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Synthesis of Monohalogeno Derivatives of *closo*-$[B_9H_9]^{2-}$. Crystal Structures of $(Ph_4P)_2[1\text{-}XB_9H_8]\cdot CH_3CN$ (X = Cl, Br, I)

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By reaction of $Na_2[B_9H_9]$ with the appropriate *N*-halogenosuccinimide, the monohalogenated anion $[1\text{-}XB_9H_8]^{2-}$ (X = Cl, Br, or I) is formed. The X-ray diffraction analyses performed on single crystals of $(Ph_4P)_2[1\text{-}XB_9H_8]\cdot CH_3CN$ (X = Cl, Br, I) reveal that the tricapped trigonal prismatic geometry of the cluster is retained after substitution in the 1-position. Crystallographic data are as follows for $(Ph_4P)_2[1\text{-}XB_9H_8]\cdot CH_3CN$. X = Cl, Br: monoclinic, space group $P2_1$, $a = 10.7$ Å, $b = 32.9$ Å, $c = 13.8$ Å, $\beta = 96°$, $Z = 4$, R1 = 0.038 and R1 = 0.036, respectively. X = I: monoclinic, space group $P2_1/n$, $a = 10.5$ Å, $b = 13.6$ Å, $c = 33.4$ Å, $\beta = 94°$, $Z = 4$, R1 = 0.094. The compounds have been characterized by vibrational and ^{11}B NMR spectroscopy as well.

Introduction

Only few derivatives of nonahydro-*closo*-nonaborate, $[B_9H_9]^{2-}$, are known compared with the case of other *closo*-borates, such as $[B_6H_6]^{2-}$, $[B_{10}H_{10}]^{2-}$, and $[B_{12}H_{12}]^{2-}$. The perhalogenated species $[B_9X_9]^{2-}$ (X = Cl, Br, I) were prepared in 1980,[1] and $(n\text{-}Bu_4N)_2[B_9Br_9]$ was characterized by an X-ray structure determination in 1999.[2] The borates $[B_9Br_6H_3]^{2-}$ and $[B_9Cl_8H]^{2-}$ were established by chemical analyses and spectroscopy.[3] Lower substituted derivatives were synthesized by reactions with dimethyl sulfoxide and hydroxylamine-*O*-sulfonic acid,[4,5] and $B_9H_7[S(CH_3)_2]_2$ was characterized by an X-ray structure determination, showing one dimethyl sulfide group linked to a capping boron and the other to a trigonal prismatic boron.[6]

In this paper, we report the syntheses of the first monohalogenated borates $[1\text{-}XB_9H_8]^{2-}$ (X = Cl, Br, I). The X-ray diffraction analyses performed on single crystals of $(Ph_4P)_2[1\text{-}XB_9H_8]\cdot CH_3CN$ (X = Cl, Br I) reveal that the trigonal prismatic geometry of the B_9 cluster is retained after substitution in the 1-position.

Experimental Section

General Procedures. The organic solvents were dried by standard procedures. Unless otherwise noted, reagents were obtained from commercial suppliers and used as received. $Cs_2[B_9H_9]$ was prepared according to literature procedures.[3b,7] Instrumentation: ^{11}B NMR, Bruker AM 400 (128.38 MHz); IR, Matson Genesis FT IR; Raman, IFS 66 FT Bruker.

Syntheses. A sample of $Cs_2[B_9H_9]$ (0.5 g, 1.3 mmol) was converted by ion exchange to $Na_2[B_9H_9]\cdot xH_2O$. The white powder was dissolved in 0.7 N NaOH (30 mL), and the solution was cooled in an ice bath. The appropriate *N*-halogenosuccinimide (4 mmol) was added, and the mixture was stirred for 4 h, after which the monohalogenated compound was directly isolated by ion-exchange chromatography (IEC) on (diethylamino)ethyl (DEAE) cellulose (0.5 M NaCl, 25 cm in length, 2.5 cm in diameter) from the starting compound.

