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A Simple Way to Obtain a Decachloro Derivative of Cobalt Bis(dicarbollide)

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Abstract: A simple synthetic way to obtain a decachloro derivative of cobalt bis(dicarbollide) has been found. The reaction of cesium salt of cobalt bis(dicarbollide) anion with aluminum chloride in chloroform under reflux conditions results in Cs[3,3′-Co(4,7,8,9,12-Cl_5-1,2-$C_2B_9H_6$)$_2$] of high purity and good yield.

Keywords: carboranes; metallacarboranes; cobalt bis(dicarbollide); chlorinated derivatives

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1. Introduction

Cobalt bis(dicarbollide) anion [3,3′-Co(1,2-$C_2B_9H_{11}$)$_2$]$^-$ is the most important representative of the sandwiched metallacarboranes [1,2]. The synthesis of this complex was first reported as early as 1965 [3,4], and the intensive study of its chemistry continues to this day. Nowadays, cobalt bis(dicarbollide) and its derivatives find applications in many different fields from medicine [5–14] to material science [15–21].

An important field of using cobalt bis(dicarbollide) and its derivatives is the solvent extraction of radionuclides. Since the first publication of alkali metals extraction by polyhedral borate anions [22] up to now, more than a hundred articles and patents have been published on this subject (see [1] and references therein). The approach is based on the extremely hydrophobic properties of cobalt bis(dicarbollide) anion, which enters the organic phase of moderate polarity as an ion pair with the least hydrated cations (first of all, Cs^+ and Sr^{2+}). In order to increase the chemical stability of cobalt bis(dicarbollide) in strong acidic media [23], which is used in the process, the hydrogen atoms at the most reactive BH-vertexes (positions 8,8′ and 9,9′,12,12′) are substituted to other groups, such as, for example, halogens. The hexachloro derivative of cobalt bis(dicarbollide) anion [3,3′-Co(8,9,12-Cl_3-1,2-$C_2B_9H_8$)$_2$]$^-$ is well known by its high affinity and selectivity for Cs^+ in nuclear application (see, for example, [24,25]) and is also used as one of the components of synergistic extraction mixture in the Universal Solvent Extraction (UNEX) process [26].

For many years, the hexachloro derivative was known as the derivative with the highest substitution degree; however, very recently it was reported that the reaction of cobalt bis(dicarbollide) with sulfuryl chloride in the presence of $AlCl_3$, depending on the amount of reagents and reaction time, results in the formation of octa-, deca-, and dodecachloro derivatives of cobalt bis(dicarbollide) [27]. In this contribution, we describe a simple and convenient method for obtaining decachloro cobalt bis(dicarbollide) Cs[3,3′-Co(4,7,8,9,12-Cl_5-1,2-$C_2B_9H_6$)$_2$] without using toxic, corrosive, and lachrymatory sulfuryl chloride.

2. Materials and Methods

2.1. General Methods

Cesium salt of cobalt bis(dicarbollide) was obtained using standard literature methods [3]. Chloroform, 99.85% was purchased from Component-Reaktiv (water content < 0.05%, HCl content < 0.001%). Aluminum chloride was purchased from ABCR and used without

additional purification. The NMR spectra at ^{1}H (400.1 MHz), ^{11}B (128.4 MHz), and ^{13}C (100.0 MHz) were recorded with a Varian Inova 400 spectrometer. Me_4Si was taken as the internal standard for ^{1}H and ^{13}C NMR spectra. $BF_3 \cdot Et_2O$ was used as an external standard for ^{11}B NMR spectra. Infrared spectra were collected on an FSM-2201 (INFRASPEC) instrument. UV/Vis spectra in chloroform were recorded with an SF-2000 spectrophotometer (OKB SPECTR LLC) using 1 cm cuvettes. Mass spectra (MS) were measured using a Shimadzu LCMS-2020 instrument with DUIS 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 (https://www.sisweb.com/mstools/isotope.htm, accessed on 26 December 2022).

