Russian Chemical Bulletin, International Edition, Vol. 50, No. 6, pp. 1115—1116, June, 2001 1115

Regioselective hydrogen—deuterium exchange in the $[B_{10}H_{10}]^{2-}$ anion. Syntheses of $[1,10\text{-}B_{10}H_8D_2]^{2-}$ and $[2,3,4,5,6,7,8,9\text{-}B_{10}H_2D_8]^{2-}$

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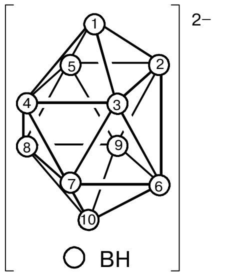
Decahydro-*closo*-decaborate anion, $[B_{10}H_{10}]^{2-}$, undergoes regioselective deuterio-exchange in methanol-d_4. Selectively deuterated derivatives $[1,10\text{-}B_{10}H_8D_2]^{2-}$ and $[2,3,4,5,6,7,8,9\text{-}B_{10}H_2D_8]^{2-}$ were synthesized.

Key words: decahydro-*closo*-decaborate anion, deuterio-exchange, regioselectivity.

The decahydro-*closo*-decaborate anion $[B_{10}H_{10}]^{2-}$ first obtained in 1959 [1] still attracts attention of chemists.



One of the most interesting problems in chemistry of the *closo*-decaborate anion is the study of its interaction with acids. It has been shown previously[2] that the decahydro-*closo*-decaborate anion undergoes fast deuterio-exchange in D_2O in the presence of an acid to form the perdeuterated derivative $[B_{10}D_{10}]^{2-}$. It was supposed[3] that the deuterio-exchange, like some substitution reactions in an acidic medium, occurs through the formation of the $[B_{10}H_{11}]^-$ anion. Later, this assumption was confirmed by ^{11}B NMR spectroscopy (see Ref. 4). According to the quantum-chemical calculations of the $[B_{10}H_{11}]^-$ anion in the MNDO approximation[5] confirmed later by X-ray diffraction studies,[6] the energy minimum corresponds to the structure with an additional proton "capping" a polar face. Fast proton exchange between all polar faces occurs in a solution. However, the action of strong acids, such as trifluoromethanesulfonic acid, can result in the *closo*-borate cage opening to form decaborane(14) derivatives, *viz.*, *nido*-6-R-$B_{10}H_{13}$ (R = C_6H_5, C_6H_{13}, OSO_2CF_3).[7]

The interaction of the *closo*-decaborate anion with weak XH acids (X = O, N), *viz.*, alcohols, phenols, indols, has not virtually been studied. The shortened N—H...H—B contacts were observed in crystals of the $(R_3NH)_2[B_{10}H_{10}]$ salts, which points to the presence of H bonds between $[B_{10}H_{10}]^{2-}$ and a protonated tertiary amine R_3NH^+.[8] However, it is difficult to estimate the contribution of the electrostatic and packing factors to this interaction in compounds with this composition.

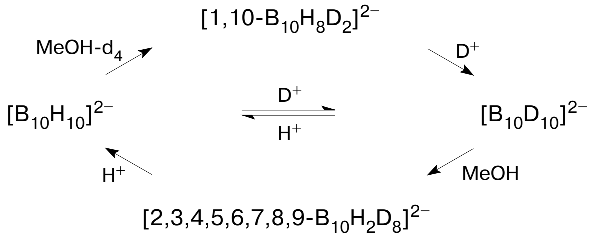
We began studies of the reactions of the *closo*-decaborate anion with neutral proton donors of different strengths in solution[9] in order to determine the conditions of H bond formation and obtain data on their energies and the role of these interactions in proton transfer from the acid to the boron cage.

The purpose of this work is to synthesize the selectively deuterated *closo*-decaborate anion, which is necessary to distinguish the contributions from the apical and equatorial BH groups to the formation of H...H bonds.

Our attempts to synthesize $[1,10\text{-}B_{10}H_8D_2]^{2-}$ by the substitution of the diazo groups in the bis(diazonium) derivative $[1,10\text{-}B_{10}H_8(N_2)_2]$ described previously[10] using $NaBD_4$ and $LiAlD_4$ as sources of the deuteride ion failed. However, we found that the decahydro-*closo*-decaborate anion undergoes slow hydrogen—deuterium exchange in methanol-d_4 at ~20 °C at the apical positions to form $[1,10\text{-}B_{10}H_8D_2]^{2-}$. The ^{11}B NMR spectrum of $[1,10\text{-}B_{10}H_8D_2]^{2-}$ in methanol-d_4 consists of a singlet at δ −1.6 and a doublet at δ −29.8 (J = 126 Hz) with a ratio of integral intensities of 1 : 4. The IR spectrum of $(Bu_4N)_2[1,10\text{-}B_{10}H_8D_2]$ in Nujol contains absorption bands of equatorial vibrations $\nu(B—H_{eq})$ at 2442 cm^{-1} and apical vibrations $\nu(B—D_{ap})$ at 1871 cm^{-1}.

On the other hand, the decadeuterio-*closo*-decaborate anion $[B_{10}D_{10}]^{2-}$ in methanol gives the corresponding product of deuterium—hydrogen exchange at apical positions, *viz.*, $[2,3,4,5,6,7,8,9\text{-}B_{10}H_2D_8]^{2-}$. (The ^{11}B NMR spectrum: a doublet at δ −1.6 (J = 145 Hz) and a singlet at δ −29.8 with a ratio of integral intensities of 1 : 4; IR

Scheme 1



Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1065—1066, June, 2001.

1066-5285/01/5006-1115 $25.00 © 2001 Plenum Publishing Corporation

spectrum, ν(B—H_{ap}) at 2474 cm^{-1} and ν(B—D_{eq}) at 1830 cm^{-1}). Thus, the hydrogen—deuterium exchange in the *closo*-decaborate system occurs as depicted in Scheme 1.

Experimental

$(Bu_4N)_2[B_{10}D_{10}]$ was synthesized by a previously published procedure.[2] ^{11}B NMR spectra were recorded on a Bruker AMX-400 instrument (128.3 MHz). IR spectra of samples in Nujol were obtained on a Specord M-82 spectrophotometer.

Synthesis of $(Bu_4N)_2[1,10\text{-}B_{10}H_8D_2]$. A solution of $(Bu_4N)_2[B_{10}H_{10}]$ (1.20 g, 2.0 mmol) in methanol-d_4 (15 mL) was stored for 3 days at 20 °C and the solvent was distilled off at a reduced pressure and ~20 °C. The product was obtained in 100% yield (1.20 g).

Synthesis of $(Bu_4N)_2[2,3,4,5,6,7,8,9\text{-}B_{10}H_2D_8]$. A solution of $(Bu_4N)_2[B_{10}D_{10}]$ (0.61 g, 1.0 mmol) in methanol (10 mL) was stored for 3 days at 20 °C and the solvent was distilled off at a reduced pressure and ~20 °C. The product was obtained in 100% yield (0.61 g).

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 98-03-33037 and 99-03-33073) and the Federal Target Program "Integration" (Project No. AO115).

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Received January 15, 2001;
in revised form March 30, 2001