



Synthesis, Crystal Structure, and Some Transformations of 9,12-Dichloro-*ortho*-Carborane

Sergey A. Anufriev ¹, Sergey V. Timofeev ¹, Olga B. Zhidkova ¹, Kyrill Yu. Suponitsky ^{1,2} and Igor B. Sivaev ^{1,2,*}

- ¹ A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov Street, 119991 Moscow, Russia
- ² Basic Department of Chemistry of Innovative Materials and Technologies, G.V. Plekhanov Russian University of Economics, 36 Stremyannyi Line, 117997 Moscow, Russia
- * Correspondence: sivaev@ineos.ac.ru

Abstract: Reaction of *ortho*-carborane with anhydrous $AlCl_3$ in chloroform results in a mixture of 9-chloro, 9,12-dichloro, and 8,9,12-trichloro derivatives with 9,12-dichloro-*ortho*-carborane being the main product. Molecular crystal structure of 9,12-dichloro-*ortho*-carborane was determined by the single crystal X-ray diffraction. The crystal structure of 9,12-Cl₂-1,2-C₂B₁₀H₁₀ appeared to be nearly isostructural to 9,12-dibromo-*ortho*-carborane: the crystal packing is built of layers in which molecules are connected via weak hydrogen and halogen bonds. A synthetic scheme for preparation of the hexachloro derivative of cobalt bis(dicarbollide) Cs[8,8',9,9',12,12'-Cl₆-3,3'-Co(1,2-C₂B₉H₈)₂] from 9,12-dichloro-*ortho*-carborane has been proposed.

Keywords: carborane; chloro derivatives; synthesis; NMR spectra; single crystal X-ray diffraction



Citation: Anufriev, S.A.; Timofeev, S.V.; Zhidkova, O.B.; Suponitsky, K.Y.; Sivaev, I.B. Synthesis, Crystal Structure, and Some Transformations of 9,12-Dichloro-*ortho*-Carborane. *Crystals* 2022, *12*, 1251. https:// doi.org/10.3390/cryst12091251

Academic Editor: Simon Duttwyler

Received: 1 August 2022 Accepted: 31 August 2022 Published: 2 September 2022

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1. Introduction

Chlorination was the first described substitution reaction at boron atoms in carboranes $C_2B_{10}H_{12}$. However, despite the fact that the synthesis of chloro derivatives of *ortho*-carborane was first described almost 60 years ago [1–5], so far only two of its chloro derivatives, namely, 1,2- $C_2B_{10}H_4$ -4,5,7,8,9,10,11,12- Cl_8 [6,7] and 1,2- $C_2B_{10}H_2$ -3,4,5,6,7,8,9,10,11,12- Cl_{10} (the last one as a complex with DMSO) [8], have been characterized by single crystal X-ray diffraction. Moreover, to the best of our knowledge, the structures of only two chloro derivatives of C-substituted carboranes have been determined [9,10]. This contrasts sharply with both the well-developed chemistry of iodo derivatives of *ortho*-carborane [11–22] and the chemistry of chloro derivatives of their structural analogs carba-*closo*-dodecaborate $[CB_{11}H_{12}]^{-}$ [23–25] and *closo*-dodecaborate $[B_{12}H_{12}]^{2-}$ [26,27] anions, polychlorinated and perchlorinated derivatives of which are widely used as weakly coordinating anions [28–34].

One of the reasons for the poor study of chloro derivatives of *ortho*-carborane is the rather low selectivity of the chlorination reaction, which leads already at the first stage of substitution to the formation of hardly separable mixtures of 8- and 9-chloro derivatives, with the content of the minor 8-isomer varying depending on the reaction conditions from approx. 10 to 50% [35,36]. A further chlorination leads to the formation of complex mixtures of chloro derivatives of carborane with higher substitution degrees [37,38].

Recently, an efficient method for the synthesis of 9-chloro-*ortho*-carborane has been proposed and its complete characterization by multinuclear NMR spectroscopy has been carried out [39]. As for 9,12-dichloro-*ortho*-carborane, some of its NMR data have recently been reported, but the experimental procedure for its synthesis has not been described in detail [40].