2.2. Synthesis of Cs[3,3′-Co(4,7,8,9,12-Cl$_5$-1,2-C$_2$B$_9$H$_6$)$_2$]

To a suspension of cesium salt of cobalt bis(dicarbollide) (0.50 g, 1.10 mmol) in chloroform (25 mL), anhydrous $AlCl_3$ (0.20 g, 1.50 mmol) was added by one portion. The reaction mixture was heated under reflux for 4 h, cooled to room temperature, and concentrated under reduced pressure. The crude product was washed with water, filtered, and dried on air to give 0.81 g (92% yield) of Cs[3,3′-Co(4,7,8,9,12-Cl_5-1,2-$C_2B_9H_6)_2$] as orange crystals. ^{1}H NMR (acetone-d_6, ppm): δ 5.45 (2H, br s, C*H*$_{carb}$), 4.24 (2H, br s, C*H*$_{carb}$), 3.7 ÷ 0.8 (8H, br m, B*H*). ^{13}C NMR (acetone-d_6, ppm): δ 49.0 (C*H*$_{carb}$), 46.9(C*H*$_{carb}$). ^{11}B NMR (acetone-d_6, ppm): δ 11.2 (2B, s), 6.0 (2B, s), 5.0 (2B, s), 4.0 (2B, s), 0.3 (2B, s), –1.0 (2B, d), –15.6 (2B, d, *J* = 170 Hz), –18.5 (2B, d, *J* = 155 Hz), –29.1 (2B, d, *J* = 167 Hz). IR (film, cm^{-1}): 3066 (ν_{C-H}), 3046 (ν_{C-H}), 2617 (br, ν_{B-H}), 2591 (br, ν_{B-H}). UV (acetone, nm): λ 277, 239. MS (DUIS) for $C_4H_{12}B_{18}Cl_{10}Co$: calcd. *m/z* 668 [M]$^-$, obsd. *m/z* 668 [M]$^-$. The spectral data are in good agreement with those described in the literature [27].

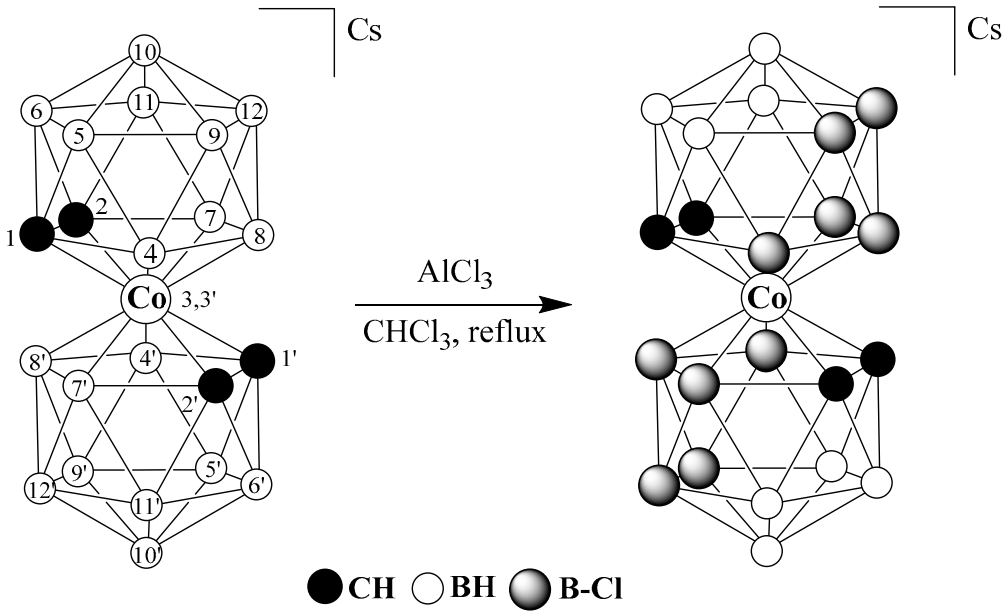
3. Results and Discussion

There are two main approaches for obtaining chloro derivatives of cobalt bis(dicarbollide) anion. The first approach includes the preliminary chlorination of *closo*-carborane, followed by its conversion to *nido*-carborane and the subsequent insertion of cobalt by the reaction with cobalt salts (typically with $CoCl_2$ or $CoBr_2$) [28,29]. Another method is based on the direct chlorination of cobalt bis(dicarbollide) anion [28,30–32]. The combination of these two approaches is also possible [29]. Most of these methods make it possible to introduce from one to six chlorine atoms to the cobalt bis(dicarbollide) anion.

It has recently been demonstrated that the reaction of the cobalt bis(dicarbollide) anion with sulfuryl chloride in the presence of $AlCl_3$ in an Ace pressure tube, depending on the amount of reagents and reaction time, results in the formation of chlorinated derivatives with a higher degree of substitution, such as Cl-8, Cl-10, and Cl-12 derivatives [27]. This work is the first example of the synthesis of pure chloro derivatives with a high degree of halogenation, in contrast to the previously described preparation of inseparable mixtures of chlorinated derivatives of cobalt bis(dicarbollide) (up to Cl-9) [33]. However, the proposed approach requires the use of dangerous sulfuryl chloride as well as special equipment for synthesis under pressure. In this contribution, we present a simple method for obtaining a decachloro derivative of cobalt bis(dicarbollide) that does not require the use of sulfuryl chloride, nor any special devices or inert atmosphere.

