thiourea under electrochemical oxidation conditions followed by hydrolysis of the resulting compound [79]. The SH-substituted derivative $[B_{12}H_{11}SH]^{2-}$ was used in **ruthenium(III)** complexation; complex $[Ru[SB_{12}H_{11}](NH_3)_5]\cdot 2H_2O$ (Figure 10) was isolated when the salt of the substituted boron cluster was allowed to react with $[RuCl(NH_3)_5]Cl_2$. The metal atom coordinates five NH_3 groups and the substituent via the S atom [80] (S–B 1.878 Å, Ru–S 2.240 Å).

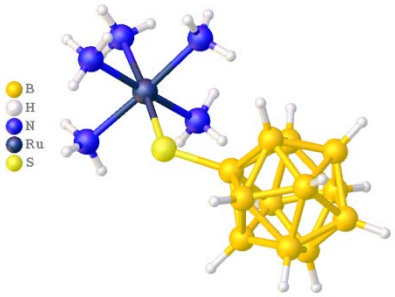


Figure 10. Structure of ruthenium(III) complex $[Ru[SB_{12}H_{11}](NH_3)_5]\cdot 2H_2O$ (water molecules are omitted).

2.7. Oxonium Substituents

The introduction of cyclic ether molecules as an exo-polyhedral substituent into the boron cluster results in reduction of the total charge of the derivatives of the *closo*-decaborate anion. Thus, the reaction of salts of the undecahydrodecaborate anion $[B_{10}H_{11}]^-$ with 1,4-dioxane and tetrahydropyran gives derivatives of the *closo*-decaborate anion containing the organic molecules as substituents in position B(2) of the polyhedron [65,81]. These derivatives react with $[Ag(PPh_3)_3]NO_3$ to form the corresponding silver(I) complexes $[Ag(PPh_3)_4][2\text{-}B_{10}H_9O(CH_2)_5]\cdot CH_2Cl_2$ and $[Ag(PPh_3)_4][2\text{-}B_{10}H_9O(CH_2)_4O]$. In both complexes, silver coordinates four molecules of Ph_3P forming cationic complex $[Ag(PPh_3)_4]^+$ [65], while the substituted derivative plays the role of a counterion. Both compounds are additional evidence that the silver(I) atom tends to form salts with monocharged derivatives of the boron clusters instead of forming complexes with them.

2.8. Opening of the Cyclic Substituent

Activation of the coordination ability of the oxonium derivatives of the boron clusters can be realized by opening of the cyclic ether substituent. In this case, the resulting derivative acquires the double negative charge and all the O atoms present in the structure of the resulting derivative potentially can be coordinated by the metal atom.

Particularly, reactions of the 1,4-dioxane derivative of the $[B_{10}H_{10}]^{2-}$ anion with ethylenediamine in ethanol lead to the formation of the derivative of the *closo*-decaborate anion **$2\text{-}B_{10}H_9O(CH_2)_2O(CH_2)_2NH(CH_2)_2NH_2)]^{2-}$ with pendant ethylenediamine (en) group** separated from the boron cluster by an alkoxy spacer. This anion was used in nickel(II) complexation [82]. In the compounds obtained, the metal atom coordinates only the substituent introduced into the boron cluster, whereas all BH groups remain uncoordinated. Complexes $[Ni(en)[2\text{-}B_{10}H_9O(CH_2)_2O(CH_2)_2NH(CH_2)_2NH_2)]] \cdot H_2O$ and $[Ni(H_2O)(en)_3[2\text{-}B_{10}H_9O(CH_2)_2O(CH_2)_2NH(CH_2)_2NH_2)]]$ were isolated. The complexes were obtained by heterophasic (using $NiCO_3$–$Ni(OH)_2$) and homophasic reactions, respectively. In the first complex, the water molecule is located in the outer sphere, whereas nickel(II) coordinates two O atoms and two N atoms of the substituent chain. In the second, nickel(II) coordinates two N atoms and one O atom of the substituent, two N atoms of ethylenediamine, and one O atom of coordinated water. The complexes are hydrated isomers resulting from the changed denticity of the substituted boron ligand (Figure 11).

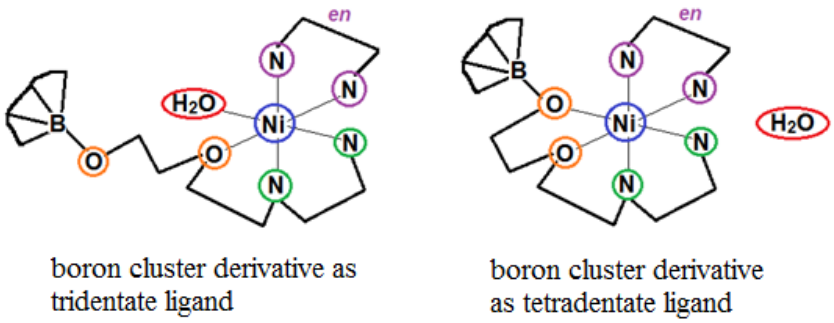


Figure 11. Schematic representations of the structures of nickel(II) complexes $[Ni(H_2O)(en)_3[2\text{-}B_{10}H_9O(CH_2)_2O(CH_2)_2NH(CH_2)_2NH_2)]]$ (**left**) and $[Ni(en)[2\text{-}B_{10}H_9O(CH_2)_2O(CH_2)_2NH(CH_2)_2NH_2)]] \cdot H_2O$ (**right**).

The opening of the cyclic substituent in the $[2\text{-}B_{10}H_9O(CH_2)_2O]^-$ anion using the ethylate ion leads to the formation of **the $[2\text{-}B_{10}H_9O(CH_2CH_2)_2OEt]^{2-}$ derivative with the pendant ethoxy group** separated from the boron cluster by an alkoxy spacer. Lead(II) complex $[Pb(Bipy)[2\text{-}B_{10}H_9O(CH_2CH_2)_2OEt)]]_2 \cdot 0.5DMF$ was obtained in lead complexation in the presence of Bipy [83] (Figure 12). In the crystal, Pb(II) coordinates two N atoms of Bipy (Pb–N 2.470(4), 2.483(5) Å) and three O atoms of the alkoxy spacer of the substituent (Pb–O 2.497(4)–2.859(4) Å). In addition, Pb(II) coordinates the apical BH group of one boron cage and the apical edge of the other (Pb–B 3.128(6) and 3.288(7) Å, Pb–H 2.70(5) and 2.73(6) Å).

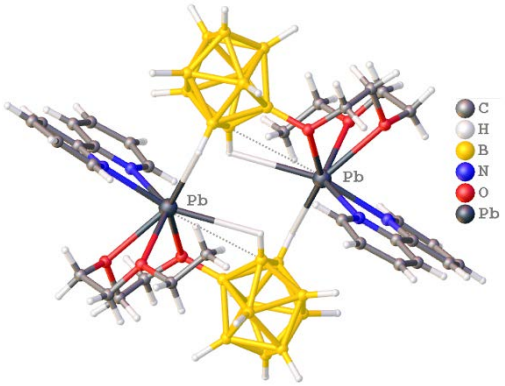


Figure 12. Structure of lead(II) complex $[Pb(Bipy)[2\text{-}B_{10}H_9O(CH_2CH_2)_2OEt]]_2 \cdot 0.5DMF$.

It was found that a monosubstituted derivative of the *closo*-decaborate with 1,4-dioxane $[B_{10}H_9O(CH_2)_4O]^-$ reacts with polyhydric alcohols (ethylene glycol, glycerol, triethanolamine), giving **derivatives with pendant hydroxy groups $[B_{10}H_9OCH_2CH_2OCH_2CH_2OR]^{2-}$** ($R = CH_2OH$, $CH(OH)CH_2OH$, $CH_2N(CH_2CH_2OH)_2$) [84]. On the basis of these compounds, **gadolinium(III)** complexes $Gd_2[B_{10}H_9OCH_2CH_2OCH_2CH_2OR]_3$ were obtained when reacting with gadolinium(III) carbonate. The final compounds were characterized by NMR and IR spectroscopies as well as mass-spectrometry [84]. According to the data obtained, it seems that the *closo*-decaborate derivatives are coordinated by the substituents.

Thus, it is obvious that lead(II) coordinates the discussed derivatives of the boron clusters with the B–O bonds via the 3c2e PbHB bonds and functional groups of the substituents, whereas nickel(II) and gadolinium(III) are too hard to coordinate the boron cage and are able to coordinate the substituents.

2.9. S-thiocyanato Substituents

The reaction between *closo*-dodecaborate and dirodane in dichloromethane afforded **the S-thiocyanato-derivative of the *closo*-decaborate anion $[B_{12}H_{11}SCN]^{2-}$** [81]; its interaction

with trinuclear mercury complex (*o*-$C_6F_4Hg)_3$ yielded half-sandwich and sandwich mercury complexes $\{(o\text{-}C_6F_4Hg)_3[B_{12}H_{11}SCN]\}^{2-}$ and $\{[(o\text{-}C_6F_4Hg)_3]_2[B_{12}H_{11}SCN]\}^{2-}$ [85,86]. The latter complex (Figure 13) has the structure of a wedge-shaped sandwich with $[B_{12}H_{11}SCN]^{2-}$ located between two (*o*-$C_6F_4Hg)_3$ molecules (Hg–H 2.56–3.18 Å, Hg–B 3.317(10)–3.546(11) Å).

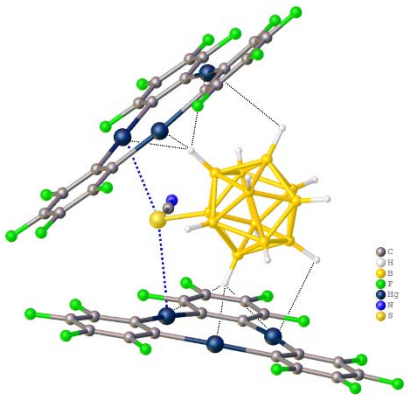
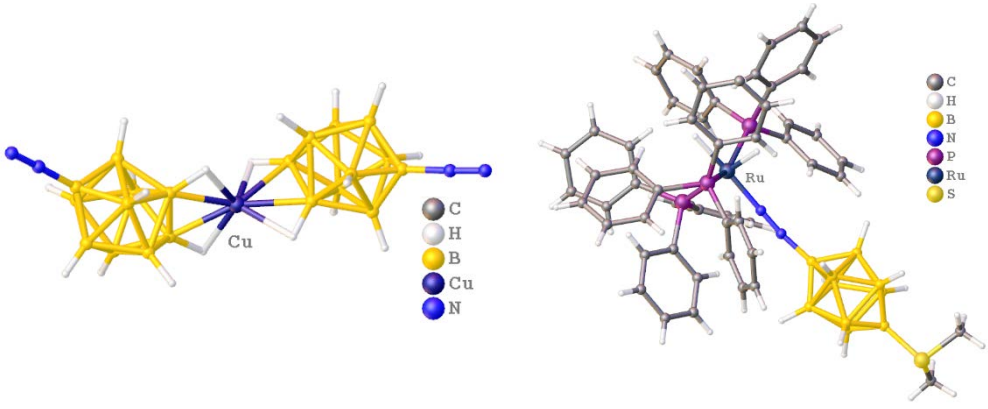


Figure 13. Structure of mercury complex in $(Bu_4N)_2[[(o\text{-}C_6F_4Hg)_3]_2[B_{12}H_{11}SCN]]$.

2.10. Diazo Substituents

The reaction of triethylammonium *closo*-decaborate with 2,4,6-tribromophenyldiazonium tetrafluoroborate in acetonitrile leads to the formation of triethylammonium 1-diazo-*closo*-decaborate $(Et_3NH)[1\text{-}B_{10}H_9N_2]$. When it reacted with copper(I) chloride, copper(I) complex $[Et_3NH][Cu[1\text{-}B_{10}H_9N_2]_2]$ with a **singly charged diazo-substituted derivative $[\mathbf{1\text{-}B_{10}H_9N_2}]^-$** was isolated [87] containing a linear B–N≡N group. This complex is built of copper(I) anionic complex $[Cu[1\text{-}B_{10}H_9N_2]_2]^-$ (Figure 14a), in which copper(I) coordinates two $[1\text{-}B_{10}H_9(N_2)]^-$ monoanions along the apical edge (Cu–B 2.184(9), 2.168(8) Å; Cu–H 1.96, 1.99Å), opposite to the introduced N≡N substituent.