In this contribution we describe the synthesis of 9,12-dichloro-*ortho*-carborane and its characterization by NMR spectroscopy and single crystal X-ray diffraction.

2. Results and Discussion

9,12-dichloro-*ortho*-carborane was prepared by heating of the parent *ortho*-carborane with anhydrous AlCl₃ in chloroform or carbon tetrachloride similar to reported by Za-kharkin et al. (Scheme 1) [2]. The separation of the reaction mixture using column chromatography on silica with chloroform as eluent gave 11% of 9-Cl-1,2-C₂B₁₀H₁₁ (1), 53% of 9,12-Cl₂-1,2-C₂B₁₀H₁₀ (2), and 21% of 8,9,12-Cl₃-1,2-C₂B₁₀H₉ (3) as white solids.



Scheme 1. Synthesis of 9,12-Cl₂-ortho-C₂B₁₀H₁₀.

The NMR spectral data of the monochloro derivative **1** (See SI) correspond to the literature data [39]. The ¹H NMR spectrum of the dichloro derivative 9,12-Cl₂-*ortho*-C₂B₁₀H₁₀ (**2**) in CDCl₃ contains signals of the *CH* groups at 3.50 ppm and the signals of *BH* groups in the region of 1.5–3.2 ppm. Note the downfield shift of the signal of the *CH* carborane groups compared to the parent *ortho*-carborane (3.56 ppm), which indicates a decrease in the electron-withdrawing effect of the carborane fragment. The ¹³C NMR spectrum contains signal of the carborane carbons at 43.6 ppm. The ¹¹B NMR spectrum contains one singlet at 6.7 ppm and three doublets at -8.3, -15.3, and -18.3 ppm with the integral intensity ratio of 2:2:4:2. All these data are close to reported in the literature [40].

The ¹¹B NMR spectrum of the trichloro derivative **3** consists of two singlets at 6.0 and 0.2 ppm and five doublets at -9.9, -15.1, -17.2, -18.6, and -18.3 ppm with the integral intensity ratio of 2:1:2:2:1:1. The position of the substitution in compound **3** is unambiguously confirmed by its ¹¹B-¹¹B DQCOSY spectrum (Figure 1), which shows strong cross-peaks of the signals of substituted boron atoms. The ¹H NMR spectrum of the trichloro derivative 8,9,12-Cl₃-*ortho*-C₂B₁₀H₉ (**3**) contains signals of the *CH* groups at 3.54 ppm and the signals of *BH* groups in the region of 1.5–3.3 ppm. It should be noted that a slight decrease in the electron-withdrawing effect of the carborane cage, observed when chlorine atoms are introduced into positions 9 and 12, is almost completely compensated by the introduction of one more chlorine atom into position 8. The ¹³C NMR spectrum contains signal of the carborane carbons at 41.0 ppm.

Recently, interest has increased in studying the role of weak non-covalent interactions, including dihalogen and hydrogen bonds, in the stabilization of the crystal packing of halogen derivatives of carboranes. Such types of bonding were found earlier in the crystal structures of some iodo [41,42] and bromo [43,44] derivatives of *ortho*-carborane. In general, dihalogen bonds (X...X contacts of type II) are known to be most favored in iodo derivatives, less in bromo derivatives, and the least in chloro derivatives [45]. Nevertheless, the intermolecular Cl...Cl dihalogen bonds have been found in the solid-state structures of 4,5,7,8,9,10,11,12-Cl₈-1,2-C₂B₁₀H₄ [6,7] and 3,4,5,6,7,8,9,10,11,12-Cl₁₀-1,2-C₂B₁₀H₂·DMSO [8,46], as well as in the structure of perchloro 1,7-diphosphaborane 1,7-P₂B₁₀Cl₁₀·toluene [47]. In this case, only a part of the chlorine atoms participates in the formation of the dihalogen bonds. Therefore, it was interesting to study the crystal structure of 9,12-Cl₂-1,2-C₂B₁₀H₁₀ from the point of view of the possibility of the formation of Cl...Cl dihalogen bonds.