We found that the reaction of cesium salt of cobalt bis(dicarbollide) anion with excess $AlCl_3$ in chloroform solution under reflux condition for 4 h results in the formation of Cs[3,3′-Co(4,7,8,9,12-Cl_5-1,2-$C_2B_9H_6)_2$] as a single product (Scheme 1).

The isolation of the target product was carried out by concentrating the reaction mixture under vacuum and washing the dry residue with water to remove the unreacted aluminum chloride. According to NMR spectra and other analytical data, the main product of the reaction represents the decachloro derivative of cobalt bis(dicarbollide). However, trace amounts of Cl-9, Cl-11, and Cl-12 derivatives can also be detected in the mass spectrum of the compound.



Scheme 1. Synthetic rout to Cs[3,3′-Co(4,7,8,9,12-Cl_5-1,2-$C_2B_9H_6)_2$].

The $^{11}B\{^1H\}$ and ^{11}B NMR spectra (Figure 1) of the prepared complex consist of nine groups of signals in the range 11.2 ÷ (−29.1) ppm, which corresponds to the spectral region of cobalt bis(dicarbollide) derivatives and indicates the presence of symmetry in the molecule. Five signals at 11.2, 6.2, 5.0, 4.0, and 0.3 ppm represent singlets and correspond to the signals of boron atoms substituted with chlorine (positions 4,4′; 7,7′; 8,8′; 9,9′; and 12,12′). Five other signals appear as doublets and represent signals from unsubstituted boron atoms.

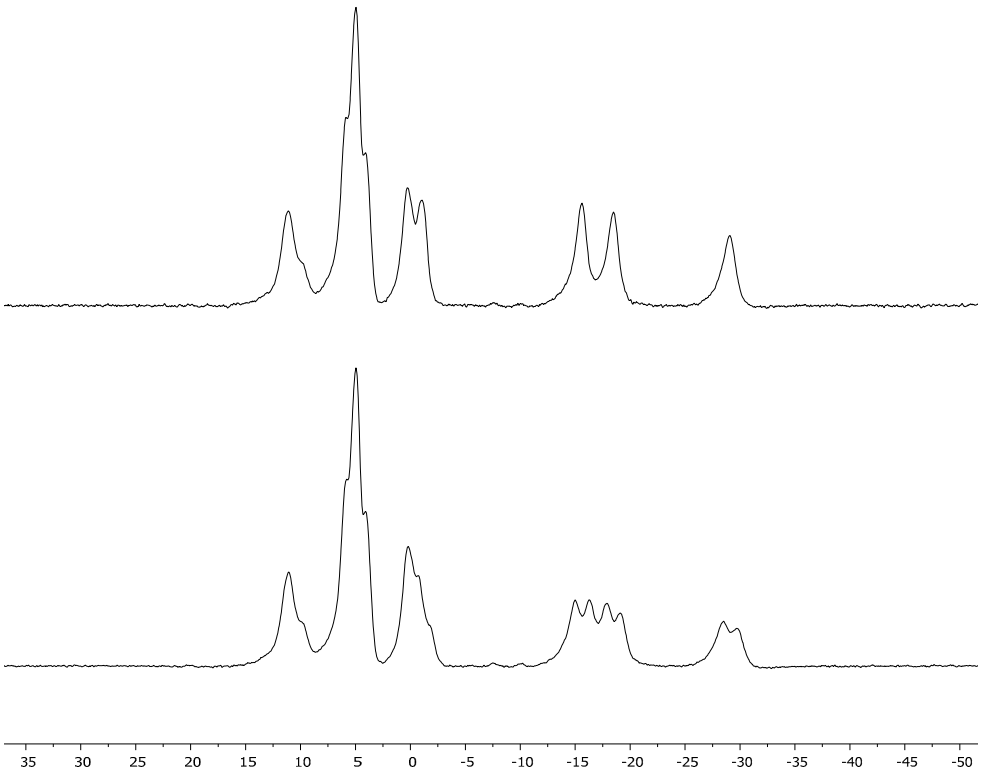


Figure 1. The $^{11}B\{^1H\}$ (**top**) and ^{11}B (**bottom**) NMR spectra of Cs[3,3′-Co(4,7,8,9,12-Cl_5-1,2-$C_2B_9H_6)_2$].

