SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

Reaction of the *closo*-Decaborate Anion $B_{10}H_{10}^{2-}$ with Dichloroethane in the Presence of Hydrogen Halides

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Abstract—The reactions of the *closo*-decaborate anion with hydrogen halides and dichloroethane have been studied. Irrespective of the hydrogen halide used (HCl, HBr, HI), chlorination to give mono-, di-, and trihalo-substituted products is the major process. The product ratio depends on the hydrogen halide used and on the synthesis temperature and time. The products have been identified by ¹¹B NMR, IR, and ESI mass spectra. The structure of $(Ph_3(NaphCH_2)P)_2B_{10}H_8Cl_2$ has been studied by X-ray diffraction. The geometry distortion of the *closo*-decaborate core found in the chlorinated derivatives is retained on further chemical transformations of the compound.

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The closo-decaborate anion is a pseudoaromatic system prone to numerous reactions involving replacement of exopolyhedral hydrogen atoms, including chlorination. It is known from published data that halogenation of the *closo*-decaborate anion with free halogen in an aqueous solution of the ammonium salt $(NH_4)_2B_{10}H_{10}$ [1] results in mono- and dihalogenated anions $B_{10}H_{10-n}X_n^{2-}$, where X = Cl, Br, I; n = 1, 2, which were identified by NMR, IR, and Raman spectroscopy. The structure of monohalogenated derivatives *closo*-decaborate of the anion $[(C_5H_5N)_2CH_2][2-XB_{10}H_9]$, where X = Cl, Br, I, was determined more precisely by X-ray diffraction [2, 3]. These products are formed upon the reaction of $B_{10}H_{10}^{2-}$ with chlorine, bromine, or iodine or with N-halosuccinimide and can be separated from the unreacted starting anions or highly substituted halo derivatives by ion exchange chromatography. Halogenation processes of the *closo*-decaborate anion have not been adequately studied; therefore, it is pertinent to carry out further studies of this process and to search for new halogenation methods under different conditions in order to avoid the formation of product mixtures with different degrees of substitution.

Previously, we reported the reaction of the *closo*-dodecaborate anion $B_{12}H_{12}^{2-}$ with hydrogen halides in dichloroethane [4] giving mono- and dichlorinated products. The present work continues this study and deals with the reaction of the *closo*-decaborate anion $B_{10}H_{10}^{2-}$ with hydrogen halides.

EXPERIMENTAL

The $[B_{10}H_{10}]^{2-}$ anion was synthesized by a reported procedure [5] via 1,6-bis(triethylaminedecaborane).

The hydrogen halides used in the reaction were prepared by known procedures [6]: HCl was obtained by the reaction of sodium chloride with sulfuric acid; HBr and HI were obtained by the reaction of an aqueous solution of the respective hydrohalic acid with phosphorus(V) oxide or by the reaction of bromine or iodine with tetralin.

Prior to being supplied to the reactor, the hydrogen halide gas was passed through two absorption tubes with phosphorus(V) oxide for complete drying.

Chlorination of the $[B_{10}H_{10}]^{2-}$ **anion.** A solution of tetrabutylammonium decaborate (1.0 g) in dichloroethane (30 mL) was placed into a three-necked flask equipped with a bubbling device, a reflux condenser, a thermometer, and a stirrer, and the mixture was heated to 40–60°C. Thoroughly dried hydrogen halide was bubbled continuously through the mixture for 1–5 h. The yellow reaction mixture was concentrated on a rotary evaporator until a precipitate formed. The reaction conditions, the reactants, and the products are summarized in Table 1.

Synthesis of $(Ph_3(NaphCH_2)P)_2B_{10}H_8Cl_2$. The reaction mixture (0.8 g) was dissolved in CH₃CN (25 mL). A solution of $(C_6H_5)_3(CH_2C_{10}H_7)PCl$ (2.0 g in 20 mL of H₂O) was added with stirring to the resulting solution. After 24 h, a white finely crystalline precipitate formed, which was filtered off and recrystallized from acetonitrile to give white crystals.