Figure 1. ¹¹B-¹¹B DQCOSY NMR spectrum of 8,9,12-Cl₃-1,2-C₂B₁₀H₉ in CDCl₃.

Crystal structure of 9,12-dichloro-*ortho*-carborane was determined by the single crystal X-ray diffraction. General view of the molecule is presented in Figure 2. The B-Cl bond lengths are 1.798(2) Å. The crystal structure of 9,12-Cl₂-1,2-C₂B₁₀H₁₀ appeared to be nearly isostructural to recently studied 9,12-dibromo-*ortho*-carborane [44].



Figure 2. General view of 9,12-Cl₂-1,2-C₂B₁₀H₁₀ showing atomic numbering. Thermal ellipsoids are drawn at 50% probability level. The B9-Cl1 and B12-Cl2 distances are equal to each other (1.798(2) Å).

Crystal packing can be described as built up of layers in which molecules are connected via weak halogen bond and weak hydrogen bonds (Figure 3) as it was observed for the dibromo derivative 9,12-Br₂-1,2-C₂B₁₀H₁₀. Since the chlorine atom is both weaker donor and acceptor of the lone pair in comparison to the bromine, the strength of Cl...Cl and Cl...H contacts might appear to be somewhat weaker. In fact, the shortest H...Br nonbonded contacts (2.82 Å) in 9,12-Br₂-1,2-C₂B₁₀H₁₀ are somewhat longer than sum of van-der-Waals radii (2.72 Å) [48], while in 9,12-Cl₂-1,2-C₂B₁₀H₁₀ similar contacts (H2...Cl1, 2.61(2) Å) are somewhat shorter than sum of van-der-Waals radii (2.67 Å). At the same time, the Br...Br interactions (the Br...Br distance is 3.796 Å, sum of van-der-Waals radii is 3.79, B-Br...Br angle is 148.4°) in the dibromo derivative 9,12-Br₂-1,2-C₂B₁₀H₁₀: the Cl...Cl distance is 3.751(2) Å (sum of van-der-Waals radii is 3.65 Å) and the B-Cl...Cl angle is 145.8(2)°. Those differences, however, are rather small and the behavior of the chlorine and bromine atoms in the dihalogen derivatives can be considered to be quite similar.



Figure 3. Crystal packing fragment of 9,12-Cl₂-1,2-C₂B₁₀H₁₀. Trimeric associate formed via Cl...Cl dihalogen and H...Cl hydrogen bonds. Projection onto *bc* plane.

In the crystal of the 8,9,12-trichloro derivative **3** (Figure 4), the Cl8 atom is disordered over two cites: at B8 and B10 atoms in the ratio of 84:16. In fact, two disordered molecules are the same and are related by the mirror plane.

For the crystal packing description, we used major part of the disordered molecule. As in the 9,12-dihloro derivative **2**, no any strong Cl...Cl halogen bonds of type II are observed in the crystal of compound **3**. Each Cl atom forms two Cl...Cl dihalogen bonds being both lone pair donor and acceptor (Table 1) which leads to a formation of halogen-bonded layers (Figure 5). Each Cl atom participates in three Cl...H contacts however their distances are in the range of 2.87–3.29 Å which are longer than sum of van-der-Waals radii.

The use of the hexachloro derivative of cobalt bis(dicarbollide) $Cs[8,8',9,9',12,12'-Cl_6-3,3'-Co(1,2-C_2B_9H_8)_2]$ in the extraction processing of nuclear waste has previously been described [49,50]. The hexachloro derivative of cobalt bis(dicarbollide) can be obtained by direct chlorination of cobalt bis(dicarbollide) with chlorine [51] or sulfuryl chloride [52]; however, both these methods, along with the hexachloro derivative, lead to the formation of derivatives with higher degrees of substitution, which makes it difficult to purify the target product. This prompted us to develop a scheme for the synthesis of the hexachloro derivative of cobalt bis(dicarbollide) based on the dichloro derivative of *ortho*-carborane **2** (Scheme 2).