Despite the fact that the obtained complex is substituted symmetrically, the signals from four CH groups in its ^{1}H NMR spectrum appear as two separate broad singlets at 5.45 and 4.24 ppm, whereas it was expected that they should be equivalent. Similarly, ^{13}C NMR spectrum consists of two signals from CH groups at 49.0 and 46.9 ppm (see Figure S1 and Figure S2, respectively, in the Supplementary Materials). These spectral data indicate that the complex is a gauche rotamer, which can also be confirmed by X-ray structural data obtained for $NMe_4[3,3'$-Co(4,7,8,9,12-Cl_5-1,2-$C_2B_9H_6)_2$] earlier [27].

To understand the possible mechanism of cobalt bis(dicarbollide) chlorination by $AlCl_3$ in chloroform solution, it is necessary to consider some similar processes. In the middle of the 20th century, the ionization of polychloromethanes by aluminum chloride at low temperatures had been described [34]. The thermodynamic stability of the CCl_3^+ cations as opposed to the CH_3^+ cation is explained by the efficient p-n interaction between the nonbonded electron pairs of the halogens and the positively charged carbon atom [35,36]. Therefore, the trichloromethyl cation itself should not be a highly reactive electrophile. This made it possible to isolate and structurally characterize their salts with weakly coordinating anions [37,38]. However, it was found that $CCl_4/AlCl_3$ is an extremely reactive hydride abstracting and ionic chlorinating system for adamantane [39] and carboranes [40].

The combinations of polyhalomethanes with aluminum halides ($CBr_4{\cdot}nAlBr_3$, $CHBr_3{\cdot}nAlBr_3$, $CCl_4{\cdot}nAlBr_3$, $CHCl_3{\cdot}nAlBr_3$, and $CH_2Br_2{\cdot}nAlBr_3$) are considered to be organic superacids, which catalyze efficiently the cracking, isomerization, and oligomerization of alkanes and cycloalkanes under mild conditions [41,42]. It was shown that the reactivity of chloromethyl cations in hydride abstraction reactions with hydrocarbons in superacid media decreased in the order $CCl_3^+ > CHCl_2^+ >> CH_2Cl^+$ [43]. This could not be expected, since the stability of the chloromethyl cations decreases in the same order as the number of 3p-donor chlorine atoms decreases. Based on this, CCl_3^+ should be the least reactive species among other in the series. To explain this unusual behavior, protosolvation or superelectrophilic activation [44–46] of chlorine atoms in a superacid was proposed. Protosolvation should enhance the electrophilic character of the carbon in the corresponding halomethyl ion, resulting in a higher reactivity in the hydride abstraction.

Since the dichloromethane cation $CHCl_2^+$ is less stable and less reactive than the trichloromethane one, reactions involving it are much less studied. It is known that reactions of $CHCl_3$ with aromatics in the presence of $AlCl_3$ proceed according to the electrophilic substitution mechanism through the formation of the $[CHCl_2]^+[AlCl_4]^-$ complex at the first stage [47]. At the same time, the reaction with carboranes under similar conditions, due to the hydride nature of the hydrogen atoms, proceeds according to the mechanism of electrophilic-catalyzed nucleophilic substitution, leading to halogen derivatives [40].

Summarizing the above, we believe that the reaction mechanism involves at the first stage the chloride abstraction by $AlCl_3$ from chloroform with the formation of $[CHCl_2]^+[AlCl_4]^-$. The resulting $CHCl_2^+$ carbocation removes the most hydridic hydrogen atoms from cobalt bis(dicarbollide). The quasi-borinium cation formed upon the removal of the hydride from cobalt bis(dicarbollide) is a very strong Lewis acid [48], capable of abstracting the chloride ion from $AlCl_4^-$. The first steps of this process are shown in Figure 2. To confirm our suggestion, it should be noted that in the ^{1}H NMR spectrum of the reaction mixture, there is the signal from CH_2Cl_2 that is formed in the reaction.