(**a**) (**b**)

Figure 14. (**a**) Anionic copper(I) complex in $[Et_3NH][Cu[1\text{-}B_{10}H_9N_2]_2]$ and (**b**) molecular ruthenium(II) complex $[RuH_2[N_2B_{10}H_8SMe_2](Ph_3P)_3]\cdot 3C_6H_6$.

Ruthenium complexation starting from $[RuH_2(N_2)(PPh_3)_3]$ with the **neutral disubstituted derivative 1,10-(dimethylsulfonio)diazo-*closo*-decaborane $[\mathbf{N_2B_{10}H_8SMe_2}]$** gave ruthenium(II) complex $[RuH_2[N_2B_{10}H_8SMe_2](Ph_3P)_3]\cdot 3C_6H_6$ [88]. In this complex, the Ru–N≡N–B group is linear according to X-ray diffraction (Figure 14b) (Ru–N 1.889 Å; Ru–H 1.53(7), 1.74(7); B–N 1.498 Å).

Thus, copper(I) coordinates the diaza-substituted monocharged derivative forming 3c2e CuHB bonds, whereas ruthenium(II) coordinates the neutral derivative with additional dimethylsulfonium substitution by the diaza-group. The absence of RuHB bonds can be

explained by two hydride atoms bonded with the metal atom and the neutral charge of the boron cage.

2.11. Cyano-Substituents

The **1,10-dicyano-*closo*-decaborate ion [1,10-$B_{10}H_8(CN)_2$]$^{2-}$** was obtained by heating the [1,10-$B_{10}H_8(CONH_2)_2$]$^{2-}$ derivative, which in turn is formed upon sequential processing of the *closo*-decaborate anion with nitric acid followed by reduction with sodium borohydride to obtain a neutral compound [1,10-$B_{10}H_8(CO)_2$] and its further interaction with ammonia [89–91]. The disubstituted derivative [1,10-$B_{10}H_8(CN)_2$]$^{2-}$ was used in iron(III) complexation in the presence of cyclopentadienyl and phosphine ligands, which resulted in a binuclear iron(III) complex with linear Fe–N≡C–B bond of the composition [(*Cp*)(dppe)Fe}$_2$[1,10-$B_{10}H_8(NC)_2$]·H_2O [91]. In the resulting complex, the disubstituted derivative of the boron cluster bridges two metal atoms (Figure 15). In this compound, the derivative is coordinated only by the functional groups of the substituent (Fe–N 1.9102(17) Å, N–C 1.152(3) Å).

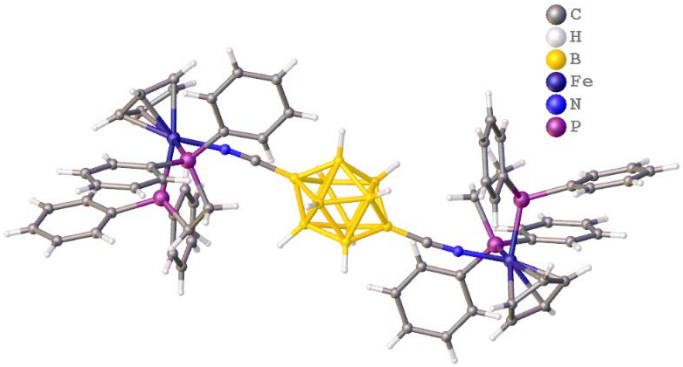


Figure 15. Structure of iron(III) complex [(*Cp*)(dppe)Fe}$_2$[1,10-$B_{10}H_8(NC)_2$]·H_2O with linear M–N≡C–B groups. Solvent molecules are omitted.

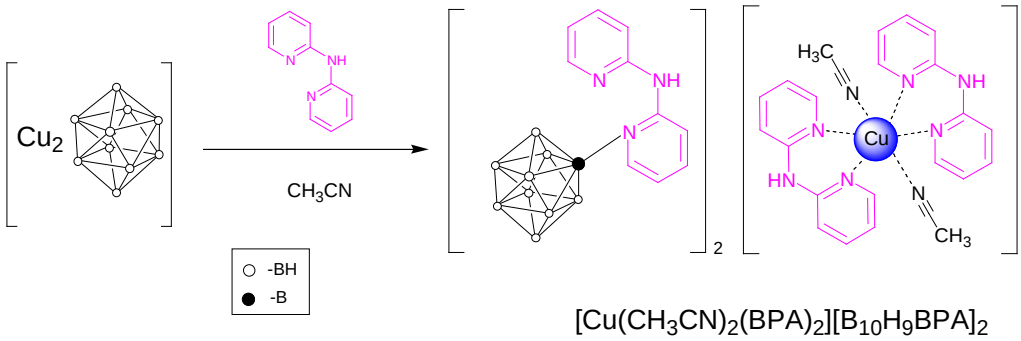
The obtained complex is the first iron(III) complex with boron clusters. Usually, boron clusters reduce metal(III) to metal(II) in the course of complexation (as was observed for cobalt and iron); the presence of the substituent and shielding the metal by the cyclopentadienyl and phosphine ligands resulted in the preparation of iron(III) complex.

2.12. Azaheterocycles as Substituents

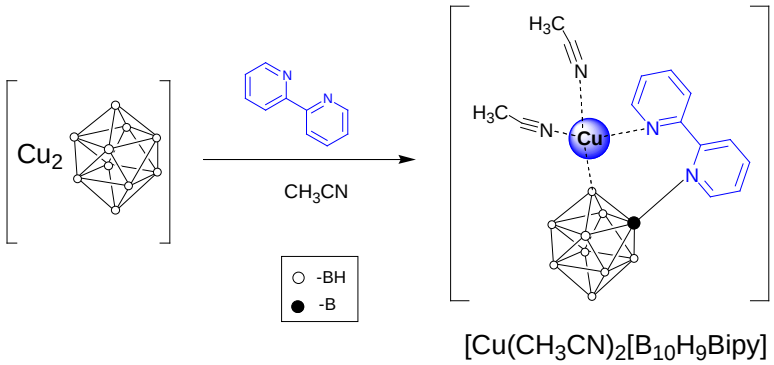
The ability of the *closo*-decaborate anion to participate in reactions of the substitution of hydrogen atoms in the course of copper(II) complexation was mentioned above for the OH-substituted derivative. Another example of substitution reactions accompanying the complexation is the reaction of copper(I) complex [$Cu_2[B_{10}H_{10}]$] with 2,2′-bipyridylamine BPA [92,93] which resulted in redox reaction and afforded copper(II) complex [$Cu(BPA)_2(NCCH_3)_2$][2-$B_{10}H_9BPA]_2 \cdot 2H_2O$ (Scheme 1).

The BPA molecule is bonded to equatorial position B(2) of the boron cage and plays the role of a substituent. The **monosubstituted N-dipyridylamine derivative [2-$B_{10}H_9BPA$]$^-$** acts as a counter ion for the mixed-ligand mononuclear cationic Cu(II) complex [$Cu(BPA)_2(NCCH_3)_2$]$^{2+}$ [92]. Copper coordinates two chelating BPA ligands, and acetonitrile complete the coordination sphere of the metal to a distorted octahedron (4 + 2).

The **monosubstituted N-bipyridyl derivative [$B_{10}H_9Bipy$]$^-$** was found to form in situ in copper(I) complexation with the unsubstituted *closo*-decaborate anion [93]. In this reaction (Scheme 2), the process of substitution of an exo-polyhedral hydrogen atom for the ligand molecule is observed, which accompanies the copper(I) complexation.



Scheme 1. Preparation of complex $[Cu(BPA)_2(NCCH_3)_2][2\text{-}B_{10}H_9BPA]_2$.



Scheme 2. Preparation of complex $[Cu(CH_3CN)_2[B_{10}H_9Bipy]$.

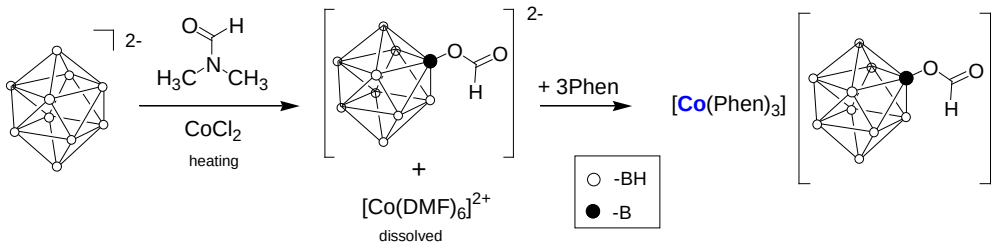
The substituted derivative $[2\text{-}B_{10}H_9Bipy]^-$ in the complex is coordinated by the metal atom via nitrogen atoms (Cu–N 2.028(2) Å) and apical BH group (Cu–B(H) 2.601(3), Cu–H(B) 1.85(3)Å). In addition, two acetonitrile molecules are involved in copper(I) coordination (Cu–N 1.995(3), 1.976(3) Å).

Note that these reactions are of particular interest because the $[2\text{-}B_{10}H_9L]^{2-}$ derivatives with azaheterocyclic ligands L cannot be obtained in the course of the acid-catalyzed nucleophilic substitution [94,95]; under acidic conditions, organic ligands (Bipy, Phen, BPA) are protonated to form salts $[LH]_2[B_{10}H_{10}]$ or $[LH_2][B_{10}H_{10}]$ [96,97].

The data obtained indicate that copper(II) cannot coordinate the monocharged substituted derivatives whereas copper(I) is able to form complexes with the inner-sphere boron cluster. The possibility of the Bipy molecule to bend across the linker C–C bond allows it to be coordinated by copper(I) and simultaneously to be attached to the boron cage. Note that similar copper(I) complex with Phen ligand cannot be formed because of the rigidity of the ligand.

2.13. Carboxy Groups as Substituents

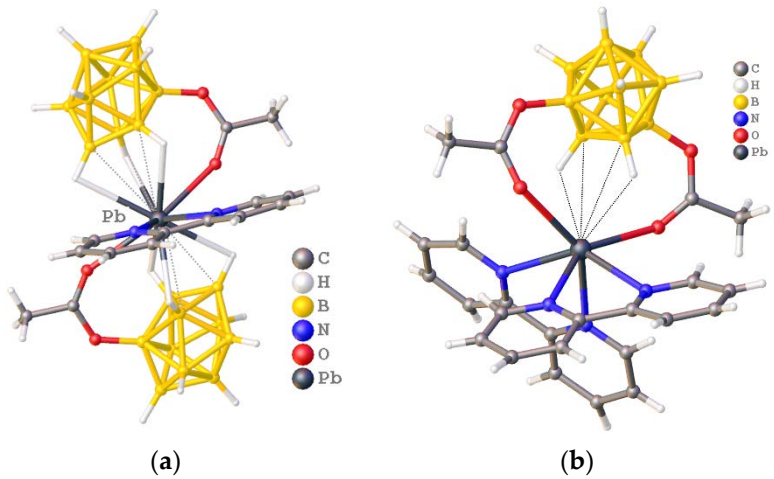
During the reactions of cobalt(II) complexation in DMF, the solvent can act as a reagent to give substituted derivatives of the boron clusters. Monosubstituted **formoxy derivative $[2\text{-}B_{10}H_9OC(H)O]^{2-}$** containing the exo-polyhedral B–O bond was isolated when $(Et_3NH)_2[B_{10}H_{10}]$ was allowed to react with $CoCl_2$ in DMF on heating (Scheme 3). The resulting boron cluster anion contains a formic acid residue –OC(H)O as a substituent. The addition of a threefold excess of Phen to the reaction mixture afforded cobalt(II) complex $[Co(Phen)_3][2\text{-}B_{10}H_9OC(H)O]\cdot 3DMF$ [98].



Scheme 3. Preparation of complex $[Co(Phen)_3][2\text{-}B_{10}H_9OC(H)O]]$.

Monosubstituted and disubstituted derivatives of the B_{10} polyhedron with acetoxy groups as exo-polyhedral substituents can be obtained by reacting salts of the $[B_{10}H_{10}]^{2-}$ anion with acetic acid varying synthesis conditions [99,100]. These derivatives were also found to act as ligands in lead(II) complexation with Bipy [101]. The target compounds were obtained when the substituted derivative was allowed to react with solid $Pb(NO_3)_2$ in organic solvent; some part of lead(II) nitrate dissolved in the reaction mixture; after filtration of the unsolved $Pb(NO_3)_2$, a Bipy solution in the same solvent was added, giving a yellow color to the resulting mixture. As a result of lead(II) complexation, the target complexes precipitated.