Figure 4. General view of 8,9,12-Cl₂-1,2-C₂B₁₀H₉ showing atomic numbering. Thermal ellipsoids are drawn at 50% probability level. Only major part of the disorder is shown. The B8-Cl8, B9-Cl1 and B12-Cl2 distances are equal to 1.774(5), 1.794(4) and 1.793(4) Å, respectively.

Table 1. Cl...Cl dihalogen bond parameters in the crystal structure of compound **3** (distances in Å, angles in deg.).

B-ClCl-B Contact	ClCl	B-ClCl	ClCl-B
B9-Cl9Cl12-B12	3.704(3)	105.4(3)	133.8(3)
B9-Cl9Cl8-B8	3.870(3)	139.4(3)	92.3(3)
B12-Cl12Cl8-B8	3.870(3)	91.0(3)	149.3(3)



Figure 5. Crystal packing fragment of 8,9,12-Cl₃-1,2-C₂B₁₀H₉. Layers parallel the *ac* plane are formed by weak Cl...Cl dihalogen bonds.



Scheme 2. Synthesis of Cs[8,8',9,9',12,12'-Cl₆-3,3'-Co(1,2-C₂B₉H₈)₂].

Deboronation of carborane **2** with KOH in refluxing aqueous ethanol followed by the treatment with Me₃NHCl in water gave the corresponding *nido*-carborane (Me₃NH)[5,6-Cl₂-7,8-C₂B₉H₁₀] (**4**) in 93% yield. The ¹¹B NMR spectrum of *nido*-carborane **4** in acetone- d_6 contains singlet at -4.0 ppm and five doublets at -11.5, -20.2, -22.3, -29.1, and -35.5 ppm with the integral intensity ratio of 2:2:1:2:1:1, which agrees well with the geometry of the symmetrically substituted *nido*-carborane. The ¹H NMR spectrum contains signals of the *CH* groups at 1.70 ppm, the terminal *BH* groups in the region of 0.0–2.8 ppm, and the bridging BHB hydrogen at -2.14 ppm. The ¹³C NMR spectrum contains signal of the *nido*-carborane carborane carbons at 36.8 ppm.

Reaction of 4 with cobalt bromide in 40% aqueous solution of potassium hydroxide resulted in the corresponding cobaltacarborane $K[9,9',12,12'-Cl_4-3,3'-Co(1,2-C_2B_9H_9)_2]$ (5) isolated in 63% yield. The NMR spectral data of the tetrachloro derivative of cobalt bis(dicarbollide) correspond to the literature data [51]. The structure of the cobalt complex was supported by single crystal X-ray diffraction study of $Cs[9,9',12,12'-Cl_4-3,3'-Co(1,2-C_2B_9H_9)_2]\cdot 2Me_2CO$ (5'). An asymmetric unit cell contains one cobaltacarborane anion, two halves of the Cs cation located at two-fold symmetry axis and two acetone molecules. The structure of the anion is shown in Figure 6. The dicarbollide ligands are rotated by 37.0(4)° to each ither so that the projection of the C1' atom onto the C1-C2-B4-B7-B8 open face appears over the center of the C2-B7 bond. A similar *cisoid* orientation of the 9,9',12,12'-tetraiodo derivative of cobalt bis(dicarbollide) (TTF)[9,9',12,12'-I_4-3,3'-Co(1,2-C_2B_9H_9)_2] [53]. The intermolecular bonding in the crystal of 5' is mostly dictated by the bonding preferences of the Cs atoms. Each Cs atom binds four chlorine and four oxygen atoms (see Figure S1 in SI), while the C1...Cl and H...Cl as well as Cl...O are secondary interactions.