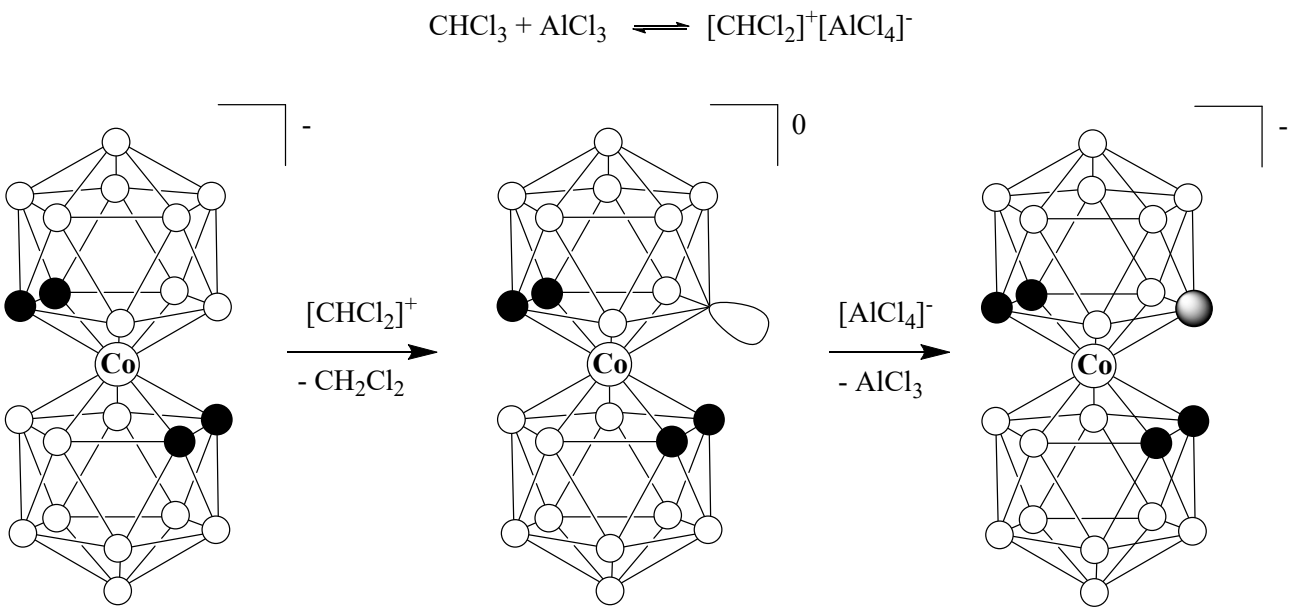


Figure 2. Proposed mechanism of the chlorination of the cobalt bis(dicarbollide) anion by $AlCl_3$ in chloroform.

4. Conclusions

In this contribution, we have described a very simple and convenient synthetic way to obtain a decachloro derivative of cobalt bis(dicarbollide) Cs[3,3′-Co(4,7,8,9,12-Cl_5-1,2-$C_2B_9H_6)_2$] by the reaction of cesium salt of the cobalt bis(dicarbollide) anion with aluminum chloride in chloroform under reflux conditions. The proposed method does not require the use of hazardous reagents or any special equipment and leads to the formation of a high-purity chlorinated complex with a good yield. A possible reaction mechanism was also discussed.

Supplementary Materials: The NMR, IR, mass, and UV/Vis spectral data for Cs[3,3′-Co(4,7,8,9,12-Cl_5-1,2-$C_2B_9H_6)_2$] can be downloaded at https://www.mdpi.com/article/10.3390/reactions4010008/s1. Figure S1. ^{1}H NMR spectrum of Cs[3,3′-Co(4,7,8,9,12-Cl_5-1,2-$C_2B_9H_6)_2$] in acetone-d_6. Figure S2. ^{13}C NMR spectrum of Cs[3,3′-Co(4,7,8,9,12-Cl_5-1,2-$C_2B_9H_6)_2$] in acetone-d_6. Figure S3. ^{11}B{^{1}H} NMR spectrum of Cs[3,3′-Co(4,7,8,9,12-Cl_5-1,2-$C_2B_9H_6)_2$] in acetone-d_6. Figure S4. ^{11}B NMR spectrum of Cs[3,3′-Co(4,7,8,9,12-Cl_5-1,2-$C_2B_9H_6)_2$] in acetone-d_6. Figure S5. ^{11}B-^{11}B COSY NMR spectrum of Cs[3,3′-Co(4,7,8,9,12-Cl_5-1,2-$C_2B_9H_6)_2$] in acetone-d_6. Figure S6. IR spectrum of Cs[3,3′-Co(4,7,8,9,12-Cl_5-1,2-$C_2B_9H_6)_2$] (thin film from acetone). Figure S7. Mass-spectrum of Cs[3,3′-Co(4,7,8,9,12-Cl_5-1,2-$C_2B_9H_6)_2$]. Figure S8. UV/Vis spectrum of Cs[3,3′-Co(4,7,8,9,12-Cl_5-1,2-$C_2B_9H_6)_2$].

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