$\mathbf{(Ph_4P)_2[1\text{-}ClB_9H_8]\cdot CH_3CN}$ **(1).** During IEC, the excess of the starting material $[B_9H_9]^{2-}$ was eluted first, after 200 mL, followed by $[1\text{-}ClB_9H_8]^{2-}$ after, 250 mL, which, upon addition of an aqueous solution of $(Ph_4P)Cl$ was precipitated as $(Ph_4P)_2[1\text{-}ClB_9H_8]$. Recrystallization from acetonitrile/ether yielded light-yellow X-ray-quality single crystals of **1**. Yield: 500 mg (46%). IR (KBr; cm^{-1}): 2493, 2449, 2423 (s, B−H), 896, 850, 809 (w, B−B). Raman (cm^{-1}): 2499, 2460, 2430 (m, B−H). ^{11}B NMR (400 MHz, $BF_3\cdot OEt_2$, CD_3CN; ppm): +0.9 (d), −5.3 (s, d), −18.0 (d), −18.5 (d), −23.2 (d).

$\mathbf{(Ph_4P)_2[1\text{-}BrB_9H_8]\cdot CH_3CN}$ **(2).** During IEC, the excess of the starting material was eluted first, after 200 mL, followed by $[1\text{-}BrB_9H_8]^{2-}$, after 350 mL, which, upon addition of an aqueous solution of $(Ph_4P)Cl$, precipitated as $(Ph_4P)_2[1\text{-}BrB_9H_8]$. Recrystallization from acetonitrile/ether yielded yellow X-ray-quality single crystals of **2**. Yield: 350 mg (31%). IR (KBr; cm^{-1}): 2450, 2424 (s, B−H), 887, 845, 801 (w, B−B). Raman (cm^{-1}): 2450, 2426 (m, B−H). ^{11}B NMR (400 MHz, $BF_3\cdot OEt_2$, CD_3CN; ppm): +0.6 (d), −5.0 (d), −9.7 (s), −18.0 (d), −22.3 (d).

$\mathbf{(Ph_4P)_2[1\text{-}IB_9H_8]\cdot CH_3CN}$ **(3).** After addition of *N*-iodosuccinimide, the ice bath was removed and the solution was stirred for 3 h. During IEC, the excess of the starting material was eluted first, after 200 mL, followed by $[1\text{-}IB_9H_8]^{2-}$, after 1500 mL, which, upon addition of an aqueous solution of $(Ph_4P)Cl$, was precipitated as $(Ph_4P)_2[1\text{-}IB_9H_8]$. Recrystallization from acetonitrile/ether yielded dark-yellow X-ray-quality single crystals of **3**. Yield: 200 mg (15%). IR (KBr; cm^{-1}): 2525, 2490, 2443 (s, B−H), 877, 833, (w, B−B). Raman (cm^{-1}): 2502, 2433 (m, B−H). ^{11}B NMR (400 MHz, $BF_3\cdot OEt_2$, CD_3CN; ppm): −0.1 (d), −3.8 (d), −16.9 (s), −18.5 (d), −21.0 (d).

Crystal Structure Determinations. Diffraction data for **1**−**3** were collected on an Enraf-Nonius CAD4 four-circle diffractometer with a monochromated Mo Kα radiation source ($\lambda = 0.710\,69$ Å). Lattice parameters were obtained, in each case, from a least-squares analyses of 25 machine-centered reflections. The intensities recorded at 208 and 193 K, respectively, were corrected for Lorentz and polarization effects. The structures were solved by using direct methods (SIR-92)[8] and

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[1] Wong, E. H.; Kabbani, R. M. *Inorg. Chem.* **1980**, *19*, 451−455.

[2] Binder, H.; Kellner, R.; Vaas, K.; Hein, M.; Baumann, F.; Wanner, M.; Winter, R.; Kaim, W.; Hönle, W.; Grin, Y.; Wedig, U.; Schultheiss, M.; Kremer, R. K.; von Schnering, H. G.; Groeger, O.; Engelhardt, G. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1059−1072.