Figure 6. General view of the $[9,9',12,12'-Cl_4-3,3'-Co(1,2-C_2B_9H_9)_2]^-$ anion showing atomic numbering. Thermal ellipsoids are drawn at 50% probability level. The B9-Cl1, B12-Cl2, B9-Cl1 and B12'-Cl2' distances are equal to 1.812(6), 1.806(6), 1.806(5) and 1.815(6), respectively.

Previously, it was shown that the chlorine atoms at positions 8 and 8' of the parent cobalt bis(dicarbollide) can be introduced using sodium hypochlorite [54]. Therefore, we decided to use a similar approach to selectively introduce two chlorine atoms into the tetrachloro derivative of cobalt bis(dicarbollide). The reaction of **5** with *t*-BuOCl in acetonitrile followed by precipitation with CsCl from aqueous solution gave the desired hexachloro derivative Cs[8,8',9,9',12,12'-Cl₆-3,3'-Co(1,2-C₂B₉H₈)₂] (**6**) in 80% yield. The ¹¹B NMR spectrum of **6** in acetone-*d*₆ contains two singlets at 6.3 and 3.2 ppm and four doublets at 1.5, -6.4, -17.8, and -24.4 ppm with the integral intensity ratio of 2:4:2:4:4:2. The ¹H NMR spectrum contains signals of the *CH* groups of cobaltacarborane at 4.39 ppm and the *BH* groups in the region of 1.0–3.9 ppm. A significant downfield shift of the signal of the CH groups of the dicarbollide ligands in the ¹H NMR spectrum of complex **6** as compared to complex **5** suggests the presence of the intramolecular CH...Cl hydrogen bonds between the dicarbollide ligands with the formation of a *transoid* conformation, which is typical for the 8,8'-dihalogen derivatives of cobalt bis(dicarbollide) [55].

3. Materials and Methods

3.1. General Methods

tert-Butylhypochlorite ^{*t*}BuOCl was synthesized according literature method [56]. All other chemical reagent were purchased from Sigma Aldrich, Acros Organics, ABCR, and other commercial vendors and used without purification. The reaction progress was monitored by thin layer chromatography (Merck F254 silica gel on aluminum plates) and visualized using 0.5% PdCl₂ in 1% HCl in aq. MeOH (1:10). The NMR spectra at 400 MHz (¹H), 128 MHz (¹¹B), and 100 MHz (¹³C) were recorded with Varian Inova 400 spectrometer.

The residual signal of the NMR solvent relative to Me₄Si was taken as the internal reference for ¹H and ¹³C NMR spectra. ¹¹B NMR spectra were referenced using BF₃·Et₂O as external standard. Mass spectra (MS) were measured using Shimadzu LCMS-2020 instrument with DUIS ionization (ESI—Electrospray ionization and APCI—Atmospheric pressure chemical ionization). The measurements were performed in a negative ion mode with mass range from m/z 50 to m/z 2000. Isotope distribution was calculated using Isotope Distribution Calculator and Mass Spec Plotter [57].

3.2. Synthetic Procedure of ortho-Carborane Chlorination and Characterization of Mono-, Di- and Trisubstituted Chloro Derivatives of ortho-Carborane

Anhydrous AlCl₃ (2.00 g, 15.0 mmol) was added to a solution of *ortho*-carborane (5.0 g, 34.7 mmol) in CHCl₃ or CCl₄ (50 mL) stirred at room temperature. The resulting mixture was heated under reflux for 4 h. Since the reaction is highly exothermic and the carborane reacts very violently at first, a 250 mL round bottom flask should be used with vigorous stirring. Then, the reaction mixture was cooled to ambient temperature and treated with a solution of 5% HCl in water (50 mL). The organic phase was separated; the aqueous fraction was extracted with CHCl₃ or CCl₄ (3 × 50 mL). The organic phases were combined, dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude product was purified twice by column chromatography on silica using CHCl₃ as eluent to give 0.70 g (11%) of 9-Cl-*ortho*-C₂B₁₀H₁₁ (1), 6.01 g (53%) of 9,12-Cl₂-*ortho*-C₂B₁₀H₁₀ (2), and 1.82 g (21%) of 8,9,12-Cl₃-*ortho*-C₂B₁₀H₉ (3) as white powders.