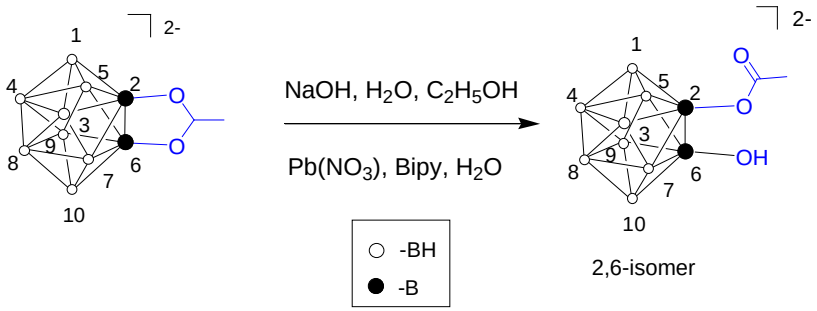
Lead(II) complex $(Ph_4P)[Pb(Bipy)[2\text{-}B_{10}H_9OC(O)CH_3)_2]_2$ [100] and $[Pb(Bipy)_2[2,7(8)\text{-}B_{10}H_8(OC(O)CH_3)_2)]$ [99] with **monosubstituted $[2\text{-}B_{10}H_9OC(O)CH_3)_2]^{2-}$ and disubstituted $[2,7(8)\text{-}B_{10}H_8(OC(O)CH_3)_2)]^{2-}$ acetoxy derivatives** are known (Figure 16). In both compounds, Pb(II) coordinates one or two Bipy molecules (Pb–N 2.551(3)–2.581(3) Å), one or two oxygen atoms of the carboxylate groups of the substituent (Pb–O 2.749(3)–2.760(3)Å), and BH groups of the boron cage forming PbHB bonds (Pb–B 2.989(5)–3.263(8) Å; Pb–H 2.60(4)–2.93(4) Å).



(**a**) (**b**)

Figure 16. Structures of lead(II) complexes (**a**) $(Ph_4P)[Pb(Bipy)[2\text{-}B_{10}H_9OC(O)CH_3)_2]_2$ (cation is omitted) and (**b**) $[Pb(Bipy)_2[2,8\text{-}B_{10}H_8(OC(O)CH_3)_2)]]$.

The **monocharged disubstituted *closo*-decaborate derivative with the bidentate acetate group Cat[2,6(9)-$B_{10}H_8$>$(O)_2CCH_3$]** (Cat = Ph_4P^+, Ph_4As^+) can be used to prepare a compound with two different substituents (Scheme 4). In the course of lead(II) complexation, it undergoes partial hydrolysis, the acetate group remains monodentately bound to the boron cluster in the B(2) position, while the OH group was found to act as a substituent in the B(6) position.



Scheme 4. Preparation of monoanion [2,6(9)-$B_{10}H_8$>$(O)_2CCH_3]^-$ = $[An]^-$ as salt Cat[An] or complex $[Pb(Bipy)_2[An]]_2$.

The resulting **derivative with two different substituents –OH and –OC(O)CH_3** was isolated as lead(II) complex $[Pb(Bipy)_2[2,6(9)\text{-}B_{10}H_8(OC(O)CH_3)(OH)]]_2 \cdot 3H_2O$ [102]. The lead(II) atom coordinates two Bipy (Pb(1)–N 2.510(6), 2.610(7) Å), the OH group (Pb(1)–O 2.85(3), 2.95(3) Å), and the BH group of the boron cage (Pb(1)–H 2.58, 2.66 Å) (Figure 17). In this case, the acetoxy substituent remains non-coordinated. It can be concluded that despite both the –OH and –OC(O)CH_3 groups being potentially active in lead(II) coordination, the hydroxyl group is more favorable for coordination, which can be explained by steric factors, as the acetoxy group create some steric hindrances for lead(II) atoms.

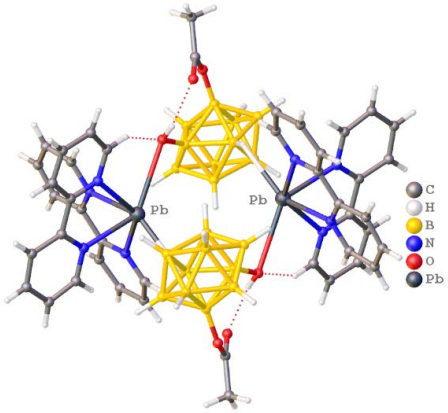
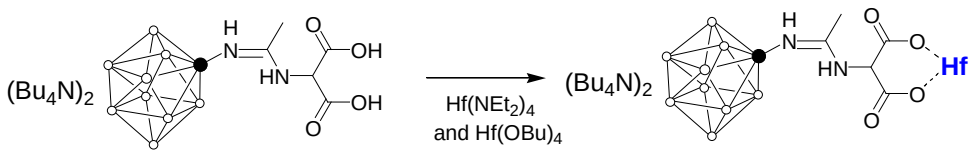


Figure 17. Structure of lead(II) complex $[Pb(Bipy)_2[2,6(9)\text{-}B_{10}H_8(OC(O)CH_3)(OH)]]_2$.

The nucleophilic addition of diethylaminomalonate to the acetonitrile derivative of the *closo*-decaborate anion and the following alkaline hydrolysis of ester groups gives the aminomalonic acid-based product $(NBu_4)[2\text{-}B_{10}H_9NHC(CH_3)NHCH(COOH)_2]$ [103]. The complexation reaction between the **derivative of the *closo*-decaborate anion with aminomalonic acid** and hafnium(IV) butoxide and hafnium(IV) diethylamide afforded **hafnium(IV) complex** $(NBu_4)_2[[2\text{-}B_{10}H_9NHC(CH_3)NHCH(COO)_2]_2Hf]$ (Scheme 5), which was characterized by IR spectroscopy, mass-spectrometry, and elemental analysis [103].



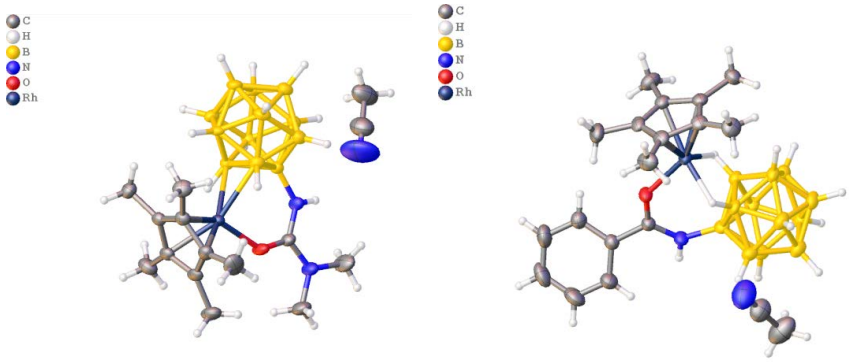
Scheme 5. Preparation of complex $(NBu_4)_2[[2\text{-}B_{10}H_9NHC(CH_3)NHCH(COO)_2]_2Hf]_2$.

Thus, in cobalt(II) complexes with carboxy substituents, boron anions act as counterions; lead(II) affords a number of complexes with combined coordination (MHB + substituent). In

hafnium(IV) complexes, the substituted derivative is assumed to be coordinated by the metal via the functional group of the substituent introduced into the boron cage.

2.14. Amide Groups as Substituents

Rhodium(III) complex $[Rh(Me_5Cp)[B_{12}H_{11}NHC(O)NMe_2]]\cdot CH_3CN$ with a cyclopentadienyl ligand and **3,3-dimethylureido-*closo*-dodecaborate anion $[B_{12}H_{11}NHC(O)NMe_2]^{2-}$** was reported [104]. This substituted derivative was prepared by successive treatment of $Cs[B_{12}H_{11}NH_3]$ with NaH and DMF. The complex was prepared by the reaction of $[B_{12}H_{11}NHC(O)NMe_2]^{2-}$ with $[Rh(Me_5Cp)(CH_3CN)_3][SbF_6]_2$ in acetonitrile. The metal coordinates the boron ligand through the O atom of the substituent (Rh–O 2.085(2) Å) and two BH groups of the boron cage (Rh–H 1.951, 1.974 Å; Rh–B 2.428(4), 2.436(4) Å) (Figure 18a).



(**a**) (**b**)

Figure 18. Structure of rhodium(III) complexes (**a**) $[Rh(Me_5Cp)[B_{12}H_{11}NHC(O)NMe_2]]\cdot CH_3CN$ and (**b**) $[Rh(Me_5Cp)[B_{12}H_{11}NHC(O)Ph]]\cdot CH_3CN$.

Later, another rhodium(III) complex with **the monosubstituted benzamido-*closo*-dodecaborate anion $[B_{12}H_{11}NHC(O)Ph]^{2-}$** was synthesized and isolated $[Rh(Me_5Cp)[B_{12}H_{11}NHC(O)Ph]]\cdot CH_3CN$ [105]. The $[B_{12}H_{11}NHC(O)Ph]^{2-}$ anion was obtained by acylation of the ammonio-*closo*-dodecaborate anion $[B_{12}H_{11}NH_3]^-$ with benzene chloride [106]. This rhodium complex was prepared by reacting tetrabutylammonium salt of the $[B_{12}H_{11}NHC(O)Ph]^{2-}$ anion with rhodium complex $[Rh(Me_5Cp)(CH_3CN)_3][SbF_6]_2$. The resulting complex also demonstrates the combined coordination of the boron cluster via two BH groups (Rh–H 1.954, 1.957 Å; Rh–B 2.427(4), 2.431(4) Å) and the O atom of the substituent (Rh–O 2.095(2) Å) (Figure 18b).

2.15. Phthalocyanine Derivatives as Substituents

A number of compounds based on boron clusters containing phthalocyanine derivatives are known. Aluminum(III) and cobalt(II) complexes with **tetrakis(methylamino-*closo*-dodecaborato)phthalocyanines and octakis(methylamino-*closo*-dodecaborato)phthalocyanines** were isolated [107]. To prepare the final compounds, anion $[B_{12}H_{11}NH_3]^-$ was reduced to $[B_{12}H_{11}NH_2]^{2-}$ with sodium hydride, and halogen-containing phthalocyanines were introduced into the resulting solution. The corresponding sodium salts were prepared (Figure 19). These derivatives of the *closo*-dodecaborate anion contain **the B–N exo-polyhedral bond**. The synthesized sodium and cesium salts are the first water-soluble phthalocyanines based on the *closo*-dodecaborate anion, almost unlimitedly soluble in water.

Zinc(II) and **cobalt(II)** complexes with **phthalocyanine derivatives containing pendant *closo*-dodecaborate anions with exo-polyhedral B–O and B–S groups** were isolated (Figure 20) [108–110]. The possibility to prepare sodium salts of the compounds under discussion soluble in water is very important for their potential application in boron-neutron capture therapy.

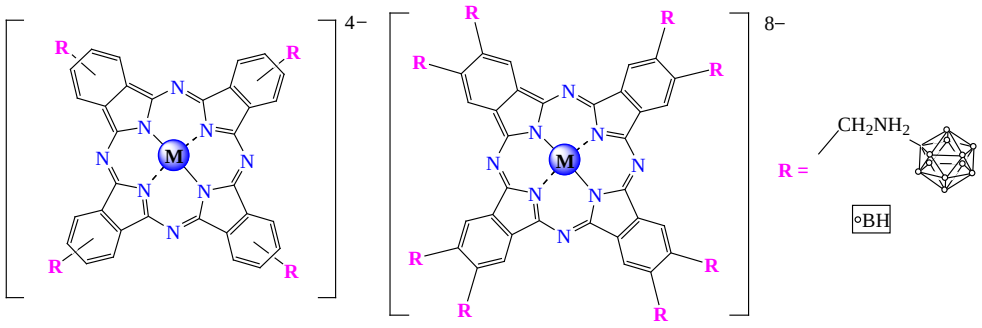


Figure 19. Structures of cobalt(II) and aluminum(III) complexes with the *closo*-dodecaborate derivatives of phthalocyanine containing B–N bonds (M = Co or AlOH).