Table 1.	Main produc	ts of the reactions	s of the $B_{10}H_{10}^{2-}$	anion salts with dichlor	oethane and hydrogen halides
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	40°C	60°C		
	Dichloroethane + hydrogen chloride ($C_2H_4Cl_2 + HCl$)			
1 h	$B_{10}H_9Cl^{2-}$	$B_{10}H_9Cl^{2-}, B_{10}H_8Cl_2^{2-}$		
5 h	$B_{10}H_9Cl^{2-}, B_{10}H_8Cl_2^{2-}, B_{10}H_7Cl_3^{2-}$	$B_{10}H_8Cl_2^{2-}, B_{10}H_7Cl_3^{2-}$		
Dichloroethane + hydrogen bromide $(C_2H_4Cl_2 + HBr)$				
1 h	$B_{10}H_9Cl^{2-}$	$B_{10}H_9Cl^{2-}, B_{10}H_8Cl_2^{2-}, B_{10}H_7Cl_3^{2-}$		
5 h	$B_{10}H_9Cl^{2-}, B_{10}H_8Cl_2^{2-}, B_{10}H_7Cl_3^{2-}$	$B_{10}H_8Cl_2^{2-}, B_{10}H_7Cl_3^{2-}, B_{10}H_7Cl_2Br^{2-}, B_{10}H_7Cl_2Br_2^{2-}, B_{10}H_6Cl_3Br^{2-}, B_{10}H_5Br_5^{2-}$		
Dichloroethane + hydrogen iodide $(C_2H_4Cl_2 + HI)$				
1 h	$B_{10}H_9Cl^{2-}$	$B_{10}H_8Cl_2^{2-}, B_{10}H_7Cl_3^{2-}$		
5 h	$B_{10}H_8Cl_2^{2-}, B_{10}H_7Cl_3^{2-}$	$B_{10}H_7Cl_2I^{2-}, B_{10}H_6Cl_3I^{2-}, B_{10}H_6Cl_2I_2^{2-}, B_{10}H_5Cl_3I_2^{2-}$		

 Table 2. Elemental analysis data for chlorinated closo-decaborates

Compound	В, %	С, %	N, %	Н, %
Compound	found/calcd.	found/calcd.	found/calcd.	found/calcd.
$\overline{(Bu_4N)_2(B_{10}H_9Cl)}$	16.92/16.96	60.21/60.28	4.34/4.39	12.78/12.81
$(Bu_4N)_2(B_{10}H_8Cl_2)$	16.02/16.09	57.15/57.19	4.15/4.17	11.95/12.00

The elemental analysis for carbon, hydrogen, and nitrogen was carried out on a CHNS-3 FA 1108 analyzer (Carlo Erba). Boron was determined by electrothermal atomization atomic absorption spectroscopy on Perkin-Elmer spectrophotometers (model 2100 with HGA-700 and model 403 with HGA-72) [7]. Elemental analysis data are presented in Table 2.

IR spectra were measured on a Infralum FT-02 spectrophotometer (the Lumeks Scientific and Production Company for Analytical Instrument Making) in the range 4000–400 cm⁻¹. The samples were prepared as mineral oil mulls. The assignment for most informative absorption bands observed in the IR spectra of chlorinated *closo*-decaborates is presented in Table 3.

The ¹¹B NMR spectra of acetonitrile solutions of the studied compounds were recorded on a Bruker AC 200 spectrometer operating at 64.297 MHz with internal deuterium lock. Boron trifluoride etherate was used as the external standard. The ¹¹B NMR data for chlorinated *closo*-decaborates are presented in Table 4.

Electrospray ionization mass spectra (microspray, 4500 V) of solutions of the compounds were recorded on a Bruker Esquire 3000 plus mass spectrometer in an acetonitrile (50%)–water mixture containing formic acid (0.2%). The average analytical concentration of the samples for ESI MS was (1.00 ± 0.20) mg/mL solution. The molecular masses of the single-charged

 Table 3. Maxima of some absorption bands in the IR spectra of chlorinated *closo*-decaborates

Compound	ν (B–H), cm ⁻¹	$\nu(BBCl), cm^{-1}$
(Bu ₄ N) ₂ (B ₁₀ H ₉ Cl)	2479	960
$(Bu_4N)_2(B_{10}H_8Cl_2)$	2475	962
(Ph ₃ (NaphCH ₂)P) ₂ B ₁₀ H ₈ Cl ₂	2476	961

anions (CatAn)⁻ determined from the spectra by analysis of reaction mixtures are given in Table 5.