9-Cl-*ortho*-C₂B₁₀H₁₁ (1): ¹H NMR (CDCl₃, ppm): δ 3.56 (1H, br s, CH_{carb}), 3.44 (1H, br s, CH_{carb}), 3.2–1.4 (9H, br m, BH). ¹¹B NMR (CDCl₃, ppm): δ 7.4 (1B, s, B(9)), –2.1 (1B, d, J = 154 Hz, B(12)), –8.8 (2B, d, J = 153 Hz, B(8,10)), –13.8 (2B, d, J = 175 Hz, B(4,5)), –15.2 (2B, d, J = 158 Hz, B(7,11)), –16.4 (2B, d, J = 169 Hz, B(3,6)). ¹³C NMR (CDCl₃, ppm): δ 52.2 (CH_{carb}), 44.5 (CH_{carb}). MS (DUIS), *m*/*z*: found: 178 (M–H)[–]; calculated for C₂H₁₀B₁₀Cl (M–H)[–] 178.0.

9,12-Cl₂-*ortho*-C₂B₁₀H₁₀ (2): ¹H NMR (CDCl₃, ppm): δ 3.50 (2H, br s, CH_{carb}), 3.2–1.5 (8H, br m, *BH*). ¹¹B NMR (CDCl₃, ppm): δ 6.7 (2B, s, *B*(9,12)), -8.3 (2B, d, J = 156 Hz, *B*(8,10)), -15.3 (4B, d, J = 169 Hz, *B*(4,5,7,11)), -18.3 (2B, d, J = 182 Hz, *B*(3,6)). ¹³C NMR (CDCl₃, ppm): δ 43.6 (CH_{carb}). MS (DUIS), *m*/*z*: found: 212 (M–H)⁻; calculated for C₂H₉B₁₀Cl₂ (M–H)⁻ 212.

8,9,12-Cl₃-*ortho*-C₂B₁₀H₉ (**3**): ¹H NMR (CDCl₃, ppm): δ 3.54 (2H, br s, CH_{carb}), 3.3–1.5 (7H, br m, *BH*). ¹¹B NMR (CDCl₃, ppm): δ 6.0 (2B, s, *B*(9,12)), 0.2 (1B, s, *B*(8)), -9.9 (1B, d, J = 159 Hz, *B*(10)), -15.1 (2B, d, J = 175 Hz, *B*(4,7)), -17.2 (2B, d, J = 175 Hz, *B*(5,11)), -18.6 (1B, d, J = 187 Hz, *B*(3)), -22.9 (1B, d, J = 182 Hz, *B*(6)). ¹³C NMR (CDCl₃, ppm): δ 41.0 (CH_{carb}). MS (DUIS), *m*/*z*: found: 246 (M–H)⁻; calculated for C₂H₈B₁₀Cl₃ (M–H)⁻ 246.

3.3. Synthesis of 9-Chloro-ortho-Carborane (1)

N-Chlorosuccinimide (1.00 g, 7.5 mmol) was added to a solution of *ortho*-carborane (1.00 g, 6.9 mmol) in glacial acetic acid (20 mL). The resulting mixture was heated under reflux for 24 h. Then, the reaction mixture was cooled and treated with water (60 mL). The white precipitate was filtered, washed with water and dried on air. Fraction crystallization from hexane gave 0.60 g (49% yield) of 9-Cl-*ortho*-C₂B₁₀H₁₁ (1) as colorless crystals.