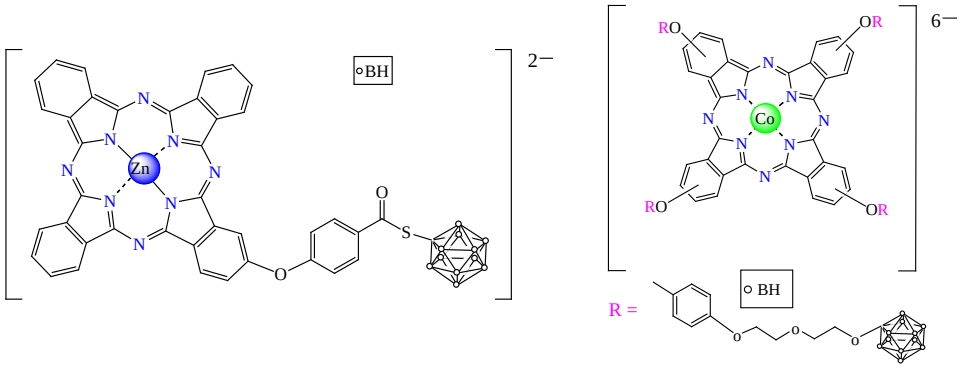


Figure 20. Structures of (**a**) zinc(II) and (**b**) cobalt(II) complexes with the *closo*-dodecaborate derivatives of phthalocyanine containing B–S and B–O bonds.

In addition, a zinc(II) complex with the *closo*-dodecaborate derivatives of phthalocyanine based on eight 1,4-dioxane derivatives of the *closo*-decaborate anion was isolated (Figure 21) in order to estimate its ability to act as a boron delivery agent for boron neutron capture therapy [111]. The compound was prepared by cyclotetramerization of 4-(3,5-dimethoxyphenoxy)phthalonitrile in the presence of zinc(II) acetate. The boronated phthalocyanine was found to accumulate in A549 human lung adenocarcinoma cells. The maximal cytoplasmic concentration was achieved at an extracellular concentration of 32 ± 3 μM. The compound was found to deliver 2.4×10^7 boron atoms per cell.

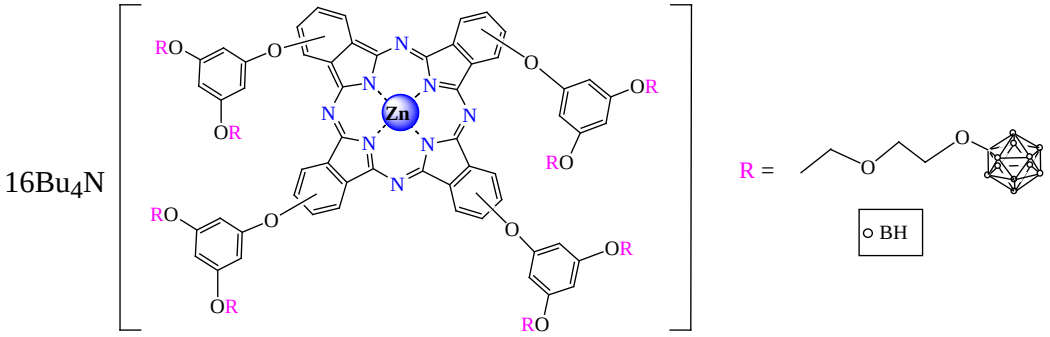


Figure 21. Structure of zinc(II) complex with the *closo*-dodecaborate derivatives of phthalocyanine containing B–O bonds.

3. Metal Complexes with B-Substituted Derivatives of Carboranes

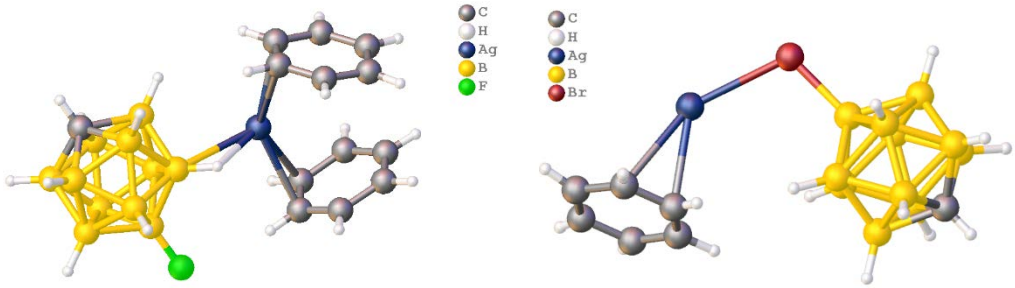
As indicated above, carboranes have a versatile chemistry involving functionalization of carbon atoms of their cage. In complexation reactions, there are a great number of complexes with derivatives containing C–X exo-polyhedral bonds. Thus, carboranylphosphine ligands (with C–P exo-polyhedral bonds) are generalized in a recent review [62]; chalcogenocarboranes with C–X bonds (X = S, Se, Te) were summarized [112–114]; carboxy [115–121], carbene [122], and acetylene [123] derivatives with the C–C exo-polyhedral bonds were discussed in the corresponding reviews. The carboranyl-based N,O-donor compounds functionalized by the carbon atom of the carborane cage have been thoroughly studied [123–129].

Here, we want to discuss the effect of the substituent attached to the boron atom on the coordination ability of the carborane cage without involving the carbon atoms in the functionalization.

3.1. Derivatives with B–Hal Bonds

Actually, there are a great number of perhalogenated carboranes and complexes based on them. The obtained compounds are weakly coordinating ligands and are studied in detail. Here, we wanted to discuss partially halogenated carboranes as well, because there are few representatives of complexes containing mono- and dihalogenated carboranes.

Monofluoro-substituted derivative of monocarborane $[CB_{11}H_{11}F]^-$ was prepared by fluorination of $Cs[CB_{11}H_{11}F]^-$ with anhydrous HF [**130**]. In **silver(I)** complex $[Ag(C_6H_6)_2$ $[12\text{-}CB_{11}H_{11}F]]$ (Figure 22a), there is no interaction between the silver ion and the fluorine atom: the carborane cage is coordinated by 3c2e BHAg bonds (Ag–H 2.181 Å, Ag–B 2.762 Å). In the related silver(I) complex with **monobrominated derivative $[CB_{11}H_{11}Br]^-$**, on the contrary, there is a strong Ag–Br interaction with the Ag–Br distance of 2.642(1) Å [131].



(**a**) (**b**)

Figure 22. Structures of (**a**) $[Ag(C_6H_6)_2[12\text{-}CB_{11}H_{11}F]]$ and (**b**) $[Ag(C_6H_6)[12\text{-}CB_{11}H_{11}Br]]$.

Disubstituted derivative of monocarborane $[CB_9H_8F_2]^-$ was used in **silver(I)** complexation, which results in silver(I) complex $[Ag(C_6H_6)_2][6,8\text{-}CB_9H_8F_2]$ [132] (Figure 23). It was found that the compound is a molecular silver(I) complex with two coordinated benzene molecules and carborane anion coordinated by two AgHB bonds (Ag–H 2.09, 2.10 Å). The coordination is similar to that observed for monofluorinated carborane in complex $[Ag(C_6H_6)_2[12\text{-}CB_{11}H_{11}F]]$.

The reaction between molybdenum complex with cyclopentadienyl ligand $[Cp(CO)_3MoI]$ and silver salt $[Ag[CB_{11}H_{11}Br]$ initially results in an intermediate dimeric **molybdenum-silver** complex $[MoCp(CO)_3IAg(CB_{11}H_{11}Br)]_2$ (Figure 24a), which has a central $\{AgI\}_2$ core appended by two carborane anions [133]. The carborane anions are coordinated by the complexing metal via the bromine atom (the Ag–Br bond is 2.6456(8) Å). Prolonged reaction results in elimination of AgI to form molybdenum complex $[MoCp(CO)_3(CB_{11}H_{11}Br)]$ (Figure 24b) with the Mo–Br bond equal to 2.6759(2) Å.

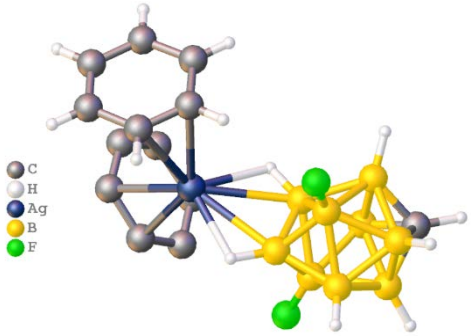
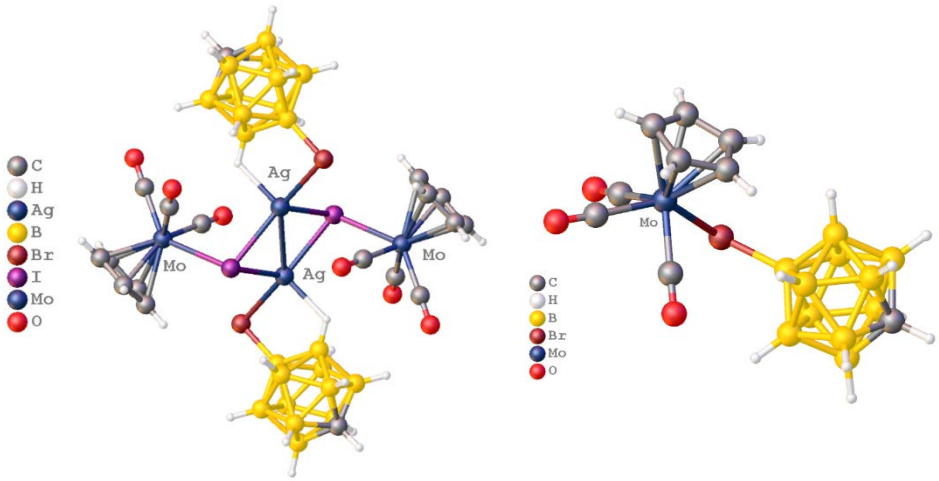


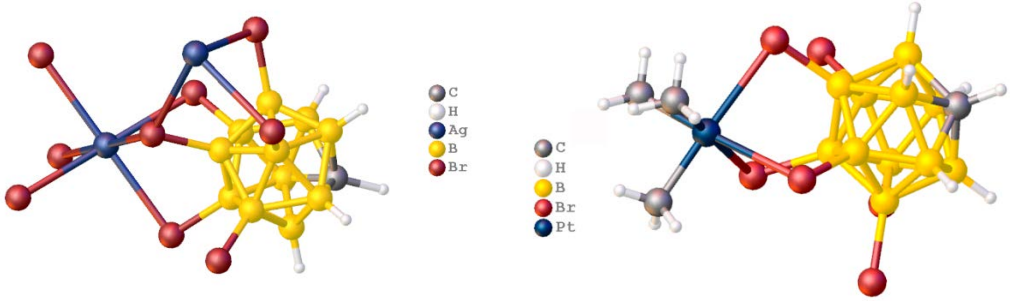
Figure 23. Structure of silver(I) complex $[Ag(C_6H_6)_2][6,8\text{-}CB_9H_8F_2]$.



(**a**) (**b**)

Figure 24. Structures of (**a**) $[MoCp(CO)_3IAg(CB_{11}H_{11}Br)]_2$ and (**b**) $[MoCp(CO)_3(CB_{11}H_{11}Br)]$.

Three isostructural polymeric **silver complexes** with **hexahalogenocarboranes $[CB_{11}H_6Hal_6]^-$** were isolated [134]: complex $[Ag(CB_{11}H_6Cl_6)(p\text{-}Me_2C_6H_4]_n$ with coordinated solvent molecules, solvent-free $[Ag(CB_{11}H_6Br_6)]_n$ (Figure 25a), and $[Ag(CB_{11}H_6I_6)]_n \cdot 0.5C_6H_6$ (Figure 25b) with non-coordinated solvent. The compounds were obtained from *p*-xylene, toluene, and benzene, respectively. In all three compounds, silver atoms coordinate two or three halogen substituents, whereas BH groups around the carbon atom remain uncoordinated. The Ag–Hal bonds are 2.640(1)–2.926(1) Å, av. 2.862(2) Å, and 2.777(4)–3.306(5) Å for Cl, Br, and I, respectively.

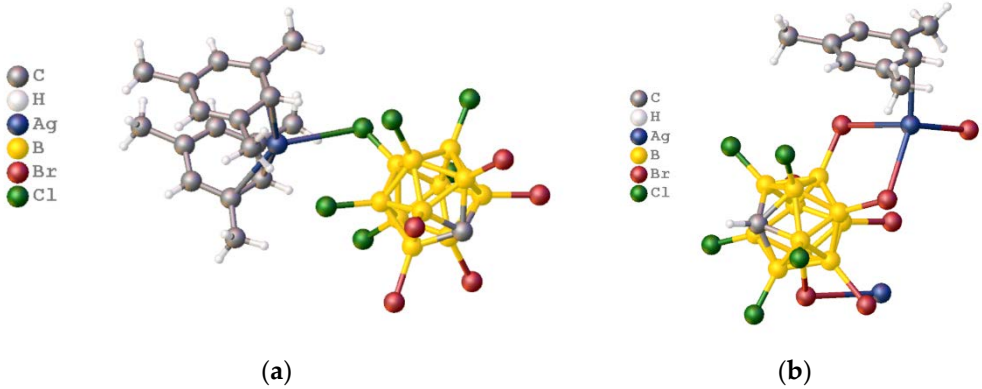


(**a**) (**b**)

Figure 25. Structures of (**a**) $[Ag(CB_{11}H_6Br_6)]_n$ and (**b**) $[(CB_{11}H_6Br_6)PtMe_3]$.