X-ray diffraction studies were carried out on an Enraf-Nonius CAD-4 automated diffractometer (λ Mo K_{α} , graphite monochromator, ω scan mode). The absorption correction was applied by azimuthal scanning. The structure was solved by direct methods. The structure solution and refinement were carried out using SHELXS97 and SHELXL97 software [8].

The set of diffraction data I(hkl) at T = 120(2) K was obtained by a standard procedure [9] on a Bruker AXS SMART 100 diffractometer (λ Mo, graphite monochromator, ω scan mode, $\theta_{max} = 30^{\circ}$) from a $0.55 \times 0.30 \times 0.15$ mm single crystal. A semiempirical correction for absorption was applied by the SADABS program [10].

Chemical shift ô, ppm	Integrated intensity	Signal multiplicity	Assignment
-2.3	2	d	B _a
-7.2	1	s	B _{Cl}
-20.7	4	d	B _e
-24.5	2	d	
-28.8	1	d	
-4.3	1	d	B _a
-7.8	1	S	B _{Cl}
-21.4	1	d	B _e
-25.1	1	d	
-30.9	1	d	
	-2.3 -7.2 -20.7 -24.5 -28.8 -4.3 -7.8 -21.4 -25.1 -30.9	Image: constraint of the system Second system -2.3 2 -2.3 2 -2.3 2 -2.3 2 -2.3 2 -2.3 2 -2.3 2 -2.3 2 -2.3 2 -2.4.5 2 -28.8 1 -4.3 1 -7.8 1 -21.4 1 -25.1 1 -30.9 1	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$

Table 4. ¹¹B NMR data for chlorinated *closo*-decaborates (in CH₃CN)

 Table 5. Data of the ESI mass spectra of some halogenated

 closo-decaborates for the (CatAn)⁻ species

Compound	Exp.	Calcd.
$(Bu_4N)_2B_{10}H_9Cl$	394.93	395.10
$(Bu_4N)_2B_{10}H_8Cl_2$	429.53	429.37
$(Bu_4N)_2B_{10}H_7Cl_3$	464.45	463.33
$(Bu_4N)_2B_{10}H_7Cl_2Br$	508.30	508.44
$(Bu_4N)_2B_{10}H_7Cl_2Br_2$	588.13	587.34
$(Bu_4N)_2B_{10}H_6Cl_3Br$	544.25	542.89
$(Bu_4N)_2B_{10}H_5Br_5$	755.92	755.14
$(Bu_4N)_2B_{10}H_7Cl_2I$	554.48	555.44
$(Bu_4N)_2B_{10}H_6Cl_3I$	590.22	589.89
$(Bu_4N)_2B_{10}H_6Cl_2I_2 \\$	681.02	681.34
$(Bu_4N)_2B_{10}H_5Cl_3I_2$	715.89	715.79

The crystal data, X-ray experiment details, and structure refinement data for $(Ph_3(NaphCH_2)P)_2B_{10}H_8Cl_2$ are presented in Table 6, and the structures of the anions present in the compound are shown in the figure.

RESULTS AND DISCUSSION

It was found that the reactions of the *closo*-decaborate anion with dichloroethane in the presence of hydrogen halides give chloro-substituted derivatives with different degrees of substitution. Analysis of the ¹¹B NMR spectra of the products (Table 4) and ESI mass spectra (Table 5) carried out at all stages of synthesis showed the presence of halogenated derivatives with degrees of substitution of mainly 1, 2 and 3.

The product ratio depends on the hydrogen halide used and on the synthesis temperature and time. The use of a heavier hydrogen halide and also an increase in the temperature and time of the synthesis promote accumulation of products with higher degrees of substitution.

The formation of the major chlorination products is always accompanied by the formation of derivatives with higher degrees of substitution, including those with different halides, which are formed when hydrogen bromide and hydrogen iodide are used.

For none of the reactions were we able to select conditions under which one chlorinated product would be formed predominantly, because the yields of products present in the reaction mixtures in all reactions were commensurable. However, the products with lower substitution degrees (1 and 2) can be easily isolated from the reaction mixture by HPLC in a 3 : 8 acetonitrile-dichloroethane system, as their retention times are shorter than that of the initial unsubstituted anion (~7 min) or than those of more halogenated products, including the products with mixed halogens (>6 min) (Table 7).