[3] (a) Forstner, J. A.; Haas, T. E.; Muetterties, E. L. *Inorg. Chem.* **1964**, *3*, 155−158. (b) Klanberg, F.; Muetterties, E. L. *Inorg. Chem.* **1966**, *5*, 1955−1960.

[4] Wong, E. H.; Gatter, M. G. *Inorg. Chim. Acta* **1982**, *61*, 95−98.

[5] Wong, E. H.; Gatter, M. G.; Kabbani, R. M. *Inorg. Chem.* **1982**, *21*, 4022−4026.

[6] Bray, D. D.; Kabbani, R. M. *Acta Crystallogr.* **1982**, *B38*, 957−959.

[7] Klanberg, F.; Muetterties, E. L. *Inorg. Synth.* **1968**, *11*, 27−30.

[8] Altomare, A.; Cascarano, G.; Giacavazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343−350.

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Table 1. Crystallographic Data for $(Ph_4P)_2[1\text{-}ClB_9H_8]\cdot CH_3CN$ (**1**), $(Ph_4P)_2[1\text{-}BrB_9H_8]\cdot CH_3CN$ (**2**) and $(Ph_4P)_2[1\text{-}ib_9H_8]\cdot CH_3CN$ (**3**)

	1	**2**	**3**
empirical formula	$C_{50}H_{51}B_9ClNP_2$	$C_{50}H_{51}B_9BrNP_2$	$C_{50}H_{51}B_9INP_2$
fw	860.60	905.06	952.05
cryst syst	monoclinic	monoclinic	monoclinic
space group (No.)	$P2_1$ (4)	$P2_1$ (4)	$P2_1/n$ (14)
a (Å)	10.658(10)	10.673(2)	10.551(5)
b (Å)	32.862(6)	32.875(3)	13.582(5)
c (Å)	13.787(5)	13.802()4	33.441(5)
β (deg)	96.470(5)	96.470(14)	94.000(5)
V (Å^3)	4798(2)	4811.9(17)	4781(5)
Z	4	4	4
$\lambda_{\text{Mo K}\alpha}$ (Å)	0.710 69	0.710 69	0.710 69
T (°C)	−65	−65	−80
ρ (g/cm^3)	1.191	1.249	1.323
GOF on F^2	1.052	1.062	1.075
final R indices^a [$I > 2\sigma(I)$]: R1, wR2	0.0388, 0.1137	0.0364, 0.0983	0.0947, 0.2468
R indices^a (all data): R1, wR2	0.0482, 0.1361	0.0496, 0.1123	0.1422, 0.2816

[a] $R1 = \sum[|F_o| - |F_c|]/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[wF_o^4]\}^{1/2}$.

Table 2. Selected Bond Lengths (Average Values, Å) for **1**−**3**, $Rb_2[B_9H_9]$ (**4**),[10] and $(n\text{-}Bu_4N)_2[B_9Br_9]\cdot CH_2Cl_2$ (**5**)[2]

	1	**2**	**3**	**4**	**5**
A (6)[a]	1.965(6)	1.951(10)	1.897(13)	1.89	1.963
B (3)[a]	1.786(8)	1.778(11)	1.865(16)	1.81	1.780
C (12)[a]	1.705(7)	1.699(10)	1.708(12)	1.71	1.675
D (1)[a]	1.854(5)	1.998(8)	2.184(11)		1.970 (9)[a]
E (8)[a]	1.18(5)	1.14(7)	1.12 (calcd)		

[a] The multiplicities of the bonds are given parentheses.