Platinum complex with **hexabromocarborane $[CB_{11}H_6Br_6]^-$** was isolated as $[(CB_{11}H_6Br_6)PtMe_3]$ when the corresponding cesium salt of the carborane reacted with $\{Me_3Pt(OTf)\}_4$ [135]. In the final complex, the complexing agent coordinates the carborane anion by three bromine atoms forming MHB bonds; the Pt–Br bond lengths are 2.7129(17)–2.7279(18) Å.

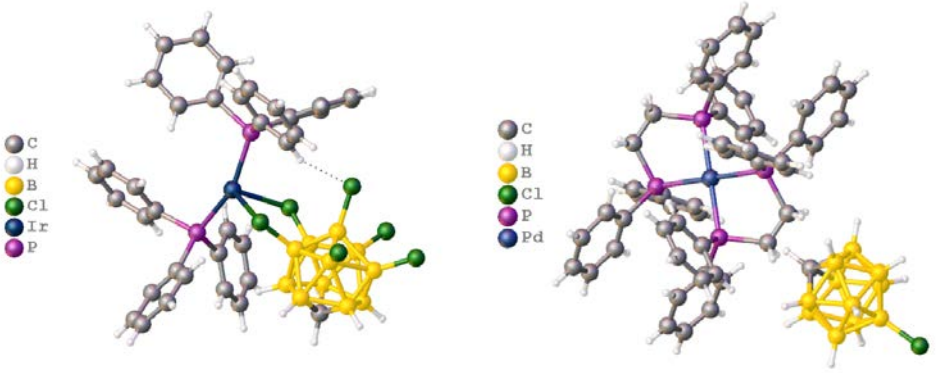
It is interesting to discuss the position of **silver(I)** atoms in **mixed halocarboranes containing both Cl and Br** substituents. Compounds $[1\text{-H-}CB_{11}Y_5X_6]^-$ (X, Y = Cl, Br, I) were prepared in high yield when $[Me_3NH][1\text{-H-}CB_{11}H_5X_6]$ (X = Cl, Br, I) was treated with proper halogenating reagents at 180–220 °C in a sealed tube [136]. Interestingly, mixed halocarboranes in silver(I) complexes are coordinated from the side opposite to the carbon atom of the carborane cage (Figure 26). Thus, carborane $[1\text{-H-}CB_{11}Br_5Cl_6]^-$ in molecular complex $[(solv)_2Ag[1\text{-H-}CB_{11}Br_5Cl_6]\cdot solv$ (solv = mesitylene) is coordinated by two chlorine atoms (Ag–Cl 2.986(2) and 2.889(2) Å), whereas $[1\text{-H-}CB_{11}Cl_5Br_6]^-$ in related polymeric complex $[(solv)_2Ag[1\text{-H-}CB_{11}Cl_5Br_6]\cdot solv$ is coordinated by two bromine atoms (Ag–Br 2.750(2)–2.873(1) Å).



(**a**) (**b**)

Figure 26. Structures of (**a**) $[(solv)_2Ag[1\text{-H-}CB_{11}Br_5Cl_6]\cdot solv$ and (**b**) $[(solv)_2Ag[1\text{-H-}CB_{11}Cl_5Br_6]\cdot solv$ (solv = mesitylene).

Iridium(III) hydridophosphine complexes $[IrL_2H_2(anion)]$ with L = PPh_3 or PMe_2Ph and **hexahalogenocarborane anions $[1\text{-}CB_{11}H_6Cl_6]^-$ and $[1\text{-}CB_{11}H_6I_6]^-$** were prepared by hydrogenation of cyclooctadiene precursor complexes [137]. In the complexes, the carborane cage is coordinated by two halogen bonds, whereas the BH groups near the *ortho*-position of the carbon atom are uncoordinated. In the structure of $[Ir(PPh_3)_2H_2(1\text{-}CB_{11}H_6Cl_6)]$ (Figure 27a), the Ir–Cl bonds are 2.680(1) and 2.655(1) Å.

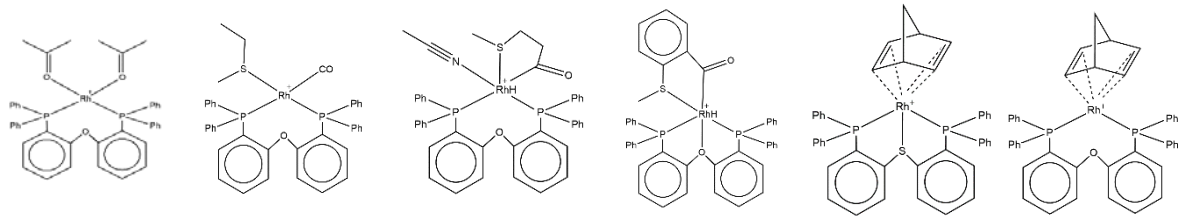


(**a**) (**b**)

Figure 27. Structures of (**a**) $[Ir(PPh_3)_2H_2(1\text{-}CB_{11}H_6Cl_6)]$ and (**b**) $[Pd(dppe)_2][CB_{11}H_{11}Cl]_2]\cdot 3CH_2Cl_2$.

Palladium(II) complex with uncoordinated **monochlorosubstituted carborane anion $[CB_{11}H_{11}Cl]^-$** was prepared when $[Pd(dppe)_2]Cl_2$ reacted with $[Ag[CB_{11}H_{12}]]$ in CH_2Cl_2 [138]. The monosubstituted derivative was isolated as complex $[Pd(dppe)_2][CB_{11}H_{11}Cl]_2]\cdot 3CH_2Cl_2$ in low yield as a result of the complexation reaction affording compound $[Pd(dppe)[CB_{11}H_{12}]]\cdot[CB_{11}H_{12}]$ as the main product. In the by-product, the monochlorosubstituted carborane anion acts as a counterion (Figure 27b).

Hexachloro- or hexabromocarboranes $[CB_{11}H_6Cl_6]^-$ or $[CB_{11}H_6Br_6]^-$ were used in **rhodium(II)** complexation with diphenylphosphine ligands present below (Scheme 6) [139,140], which were synthesized by reacting $[RhCl(nbd)]_2$ with cesium or sodium salts $[CB_{11}H_6Cl_6]^-$ or $[CB_{11}H_6Br_6]^-$ in methanol at room temperature.



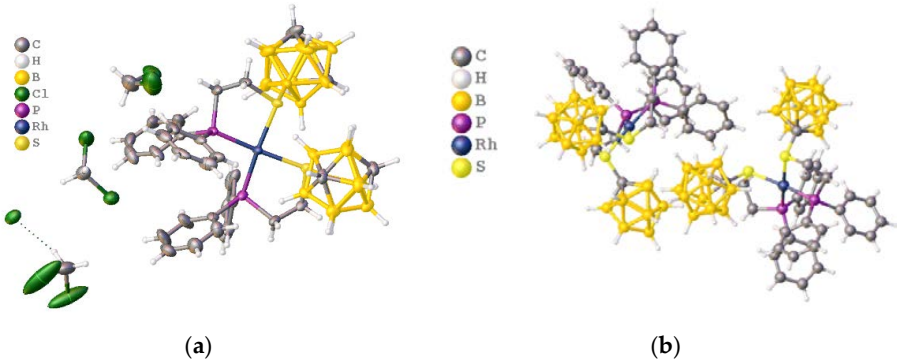
Scheme 6. Structures of ligands in complexes $[RhL][CB_{11}H_6Hal_6]$ (Hal = Cl, Br).

In all cases, rhodium(II) complexes $[RhL][CB_{11}H_6Cl_6]$ or $[RhL][CB_{11}H_6Br_6]$ with carboranes as counter ions were isolated.

When **ruthenium(I)** complex $[CpRu(NO)(CH_3)_2]$ was allowed to stand in the presence of an excess of carborane-based protonating agent $[(C_2H_5OC_2H_5)_2H][CB_{11}H_6Br_6]$ in acetonitrile, complex $[Ru(CH_3CN)_6][CB_{11}H_6Br_6]$ was isolated [141]. In the obtained complex, ruthenium(I) coordinates acetonitrile molecules, whereas hexabromocarborane $[CB_{11}H_6Br_6]^-$ acts as a counterion.

3.2. Derivatives with B–S Bonds

Rhodium(II) complex [*cis*-$Rh(Ph_2PCH_2CH_2S$-{9-*closo*-1,7-$C_2B_{10}H_{11}$}$)_2$]Cl with 2-((2-(diphenylphosphaneyl)ethyl)thio)-substituent was synthesized by the reaction between $[Rh(coe)Cl_2]$ and {9-($Ph_2PCH_2CH_2S$)-*closo*-1,7-$C_2B_{10}H_{11}$} in dichloromethane at room temperature [(coe) = cyclooctene] (Figure 28a). In this complex, the Rh atom coordinates the sulfur derivative of carborane via the substituent; the Rh–S bonds are 2.3541(16) and 2.3592(16) Å [142].



(**a**) (**b**)

Figure 28. Structures of (**a**) [$Rh(Ph_2PCH_2CH_2S$-{9-1,7-$C_2B_{10}H_{11}$}$)_2$]Cl and (**b**) [*cis*-$Rh(Ph_2PCH_2CH_2S$-{9-1,7-$C_2B_{10}H_{11}$}$)_2$][$Rh(Ph_2PCH_2CH_2S$-{1-$CB_{11}H_{11}$}$)_2$].

Complex NMe_4[*cis*-$Rh(Ph_2PCH_2CH_2S$-{1-$CB_{11}H_{11}$}$)_2$ was synthesized when $[Rh(coe)Cl_2]$ was allowed to react with NMe_4[1-($Ph_2PCH_2CH_2S$)-$CB_{11}H_{11}$] in dichloromethane at room temperature [142]. When complex [*cis*-$Rh(Ph_2PCH_2CH_2S$-{9-1,7-$C_2B_{10}H_{11}$}$)_2$]Cl reacted with

NMe_4[*cis*-Rh($Ph_2PCH_2CH_2S$-{1-$CB_{11}H_{11}$})$_2$ in methanol, compound [*cis*-Rh($Ph_2PCH_2CH_2S$-{9-1,7-$C_2B_{10}H_{11}$})$_2$][*cis*-Rh($Ph_2PCH_2CH_2S$-{1-$CB_{11}H_{11}$})$_2$] was isolated, which contains a complex cation and a complex anion. Note that in the complex anion, monocarborane is functionalized via the carbon atom; in the complex cation, the neutral dicarborane with the exo-polyhedral B–S bond is coordinated via the substituent. The Ru–S bond falls in the range 2.3585(11)–2.3612(12) Å.

Thioethyldiphenylphosphineplatinum(II) complexes based on *ortho*-carboranes were isolated [143]. Complex [*cis*-Pt($Ph_2PCH_2CH_2S$-{9-*closo*-1,7-$C_2B_{10}H_{11}$})Cl_2] (Figure 29a) was synthesized by the reaction between [Pt(cod)Cl_2] and [9-($Ph_2PCH_2CH_2S$)-*closo*-$C_2B_{10}H_{11}$] in deuterated dichloromethane. The *ortho*-dicarborane is coordinated by the substituent; the Pt–S bond is 2.2739(16) Å. In the structurally related complex with *meta*-dicarborane (Figure 29b), the Pt–S 2.2719(7) Å.