The molecular masses of the single-charged anions obtained in all syntheses were estimated from ESI mass spectra (Table 5). As a rule, these spectra of *closo*-borate anions exhibit signals for single-charged (CatAn)⁻ species. The results indicate, in all cases, the formation of $(C_4H_9)_4N[B_{10}H_9Cl]^-$, $(C_4H_9)_4N[B_{10}H_8Cl_2]^-$, and $(C_4H_9)_4N[B_{10}H_7Cl_3]^-$ anions.

The ¹¹B NMR spectra (Table 4) of mono- and dihalogenated products are the spectra of "classical" monoand disubstituted closo-decaborate anions. The ¹¹B NMR spectrum of the monochlorinated derivative exhibits five signals, one from the apical boron atoms at -3.3 ppm, one from the boron atoms bound to substituents at -7.2 ppm, and three signals at -20.7, -24.5, and -28.8 ppm due to the equatorial boron atoms. The ¹¹B NMR spectrum of the compound $(Bu_4N)_2B_{10}H_8Cl_2$ shows five signals, one from the apical boron atoms (-4.3 ppm), one from the boron atoms bound to substituents (-7.8 ppm), and three signals at -21.4, -25.0, and -31.0 ppm due to the equatorial boron atoms. In both spectra without B-H decoupling, the signals for all boron atoms that are not bound to the substituents are split into symmetrical doublets.

The IR spectra of the halogenated *closo*-decaborate (Table 3), apart from the bands at $2570-2580 \text{ cm}^{-1}$ typical of B–H stretches, contain the bands of the B–B–Cl bending modes at about 960 cm⁻¹.

For the dichloro-substituted *closo*-decaborate anion isolated by HPLC, white prismatic single crystals of the compound (Ph₃(NaphCH₂)P)₂B₁₀H₈Cl₂ were obtained (figure). The X-ray reflections were collected from a $0.15 \times 0.25 \times 0.65$ mm single crystal. The C, P, and Cl

atoms were refined in the anisotropic approximation and B atoms, in the isotropic approximation. The occupancy of the chlorine positions was first refined independently. Since the sum of position occupancies (μ) of Cl(1) and Cl(2) atoms is equal to unity, the $\mu_{Cl(2)}$ value was included in the final refinement and the occupancy of the Cl(1) position was taken to be $1 - \mu_{Cl(2)}$. All H atoms were refined by the riding model in idealized positions with isotropic thermal parameters $U_j(H) =$ $1.2U_{eq}$ (or $1.2U_{iso}$) of the corresponding non-hydrogen atom.

The structure of the compound is built of the $Ph_3(NaphCH_2)P^+$ cations and $B_{10}H_8Cl_2^{2^-}$ anions. The anions are located on a twofold axis passing through the midpoints of the B(3)–B(7) and B(5)–B(9) edges. The Cl atom is disordered over two positions (Cl(2) and Cl(1)) bound to B(2) and B(1), respectively. The occupancy ratio for the positions is Cl(2) : Cl(1) = 0.8 : 0.2. The total occupancy of the Cl atom positions is equal to unity, which corresponds to the polyhedral $B_{10}H_8Cl_2^{2^-}$ anion.

The great thermal parameters for boron atoms attest to probable overlap of the polyhedra with similar geometry. Presumably, the insignificant differences between the geometries of the decaborate polyhedra arise in different $B_{10}H_8Cl_2^{2-}$ anions under the influence of Cl atoms. Taking into account the Cl positions in the structure, four isomers are possible in which substituents can be located both at the vertices and in the belt of the *closo*-decaborate core. The content of the major 2,7-isomer is four times greater than the content of the other possible 1,10-, 1,2-, and 1,7-isomers. Determination of the exact structure of the isomers in the crystal from X-ray diffraction data is impossible.