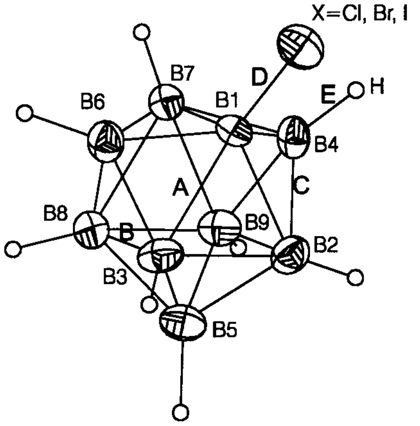

Figure 1. Molecular structure of the $[1\text{-}XB_9H_8]^{2-}$ dianion in the crystal, showing the 30% probability thermal ellipsoids.

refined by full-matrix least-squares techniques based on F^2 (SHELXL-97).[9] The positions of all non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms of the cations were placed at calculated positions. Crystallographic data are summarized in Table 1, and average values of bond lengths are presented in Table 2.

Results and Discussion

The reaction of $Na_2[B_9H_9]$ with an *N*-halogenosuccinimide in water leads to a single isomer of $[XB_9H_8]^{2-}$, identified as the 1-isomer. Compounds **1**−**3** can be separated from the starting compound by IEC on (diethylamino)ethyl (DEAE) cellulose. The isolated (Ph_4P) salts are air stable, soluble in organic solvents, and insoluble in water and 2-propanol. Slow diffusion of diethyl ether into acetonitrile solutions of **1**−**3** yields single crystals suitable for X-ray structure determinations. The general molecular structure of the dianions, with atom and bond labelings, is shown in Figure 1.

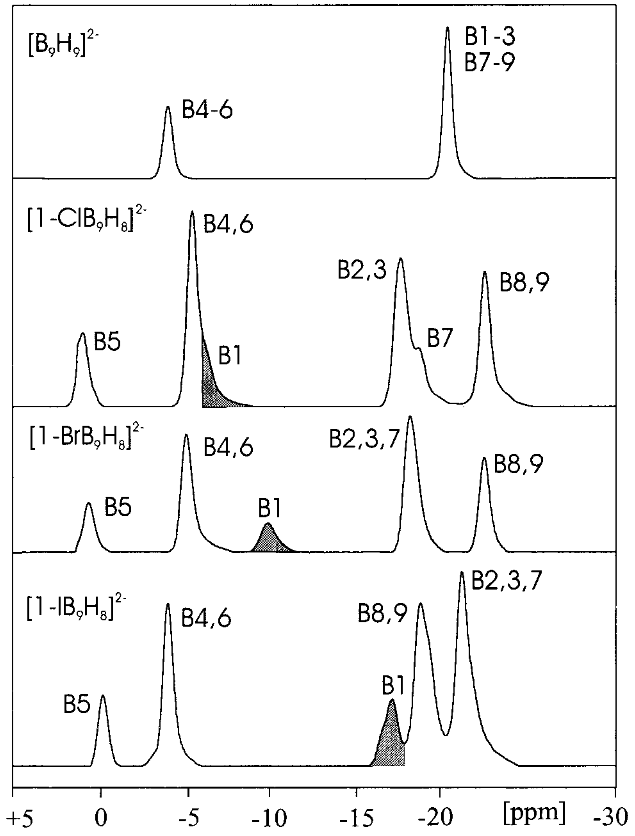

Figure 2. $^{11}B\{^1H\}$ NMR spectra of $[1\text{-}XB_9H_8]^{2-}$ (X = H, Cl, Br, I) in CD_3CN.