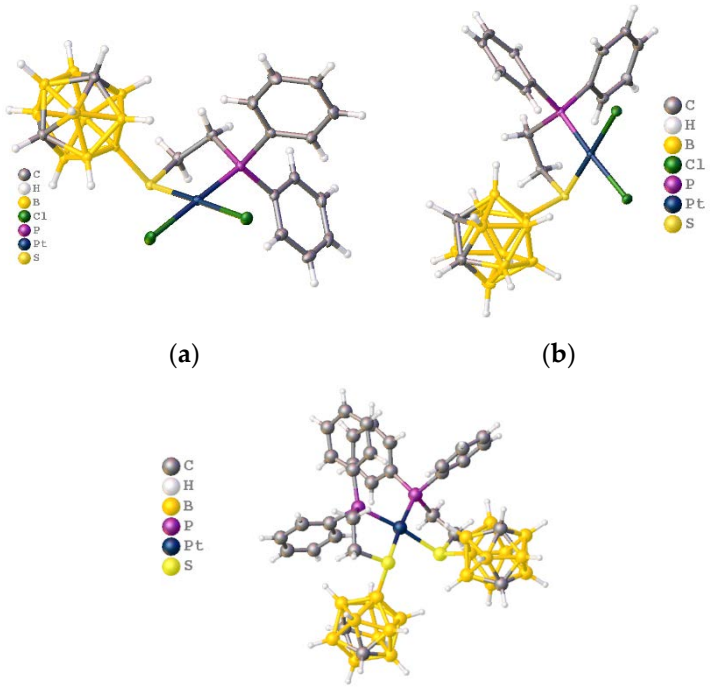


Figure 29. Structures of (**a**) [*cis*-Pt($Ph_2PCH_2CH_2S$-{9-1,7-$C_2B_{10}H_{11}$})Cl_2], (**b**) [*cis*-Pt($Ph_2PCH_2CH_2S$-{9-1,2-$C_2B_{10}H_{11}$})Cl_2], and (**c**) [*cis*-Pt($Ph_2PCH_2CH_2S$-{9-1,7-$C_2B_{10}H_{11}$})$_2$](BF_4)$_2$ (BF_4^- anions are omitted).

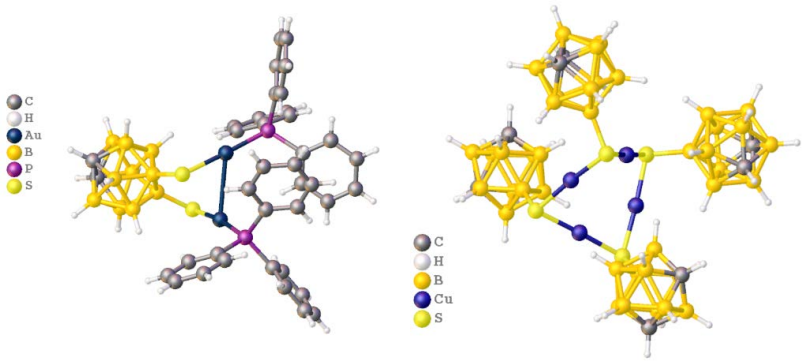
Complex [*cis*-Pt($Ph_2PCH_2CH_2S$-{9-*closo*-1,7-$C_2B_{10}H_{11}$})$_2$](BF_4)$_2$ (Figure 29c) was synthesized via the reaction between $AgBF_4$ and [*cis*-Pt($Ph_2PCH_2CH_2S$-{9-*closo*-1,7-$C_2B_{10}H_{11}$})$_2$Cl]Cl or [*cis*-Pt($Ph_2PCH_2CH_2S$-{9-*closo*-1,7-$C_2B_{10}H_{11}$})$_2Cl_2$] in deuterated dichloromethane. The platinum(II) atom coordinates the carborane derivatives by the substituent; the Pt–S bond is 2.379 and 2.377 Å.

First **gold(I)** complex with triphenylphosphine ligand [$Au_2(Ph_3P)_2S${9,12-$S_2C_2B_{10}H_{10}$] was isolated [144] (Figure 30a). In the compound, a six-member ring is formed involving the BB edge, two sulfur atoms of the substituents and two metal atoms; the Au–S bonds are 2.3171(16), 2.3161(9) Å; the Au–Au bond is 2.9937(2) Å.

Copper(I) complex [Cu-S-9-*closo*-1,7-$C_2B_{10}H_{11}$]$_4$ was synthesized by mechanochemical treatment of copper(I) ***meta*-carborane-9-thiolate** [Cu-S-9-*closo*-1,7-$C_2B_{10}H_{11}$] (Figure 30b). In the final complex, (μ-1,7-dicarba-*closo*-dodecaborane(11)-9-thiolato)-tetra-copper(I), four *meta*-carborane derivatives are coordinated by four metal atoms; the Cu–S bond falls in the range 2.163–2.176 Å [145].

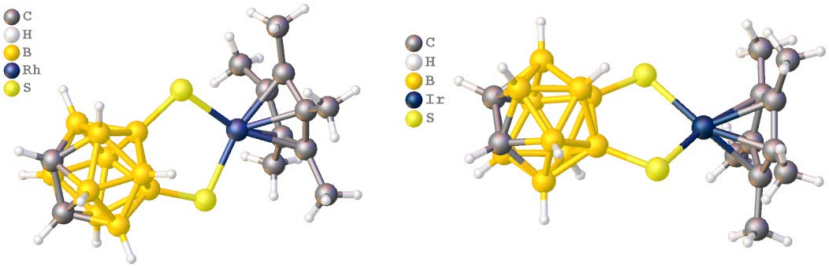
A number of **rhodium(III)** complexes with **9,12-dithiolato-1,2-dicarborane** was isolated [146,147]. Half-sandwich complex [Cp*Rh{9,12-$S_2C_2B_{10}H_{10}$}] was obtained by react-

ing *o*-carborane-9,12-dithiol with $[Cp^*RhCl_2]_2$ in the presence of a base [147]. Its structure was determined by X-ray diffraction (Figure 31b). Various complexes can be obtained based on this compound; for example, $[Cp^*Rh_2(Ph_3P)_2\{9,12\text{-}S_2C_2(B_{10}H_{10})\}]PF_6$ was isolated in the reaction with $Rh(Ph_3P)_3Cl$ in the presence of ammonium hexafluorophosphate [146].



(**a**) (**b**)

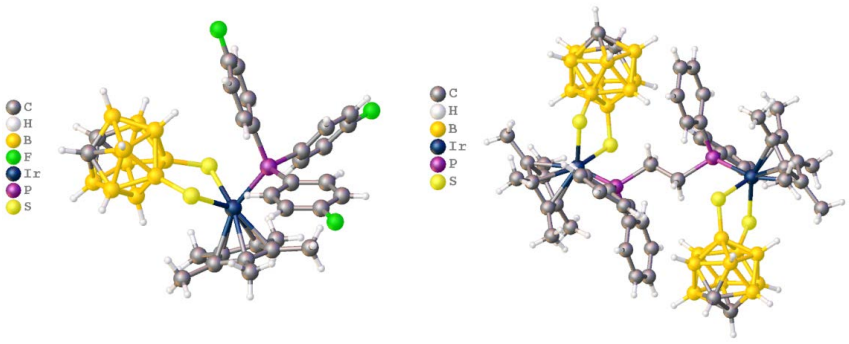
Figure 30. Structures of (**a**) gold(I) complex $[Au_2(Ph_3P)_2S\{9,12\text{-}S_2C_2B_{10}H_{10}]$ and (**b**) copper(I) complex $[Cu\text{-}S\text{-}9\text{-}closo\text{-}1,7\text{-}C_2B_{10}H_{11}]_4$.



(**a**) (**b**)

Figure 31. Structure of (**a**) rhodium complex $[Cp^*Rh\{9,12\text{-}S_2C_2(B_{10}H_{10})\}]$ and (**b**) iridium complex $[Cp^*Ir\{9,10\text{-}S_2C_2(B_{10}H_{10})\}]$.

Similar **iridium(III)** complex $[Cp^*Ir\{9,10\text{-}S_2C_2B_{10}H_{10}\}]$ (Figure 31b) was found to react with R_3P (R = Me, Et, Ph, 4-F-C_6H_4, 4-OMe-C_6H_4) at room temperature to form a series of phosphine complexes $[Cp^*Ir(R_3P)\{9,10\text{-}S_2C_2(B_{10}H_{10})\}]$ [148–150], which were characterized by X-ray diffraction. The compounds are built in a similar manner (see Figure 32a).



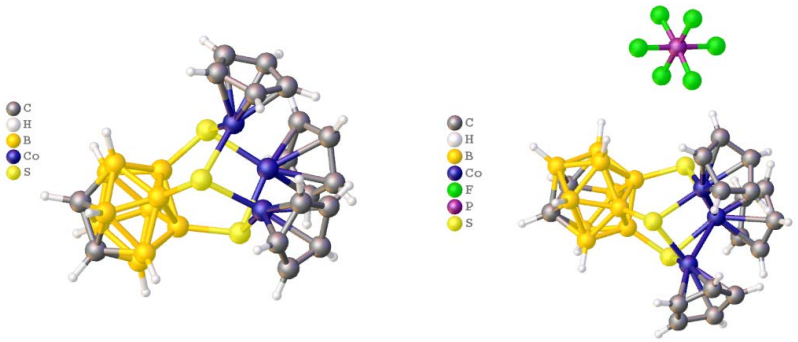
(**a**) (**b**)

Figure 32. Structures of iridium complexes (**a**) $[Cp^*Ir((4\text{-}F\text{-}C_6H_4)_3P)\{9,10\text{-}S_2C_2B_{10}H_{10}\}]$ and (**b**) $[Cp^*Ir(Ph_2PCH_2)\{9,10\text{-}S_2C_2B_{10}H_{10}\}]_2$.

It was found that [Cp*Ir{9,10-$S_2C_2B_{10}H_{10}$}] reacts with phosphine ligands L (L = Ph_3P, Me_2PhP, $MePh_2P$, $Ph_2PCH_2PPh_2$) in dichloromethane at room temperature to give complexes [Cp*Ir(L){9,10-$S_2C_2B_{10}H_{10}$}]. At the same time, the reaction of [Cp*Ir{9,10-$S_2C_2B_{10}H_{10}$}] with dppe leads to the formation of a corresponding dimeric complex [Cp*Ir(Ph_2PCH_2){9,10-$S_2C_2B_{10}H_{10}$}]$_2$ (Figure 32b), where CH ... HB, CH ... B, CH ... S, CH ... HC, and BH ... π intermolecular interactions are observed [151].

Similar **cobalt(III)** complex with cyclopentadienyl ligand [Cp*Co{9,12-$S_2C_2B_{10}H_{10}$}] was isolated and structurally characterized [152]. This complex is built similarly to the previously discussed rhodium(III) and iridium(III) complexes (see Figure 31). The Co–B bonds are 1.174(1) and 2.1735(10) Å. A series of boron-fused 1,4-dithiin compounds were prepared by the reactions of the boron-substituted half-sandwich complex [Cp*Co(9,12-$S_2C_2B_{10}H_{10}$) with alkynes.

The neutral **tricobalt(II)** complex [$(Cp)_3Co_3${9,10,12-$S_3C_2B_{10}H_9$}] (Figure 33a) was obtained by the interaction of trisubstituted *o*-carborane-9,10,12-trithiol with [$CpCo(CO)_2$] and three equivalents of $FcPF_6$ (Fc = $(C_5H_5)_2Fe$) in the presence of triethylamine in dichloromethane [153]. The addition of an excess of ferrocenium hexafluorophosphate causes a redox reaction to form salt [$(Cp)_3Co_3${9,10,12-$S_3C_2B_{10}H_9$}]PF_6 (Figure 33b).



(**a**) (**b**)

Figure 33. Structures of (**a**) [$(Cp)_3Co_3${9,10,12-$S_3C_2B_{10}H_9$}] and salt (**b**) [$(Cp)_3Co_3${9,10,12-$S_3C_2B_{10}H_9$}]PF_6.

3.3. Derivatives with B–N Bonds

From the Cambridge Structural Database, there are only three examples of carboranes with exo-polyhedral B–N bonds. The authors [154] synthesized new **B-carboranyl phosphine-iminophosphorane ligands** [3-(N=$PPh_2CH_2PPh_2$)-1,2-$B_{10}C_2H_{11}$] with the carboranyl group directly attached to the iminophosphorane nitrogen atom through the B(3) boron atom; the obtained derivative was used in **palladium(II)** complexation with [$PdCl_2(PhCN)_2$] to give complex [$PdCl_2(Ph_2PCH_2PPh_2CN)_9B_{10}C_2H_{11}$] (Figure 34). In the final compound, palladium coordinates N and P atoms of the substituent with the Pd–N bond 2.103(4) Å and Pd–P bond 2.2258(17) Å.