3.4. Synthesis of Trimethylammonium Salt of 5,6-Dichloro-nido-Carborane (4)

Potassium hydroxide (7.84 g, 140.0 mmol) was added to a solution of **2** (7.49 g, 35.2 mmol) in 70% EtOH in water (500 mL). The resulting mixture was heated under reflux for 6 h. Then, the reaction mixture was cooled and concentrated under reduced pressure. The crude product was dissolved in a water (500 mL) and a solution of NH_4Cl (11.23 g, 210.0 mmol) in water (150 mL) was added. The resulting mixture was added to a solution of Me₃NHCl (7.00 g, 73.24 mmol) in water (50 mL). The white precipitate was filtered, washed with water and dried on air to give 8.58 g (93%) of (Me₃NH)[5,6-Cl₂-*nido*-7,8-C₂B₉H₁₀] (4) as white powder.

(Me₃NH)[5,6-Cl₂-*nido*-7,8-C₂B₉H₁₀]: ¹H NMR (CD₃COCD₃, ppm): δ 3.19 (9H, s, (CH₃)₃NH), 1.70 (2H, br s, CH_{carb}), 2.8–0.0 (7H, br m, *BH*), –2.14 (1H, br m, *BH*B). ¹¹B NMR (CD₃COCD₃, ppm): δ –4.0 (2B, s, *B*(5,6)), –11.5 (2B, d, J = 140 Hz, *B*(9,11)), –20.2 (1B, d, J = 165 Hz, *B*(3)), –22.3 (2B, d, J = 151 Hz, *B*(2,4)), –29.1 (1B, dd, J₁ = 128 Hz, J₂ = 37 Hz, *B*(10)), –35.5 (1B, d, J = 145 Hz, *B*(1)). ¹³C NMR (CD₃COCD₃, ppm): δ 46.1 ((CH₃)₃NH), 36.8 (CH_{carb}). MS (DUIS), *m*/*z*: found: 202 (M)⁻; calculated for C₂H₁₀B₉Cl₂ (M)⁻ 202.

3.5. Synthesis of Potassium Salt of 9,9',12,12'-Tetrachloro Cobalt bis(Dicarbollide) (5)

Compound 4 (8.58 g, 32.7 mmol) was added to a fresh hot 40% KOH solution in water (160 mL). The resulting mixture was stirred for 30 min. Then, $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ (16.03 g, 49.2 mmol) was added and the reaction mixture was stirred at 60 °C for a week. After, the suspension was cooled, the orange precipitate was filtered, washed with 40% KOH solution in water (40% KOH washings can be used as solution for the same consecutive synthesis) and dried on air. The resulting orange solid was dissolved in acetonitrile, filtered and concentrated under reduced pressure to give 5.40 g (65%) of K[9,9',12,12'-Cl₄-closo-3,1,2-Co(1,2-C₂B₉H₉)₂] (5) as orange powder.

K[9,9',12,12'-Cl₄-*closo*-3,1,2-Co(1,2-C₂B₉H₉)₂] (**5**): ¹H NMR (CD₃COCD₃, ppm): δ 4.05 (4H, br s, CH_{carb}), 4.4–0.7 (14H, br m, *BH*). ¹¹B NMR (CD₃COCD₃, ppm): δ 6.3 (2B, d, J = 144 Hz, B(8,8')), 4.4 (4B, s, B(9,9',12,12')), 1.9 (2B, d, J = 158 Hz, B(6,6')), -7.6 (4B, d, J = 155 Hz, B(4,4',7,7')), -17.8 (4B, d, J = 164 Hz, B(5,5'11,11')), -24.4 (2B, d, J = 158 Hz, B(10,10')). ¹³C NMR (CD₃COCD₃, ppm): δ 43.7 (CH_{carb}). MS (DUIS), *m*/*z*: found: 461 (M)⁻; calculated for C₄H₁₈B₁₈Cl₄Co (M)⁻ 461.

3.6. Synthesis of Cesium Salt of 8,8',9,9',12,12'-Hexachloro Cobalt bis(Dicarbollide) (6)

^{*t*}BuOCl (14 mL, 13.42 g, 123.57 mmol) was added to a solution of **5** (5.40 g, 10.7 mmol) in acetonitrile (150 mL). The resulting mixture was stirred for 24 h and, then, concentrated under reduced pressure. The crude product was dissolved in water (200 mL), the resulting mixture was added to a solution of CsCl (6.00 g, 35.64 mmol) in water (10 mL). The orange precipitate was filtered, washed with water and dried on air to give 5.68 g (80%) of Cs[8,8',9,9',12,12'-Cl₆-closo-3,1,2-Co(1,2-C₂B₉H₈)₂] (6) as orange product.