The averaged decaborate polyhedron determined by the refinement has an irregular shape. The ranges of equivalent bonds are very broad: $B_a - B_e 1.45 - 1.74(2)$ Å, B_e-B_e 1.75–2 and 1.60–1.82(2) Å in one belt and between the belts, respectively. The greatest anomalies are observed in the bonds involving the B(3) atom, which has the greatest thermal parameter: the B(2)-B(3) bond is virtually cleaved and amounts to 2.01(2) Å; the B(1)-B(3) and B(3)-B(7) bonds are shortened to 1.45(2) to 1.60(2) Å, respectively. In addition, the polyhedron is substantially flattened along the symmetrically bound edges, B(2)-B(3) and B(8)-B(7) (the B(1)B(2)B(3)/B(2)B(3)B(6) dihedral angle is 164.6°), and the average deviation of the equatorial B(2), B(3), B(4), and B(5) atoms from the root-mean-square plane reaches 0.041 Å. The B(2)–Cl(2) and B(1)–Cl(1) bond lengths are normal (1.846(9) and 1.86(2) Å, respectively).

The structures of the *closo*-decaborate anions in $(Ph_3(NaphCH_2)P)_2B_{10}H_8Cl_2$ determined by X-ray diffraction at 120(2) K and at room temperature (293 K) are identical to within experimental error.

Table 6. Selected crystal data, X-ray experiment details, and refinement data for $(Ph_3(NaphCH_2)P)_2B_{10}H_8Cl_2$

Compound	$(Ph_3(NaphCH_2)P)_2B_{10}H_8Cl_2$
Space group	C2/c
<i>a</i> , Å	24.229(4)
<i>b</i> , Å	11.816(2)
<i>c</i> , Å	22.223(2)
β, deg	122.191(11)
$V, Å^3$	5384.4(1.5)
ρ_{calcd} , g/cm ³	1.226
Z	4
$\mu(Mo), mm^{-1}$	1.92
θ_{max} , deg	90
Number of independent reflections (N)	5107
Number of reflections with $I > 2\sigma(I) (N_{obs})$	1980
$R1$, $wR2$ for N_{obs}	0.081, 0.224
<i>R</i> 1, <i>wR</i> 2 for <i>N</i>	0.221, 0.305
GOOF	1.021

Table 7. HPLC data for the initial and some synthesized halogen derivatives of the *closo*-decaborate anion (elution with $CH_3CN : CH_2Cl_2 = 3 : 8$)

Anion	Compound	Retention time, min
$B_{10}H_{10}^{2-}$	$(Bu_4N)_2(B_{10}H_{10})$	7.1
	$(Bu_4N)_2(B_{10}H_9Cl)$	5.3
	$(Bu_4N)_2(B_{10}H_8Cl_2)$	3.3
	$(Bu_4N)_2(B_{10}H_7Cl_3)$	2.7

The geometry distortion of the *closo*-decaborate anion in an acid medium has been reported. In particular, the structure of $[(CH_3CN)_4]Cu_2B_{10}H_{10}$ obtained in the $Cu_2B_{10}H_{10}$ -CH₃CN-CF₃COOH system was determined. According to X-ray diffraction, the *closo*-decaborate anion has a similar geometry distortion, one B-B bond being almost cleaved and two such bonds being shortened. Hence, a distortion of the geometry of the *closo*-decaborate anion in a highly acidic medium appears regular.

Thus, the reactions of the *closo*-decaborate anion $B_{10}H_{10}^{2-}$ with dichloroethane and hydrogen halides yield halogenated derivatives in which chlorine atoms from dichloroethane are mainly present as substituents. The mechanism of reactions resulting in these products is as yet unknown; however, the role of hydrogen halide



Structures of the anions present in the (Ph₃(NaphCH₂)P)₂B₁₀H₈Cl₂ single crystal.

molecules is evident. Performing analogous reactions at room temperature demonstrated that chlorination of the *closo*-decaborate anion does not take place but the anion is protonated to give $B_{10}H_{11}^-$, which is confirmed

by ¹¹B NMR. This fact suggests that hydrogen halides are the protonating agents initiating halogenation, which proceeds via the protonated anion. Acid-catalyzed nucleophilic substitution of the *closo*-decaborate anion has been reported [12]; therefore, one may suggest that halogenation of the *closo*-decaborate anion by dichloroethane follows a similar mechanism (hydrogen halide initiation).

Apparently, the reaction also involves opening of the boron cluster anion. As noted above, the geometry of the *closo*-decaborate anion is distorted in highly acidic media, and the products can be isolated only in the presence of acids [11]. The *closo*-decaborate core in the compounds synthesized in this study has a similar unusual geometry, which is retained upon further chemical transformations.

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