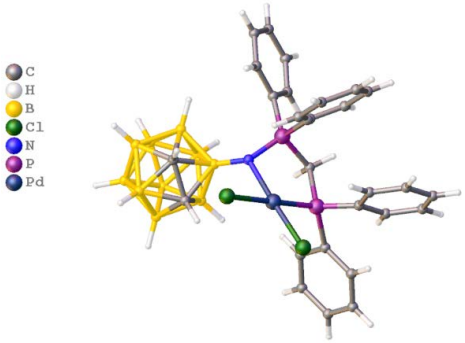
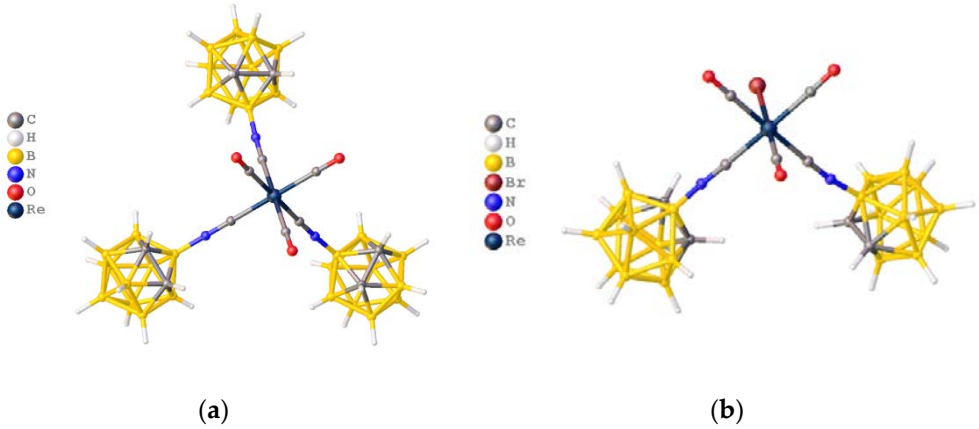


Figure 34. Structure of palladium(II) complex [$PdCl_2(Ph_2PCH_2PPh_2CN)_9B_{10}C_2H_{11}$].

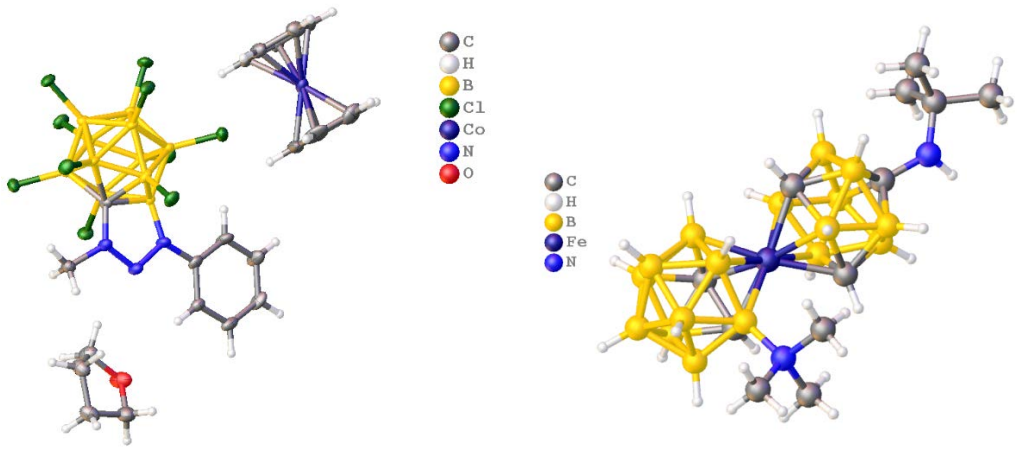
Rhenium(I) complexes with **3-isocyano-1,2-dicarba-*closo*-dodecaborane** were isolated when 3-isocyanoderivative of 1,2-carborane was allowed to react with $[NEt_4]_2[Re(CO)_3Br_3]$ and $[Re(CO)_3(solv.)_3][PF_6]$ to form final compounds $[Re(CO)_3L_3][PF_6]$ and $[Re(CO)_3L_2Br]$ (L = 3-CN-1,2-$B_{10}C_2H_{10}$] (Figure 35). In both compounds, the complexing agent coordinates carborane derivatives via the C atom of the CN substituent; the Re–C bond falls in the range 1.958(5)–2.075(2) Å [155].



(**a**) (**b**)

Figure 35. Structures of complexes (**a**) $[Re(CO)_3(3\text{-}CN\text{-}1,2\text{-}B_{10}C_2H_{10})_3][PF_6]$ (anion is omitted) and (**b**) $[Re(CO)_3(3\text{-}CN\text{-}1,2\text{-}B_{10}C_2H_{10})_2Br]$.

Among the structures closest to the systems discussed we can note the carborane-fused triazole radical anion $[1,2\text{-}(3\text{-}Ph\text{-}1\text{-}CH_3\text{-}3\text{-}N_3)\text{-}1\text{-}CB_{11}Cl_{10}]^-$, formed when 1,2-(3-phenyl-3-triazene)-decachloro-1-carba-*closo*-dodecaborate reacts with methyl phthalate [156]. When it is treated with **bis(cyclopentadienyl)cobalt**, a redox reaction occurs with the formation of compound $[Co(Cp)_2][1,2\text{-}(3\text{-}Ph\text{-}1\text{-}CH_3\text{-}3\text{-}N_3)\text{-}1\text{-}CB_{11}Cl_{10}]$ (Figure 36a). In this compound, the monocarborane anion is functionalized simultaneously via the carborane atom of the cage and adjacent BH group; thus, the obtained derivative contains the B–N and C–N exo-polyhedral bonds. The metal atom is coordinated by two cyclopentadienyl ligdns, whereas the carborane derivative acts as a counterion. The authors declare that it is an interesting example of a relatively stable radical anion that can be used to obtain functional materials.



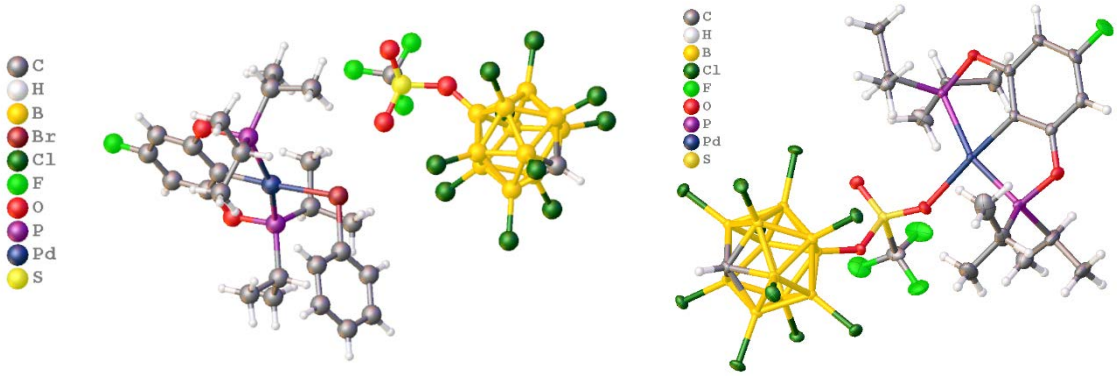
(**a**) (**b**)

Figure 36. Structures of (**a**) $[Co(Cp)_2][1,2\text{-}(3\text{-}Ph\text{-}1\text{-}CH_3\text{-}3\text{-}N_3)\text{-}1\text{-}CB_{11}Cl_{10}]$ and (**b**) $(1\text{-}BuNH\text{-}1,7,9\text{-}C_3B_8H_{10})Fe(9\text{-}N(CH_3)_3\text{-}7,8\text{-}C_2B_9H_{10})$.

Another representative of carborane-derivatives containing the B–N bond is (*t*-butylamino-1,7,9-tricarba-*nido*-undecaborato)-(9-dimethylamine-7,8-dicarba-*nido*-undecaborato)-iron [157] (Figure 36b). This compound is a metallocarborane containing a tricarborane derivative functionalized by the carbon atom and dicarborane cage with the B–N exo-polyhedral bond.

3.4. Derivatives with B–O Bonds

The complexes of this type have been isolated only for perhalogenated carboranes. Mono-triflyloxy-substituted carborane can be halogenated to form decachloro derivatives with the exopolyhedral B–OTf bond. The use of $[HCB_{11}Cl_{10}OTf]^-$ in palladium(II) complexation demonstrates that this weakly coordinating anion can act as a counterion in palladium complexes $[(POCOP)Pd(C_6D_5Br)][HCB_{11}Cl_{10}OTf]$ (Figure 37a) and binuclear [(POCOP)Pd-Cl-Pd(POCOPF)][$HCB_{11}Cl$] (POCOP is P,P-1,3-phenylene bis(P,P-diphenylphosphinite) [158]. In structurally related complex {$[(POCOP)Pd][HCB_{11}Cl_{10}OTf]$} (Figure 37b), palladium coordinated the triflyloxy-substituted carborane via the O atom of the substituent; the B–O bond is 2.2076(15) Å [159].



(**a**) (**b**)

Figure 37. Structures of palladium complexes (**a**) $[(POCOP)Pd(C_6D_5Br)][HCB_{11}Cl_{10}OTf]$ and (**b**) {$[(POCOP)Pd][HCB_{11}Cl_{10}OTf]$}.

4. Conclusions

Complexes with substituted derivatives of boron cluster anions $[B_nH_n]^{2-}$, monocarboranes $[CB_nH_{n-1}]^-$ and dicarboranes $[C_2B_nH_{n-2}]$ (n = 10, 12) isolated to date are listed in Tables 1 and 2. Analyzing the data shown, it can be concluded that the following types of complexes with substituted derivatives of *closo*-borate anions and carboranes can be isolated:

(a) Metal complexes with substituted derivatives as counterions

These compounds are built of a cationic metal complex, whereas boron clusters are not coordinated by the metal atom. Note that in these compounds, specific non-bonding interactions B–H … H–X (X = C, O, N) are usually observed between the BH group of boron clusters and ligands, organic cations, or solvent molecules;

(b) Metal complexes with coordinated substituted derivatives

These compounds contain derivatives of boron cluster anions or carboranes as coordinated ligands. Owing to the electronic and geometrical structure of boron clusters and carboranes and their chemical behavior, the following types of metal bonding with the boron cage are observed: (i) coordination via the 3c2e MHB interactions, in which the metal, boron, and hydrogen are involved in coordination; (ii) coordination of functional groups of the substituent introduced into the borane or carborane cage, while the BH groups remain non-coordinated by the metal atom; (iii) combined coordination, where the boron cluster is coordinated by 3c2e MHB bonds and the functional groups of the substituent.

The presence of 3c2e MHB bonds in the synthesized compounds is clearly manifested in the IR spectra by the appearance of absorption bands $\nu(BH)_{MHB}$ in the range 2400–2100 cm^{-1}, which correspond to the stretching vibrations of coordinated BH groups $\nu(BH)_{MHB}$; at the same time, the $\nu(BH)$ band of "non-coordinated" BH bonds is observed near 2500 cm^{-1}.

In the case of coordination of a substituted derivative due to the functional groups of the substituent, absorption bands characteristic of the corresponding groups appear in the IR spectra of complexes, but these bands are often split into several components and shift towards higher wavenumbers. These characteristic changes indicate the involvement of exo-polyhedral functional groups in coordination by metals.

Analyzing data shown in Tables 1 and 2, it is clear that substituted derivatives of the boron cluster anions give all four types of compounds, whereas compounds with carborane derivatives acting as counterions or coordinated via a substituent are generally formed (Figure 38). Several examples of compounds with MHB bonds or combined coordination were isolated for carborane derivatives, indicating that these types of compounds are not characteristic for carboranes.