Cs[8,8',9,9',12,12'-Cl₆-*closo*-3,1,2-Co(1,2-C₂B₉H₈)₂] (**6**): ¹H NMR (CD₃COCD₃, ppm): δ 4.39 (4H, br s, CH_{carb}),3.9–1.0 (12H, br m, *BH*). ¹¹B NMR (CD₃COCD₃, ppm): δ 6.3 (2B, s, *B*(8,8')), 3.2 (4B, s, *B*(9,9',12,12')), 1.5 (2B, d, J = 160 Hz, *B*(6,6')), -6.4 (4B, d, J = 157 Hz, *B*(4,4',7,7')), -17.8 (4B, d, J = 165 Hz, *B*(5,5'11,11')), -24.4 (2B, d, J = 185 Hz, *B*(10,10')). ¹³C NMR (CD₃COCD₃, ppm): δ 50.5 (CH_{carb}). MS (DUIS), *m*/*z*: found: 530 (M)⁻; calculated for C₄H₁₈B₁₆Cl₆Co (M)⁻ 530.

3.7. Single Crystal X-ray Diffraction Study

The single crystals of 9,12-Cl₂-ortho-C₂B₁₀H₁₀ and 8,9,12-Cl₃-ortho-C₂B₁₀H₉ were grown by slow evaporation of solutions of the title compounds in chloroform at room temperature, while the tiny orange prisms of Cs[9,9',12,12'-Cl₄-3,3'-Co(1,2-C₂B₉H₉)₂]·2Me₂CO were obtained by slow evaporation of a solution of the complex in acetone. Single crystal X-ray diffraction experiments were carried out using SMART APEX2 CCD diffractometer (λ (Mo-K α) = 0.71073 Å, graphite monochromator, ω -scans) at 120 K. Collected data were processed by the SAINT and SADABS programs incorporated into the APEX2 program package [58]. The structures were solved by the direct methods and refined by the fullmatrix least-squares procedure against F^2 in anisotropic approximation. The refinement was carried out with the SHELXTL program [59]. The CCDC numbers (2190099 for 2, 2202671 for 3, 2202672 for 5') contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif (accessed on 17 May 2022).

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Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/cryst12091251/s1, Crystallographic data for compounds **2**, **3**, and **5**', NMR and MS spectra of compounds **1–6**.

Author Contributions: Synthesis and NMR spectroscopy studies, S.A.A.; synthesis, S.V.T.; synthesis, O.B.Z.; single crystal X-ray diffraction experiments, K.Y.S.; supervision and manuscript concept, I.B.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the Russian Science Foundation (Grant No. 21-13-00345).

Data Availability Statement: In this section, please provide details regarding where data supporting reported results can be found, including links to publicly archived datasets analyzed or generated during the study. Crystallographic data for the structure of 9,12-Cl₂-*ortho*-C₂B₁₀H₁₀ (2), 8,9,12-Cl₃-*ortho*-C₂B₁₀H₉ (3), and Cs [9,9',12,12'-Cl₄-3,3'-Co(1,2-C₂B₉H₉)₂]·2Me₂CO (5') were deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 2190099 (for 2), 2202671 (for 3), and 2202672 (for 5'). The Supplementary Information contains crystallographic data for compounds 2, 3, and 5', and NMR and MS spectra of compounds 1–6.

Acknowledgments: The single crystal X-ray diffraction and NMR spectral data were obtained by using equipment from the Center for Molecular Structure Studies at A.N. Nesmeyanov Institute of Organoelement Compounds, operating with financial support from the Ministry of Science and Higher Education of the Russian Federation.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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