Crystallographic Studies. 1 and **2** crystallize in the same space group, $P2_1$, with similar atomic parameters and four formula units in the unit cell. The discrete anions and cations occur in two crystallographically different forms. One acetonitrile molecule cocrystallizes with each B_9 cage.. The structure of **3**, in the higher symmetric space group $P2_1/n$, consists of a cluster salt and one acetonitrile molecule which are generated four times in the unit cell. The boron cage in **1**−**3** is a tricapped trigonal prism, comparable to that in $Rb_2[B_9H_9]$.[10] The cluster anion features three types of B−B distances (see Figure 1): bonds within the triangle of the prism (A), bonds connecting the two triangles (B), and bonds from the capping borons to the prismatic boron atoms (C). Besides, there are the bonds to

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(9) Sheldrick, G. M. *SHELXL-97: Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

(10) Guggenberger, L. G. *Inorg. Chem.* **1968**, *7*, 2260−2264.

the halide (D) and to the hydrogens (E). The average values of the bond lengths are shown in Table 2. The general trend for *closo*-B_9 cages following the order A > B > C is confirmed in the present structures. The influence of the substituent on the geometry of the boron cage is very small in the cases of Cl and Br. The B−B bond lengths vary in the normal range. The structure of **3** exhibits two unusually long bond lengths, B2−B3 and B1−B7, both 2.0 Å. The B−X distances in **1**−**3** are similar to those described for other *closo*-borates. Compared with the case of $Rb_2[B_9H_9]$,[10] the influences of the substituents on the bond lengths of the cages are inconsistent. While the distances of type C are all in a small range, the type A bond lengths decrease in the order Cl, Br, J, H. In case of type B bonds, no sequence is discernible. The bond angles within the cages of **1** and **2** are similar to those that would be expected for D_{3h} symmetry. In **3**, the bond angles in the vicinity of the B−I bond are extended. Thus the angle B3−B1−B2 is 64° in **3** in contrast to 61.6° in **2**. The equivalent angles B1−B6−B7 and B1−B4−B7 are 71.9° in **3** compared to 63.2° in **2**.

NMR Spectra. The proton-coupled ^{11}B NMR spectrum of $[B_9H_9]^{2-}$ exhibits two signals at −2.7 and −20.5 ppm (128.38 MHz, $BF_3{\cdot}OEt_2$, CD_3CN) with the intensity ratio 3:6 appearing as doublets due to coupling with hydrogen. For monosubstituted B_9 clusters, six signals are expected, one singlet from the ipso boron and five doublets, with the intensity ratio 1:2:2:2:1:1. The substituents give rise to strong shielding of the ipso B1 atoms, resulting in systematic upfield shifts for the series Cl, Br, I to −5.3, −9.7, −16.9 ppm, respectively (Figure 2). The order of these shifts is due to the decreasing $-I$ effects caused by the decreasing electronegativities. Generally, the signals of the capping boron atoms B5 and B4,6 are observed in the downfield region whereas the prismatic boron atoms B2,3, B7, and B8,9 resonate at higher field. All groups of magnetically inequivalent boron atoms exhibit moderate systematic shifts depending on the substituent. Owing to similar chemical environments, the signals of B2,3 and B7 coincide, except for those of $[1\text{-}ClB_9H_8]^{2-}$. The assignments of the signals are based on two-dimensional $^{11}B-^{11}B$ NMR spectra. An antipodal effect, as observed for B_6 cages, cannot be seen in our NMR spectra.[11]

IR and Raman Spectra. The bands in the IR and Raman spectra of **1**−**3** exhibit characteristic splittings due to their lowered symmetries compared with the symmetry of the parent compound. The B−H stretching vibrations are found in the 2400−2550 cm^{-1} region. The vibrations shift to higher frequencies in the order H, Cl, Br, I. Until now, it has been impossible to prepare alkali metal salts of **1**−**3**. Due to the numerous cation bands for the (Ph_4P) salts, the assignments of modes in the framework areas below 1100 cm^{-1} are very difficult.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org. Further details of the crystal structure investigation are also available on request from the Cambridge Crystallographic Data Centre, Cambridge CB2 1EZ, U.K., on quoting the depository numbers CCDC-140143 (**1**), CCDC-140144 (**2**), and CCDC-140145 (**3**).

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(11) (a) Hermánek, S. *Chem. Rev.* **1992**, *92*, 325−362. (b) Preetz, W.; Peters, G. *Eur. J. Inorg. Chem.* **1999**, 1831−1846.