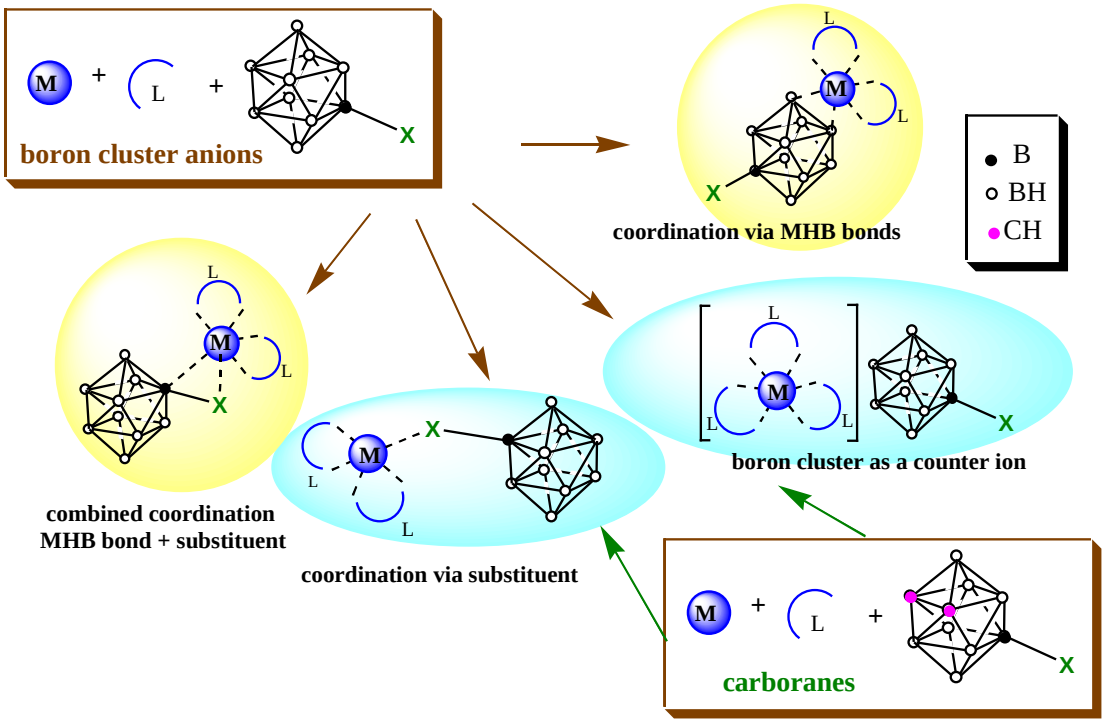


Figure 38. Coordination of the substituted derivatives of the boron clusters and carboranes.

In addition, it is clear that metals involved in the complexation of boranes and carboranes are different. Particularly, metals acting as Pearson's soft acids (Cu(I), Ag, Pb, Ru) form complexes with boron clusters coordinated via three-center two-electron MHB bonds. If the substituent reduces the total charge of the system (NH_3, thionium, oxonium groups), the coordination ability of the obtained derivatives decreases; thus, silver complexes with non-coordinated boron cluster anions are formed as end products, while Ru and Pb are still able to coordinate the singly-charged anions.

It can be concluded that lead and ruthenium demonstrate the greatest affinity for boron cluster anions: it is possible to obtain complexes of these metals with the substituted derivatives coordinated by MHB bonds, through the functional group of the substituent, and combined coordination can also be realized. Note that salts of these metals with non-coordinated boron ligands have not been obtained.

Table 1. Coordination modes found for mono- and disubstituted derivatives of boron cluster anions $[B_nH_n]^{2-}$ (n = 10, 12) in complexes. Metals are shown in bold and are highlighted using different colors in order to compare the composition of complexes with the same metal but various types of coordination.

Boron Cluster Anion as a Counterion	Coordination with the Formation of 3c2e MHB Bonds	Coordination by a Substituent	Combined Coordination: MHB + Substituent
[**Ni**(Bipy)$_3$][$B_{10}H_9OH$]	[Et_3NH][**Cu^I**[1-$B_{10}H_9N_2$]$_2$]	[Ph_3MeP)]$_2$[Cp**Ti**Cl_2[$B_{12}H_{11}OH$]	[**Cu^I**$(NCCH_3)_2$[2-$B_{10}H_9$Bipy]]
[**Ni**(Phen)$_3$][$B_{10}H_9OH$]	[**Ag**$(CH_3CN)_3]_2$[**Ag**$_2$[2-$B_{10}H_9F]_2]_n$	[**Ni**(en)[2-$B_{10}H_9O(CH_2)_2O(CH_2)_2NH(CH_2)_2NH_2$)]]	[**Ag**$_2(Ph_3P)_4$[$B_{10}H_9C(O)OCH_3$]]
[**Ni**(Bipy)$_3$][$B_{12}H_{11}Cl$]	[**Ag**$(PPh_3)_4$][($PPh_3)_2$**Ag**[$B_{10}H_9Cl$]]	[$Na_6(THF)_{15}$][**Ni**[$B_{12}H_{11}NH_2$]]$_4$	($Ph_4P)_2$[**Pb**(Bipy)[2-$B_{10}H_9OC(O)CH_3]_2$]]
[**Co**(Phen)$_3$][2-$B_{10}H_9OC(H)O$]	[**Ag**$_2(Ph_3P)_4$[$B_{12}H_{11}Cl$]]	[**Au**(PPh_3)[NH_2–$B_{12}H_{11}$]]	[**Pb**(Bipy)[2-$B_{10}H_9O(CH_2CH_2)_2$OEt]]
[**Cu^{II}**(BPA)$_2$($NCCH_3)_2$][2-$B_{10}H_9$BPA]$_2$	[**Ag**$_2$(Bipy)$_2$[2-$B_{10}H_9OH$]]	[**Ru**H_2[$N_2B_{10}H_8SMe_2$]($Ph_3P)_3$]	[**Pb**(Bipy)(DMF)[2-$B_{10}H_9OH$)]]
[**Cu^{II}**$_2$(bipy)$_4$(μ-CO_3)][2-$B_{10}H_9OH$]	[**Ag**$_2$(Bipy)$_2$[2-$B_{10}H_9S(CH_2C(O)NH_2]NO_3$	[**Ru**[$SB_{12}H_{11}$]($NH_3)_5$]	[**Pb**(Bipy)(2-$B_{10}H_9(OCH_2CH_2)_2$OEt)]
[**Ag**$(PPh_3)_4$][$B_{10}H_9NH_3$]	(Bu_4N)[[(*o*-C_6F_4**Hg**$)_3]_2$[$B_{12}H_{11}SCN$]]	[(*Cp*)(dppe)**Fe**}$_2$[1,10-$B_{10}H_8(NC)_2$]·H_2O	[**Pb**(Bipy)(DMF)[$B_{10}H_9OH$]
[**Ag**$(PPh_3)_4$][2-$B_{10}H_9S(CH_2N(CO)_2C_6H_4)_2$]	($Bu_4N)_2$[[(*o*-C_6F_4**Hg**$)_3$][$B_{12}H_{11}SCN$]]		[**Pb**(Bipy)$_2$[2,6(9)-$B_{10}H_8(OC(O)CH_3)(OH)]]_2$
[**Ag**$(PPh_3)_4$][2-$B_{10}H_9O(CH_2)_5$]	[($PPh_3)_2$Cl**Ru**[$B_{12}H_{11}(NEt_3)$]	phthalocyanine **Al(III)**, **Co(II)**, **Zn(II)** complexes	[**Pb**(Bipy)$_2$[2,7(8)-$B_{10}H_8(OC(O)CH_3)_2$)]
[**Ag**$(PPh_3)_4$][2-$B_{10}H_9O(CH_2)_4O$]	[**Pb**[2-$B_{10}H_9SH$]]	**Gd(III)** and **Hf(IV)** complexes	Bu_3MeN[**Ru**$(PPh_3)_2$Cl[$B_{12}H_{11}NH_2$]]
	[**Pb**(Bipy)$_2$[2-$B_{10}H_9SH$]]		Bu_4N[**Ru**(dppb)Cl[$B_{12}H_{11}NH_2$]]
	[**Pb**(Bipy)$_2$[1-$B_{10}H_9SMe_2]_2$]		[**Ru**$(PPh_3)_2$CO[$B_{12}H_{11}NH_2$]]
			$MePPh_3$[**Rh**$(PPh_3)_2$[$B_{12}H_{11}NH_2$]]
			[**Rh**(Me_5Cp)[$B_{12}H_{11}$NHC(O)NMe_2]]
			[**Rh**(Me_5Cp)[$B_{12}H_{11}$NHC(O)Ph]]

Table 2. Coordination modes found for mono- and disubstituted carboranes in complexes. Metals are shown in bold and are highlighted using different colors in order to compare the composition of complexes with the same metal but various types of coordination.

Boron Cluster Anion as a Counterion	Coordination with the Formation of 3c2e MHB Bonds	Coordination by a Substituent	Combined Coordination: MHB + Substituent
[**Pd**(dppe)$_2$][$CB_{11}H_{11}Cl]_2$]·3CH_2Cl_2 [(POCOP)**Pd**(C_6D_5Br)][$HCB_{11}Cl_{10}OTf$] [Ru($CH_3CN)_6$][$CB_{11}H_6Br_6$] [**Rh**L][$CB_{11}H_6Cl_6$] [**Rh**L][$CB_{11}H_6Br_6$] (L = diphenylphosphine ligands) [**Co**($Cp)_2$][1,2-(3-Ph-1-CH_3-3-N_3)-1-$CB_{11}Cl_{10}$]	[**Ag**($C_6H_6)_2$[12-$CB_{11}H_{11}F$]] [**Ag**($C_6H_6)_2$][6,8-$CB_9H_8F_2$]	[**Ag**(C_6H_6)[12-$CB_{11}H_{11}Br$]] [**Mo**Cp$(CO)_3$($CB_{11}H_{11}Br$)] [**Ir**($PPh_3)_2H_2$(1-$CB_{11}H_6Cl_6$)] [Cp***Ir**{9,10-S_2C_2($B_{10}H_{10}$)}] [Cp***Ir**(R_3P){9,10-S_2C_2($B_{10}H_{10}$)}] [Cp***Co**{9,12-$S_2C_2B_{10}H_{10}$}] [Cp***Rh**{9,12-$S_2C_2B_{10}H_{10}$}] [*cis*-**Rh**($Ph_2PCH_2CH_2S$-{9-1,7-$C_2B_{10}H_{11}$})$_2$]Cl [*cis*-**Pt**($Ph_2PCH_2CH_2S$-{1-$CB_{11}H_{11}$})$_2$] [*cis*-**Pt**($Ph_2PCH_2CH_2S$-{9-*closo*-1,7-$C_2B_{10}H_{11}$})Cl_2] [*cis*-**Pt**($Ph_2PCH_2CH_2S$-{9-*closo*-1,7-$C_2B_{10}H_{11}$})$_2$]($BF_4)_2$ [**Au**$_2$($Ph_3P)_2$S{9,12-$S_2C_2B_{10}H_{10}$}] [**Cu**-S-9-*closo*-1,7-$C_2B_{10}H_{11}]_4$ [**Pd**Cl_2($Ph_2PCH_2PPh_2CN)_9B_{10}C_2H_{11}$] [**Re**$(CO)_3L_2Br$] (L = 3-CN-1,2-$B_{10}C_2H_{10}$] {[(POCOP)Pd][$HCB_{11}Cl_{10}OTf$]}	[**Mo**Cp$(CO)_3$I**Ag**($CB_{11}H_{11}Br$)]$_2$

For carboranes, it can be seen that the series of metals forming compounds with coordinated derivatives of carboranes are platinum group metals (Ru, Rh, Pd, Ir, Pt). Only three representatives of substituted derivatives of carboranes were used in silver(I) complexation, whereas no lead(II) complexes have been isolated. It seems that this field of chemistry should be studied intensively and new compounds with MHB bonds could be prepared.

As for substituents introduced into the boron cluster, it is clear from Table 1 that the most studied are substituted derivatives of the *closo*-decaborate and *closo*-dodecaborate anions containing the chlorine atom, hydroxy group or acetoxy group. For Hal atoms, it is clear that the corresponding derivatives are coordinated (if at all) by forming MHB bonds from the side opposite to the positions of substituents introduced into the boron cage. The derivatives containing the OH and acetoxy groups are coordinated by lead forming combined coordination MHB + substituent. Some examples of lead and ruthenium complexes with S-substituted derivatives have been isolated with combined coordination of the boron cage (MHB + substituent).

An analysis of the obtained compounds shows that the most interesting combined variant of the coordination of substituted derivatives of boron cluster anions (MHB + substituent) can be expected with the introduction of substituents that do not reduce the total charge of the boron cluster, using soft acid metals according to Pearson, and using functional groups that correspond in hardness/softness to the metal.

The majority of complexes with B-substituted carboranes contain the B–Hal or B–S exo-polyhedral bonds. Compounds with other substituents are extremely rare. Analyzing Table 2, it can be concluded that carboranes have lower coordination ability; they form compounds with non-coordinated carboranes (salts) or complexes with coordination of the substituent (Figure 38). Thus, it is clear that the carborane cage should be functionalized to act as inner-sphere ligands owing to a substituent being introduced.

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Conflicts of Interest: The authors declare that they have no conflict of interest.

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