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Reaction of *nido*-[6,9-$C_2B_8H_{10}$]$^{2-}$ with Hydrogen Halides. General Synthesis of 5-Substituted Derivatives of *arachno*-6,9-$C_2B_8H_{14}$

Bohumil Štibr, Zbyněk Janoušek, Jaromir Plešek, Tomáš Jelinek, and Stanislav Heřmánek
Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, 250 68 Řež near Prague, Czechoslovakia

Stereoselective addition of hydrogen halides to the unsaturated *nido*-[6,9-$C_2B_8H_{10}$]$^{2-}$ system to give a series of *arachno*-5-X-6,9-$C_2B_8H_{13}$ (X = F, Cl, Br, or I) and 5,5′-O-(6,9-$C_2B_8H_{13}$)$_2$ compounds is reported.

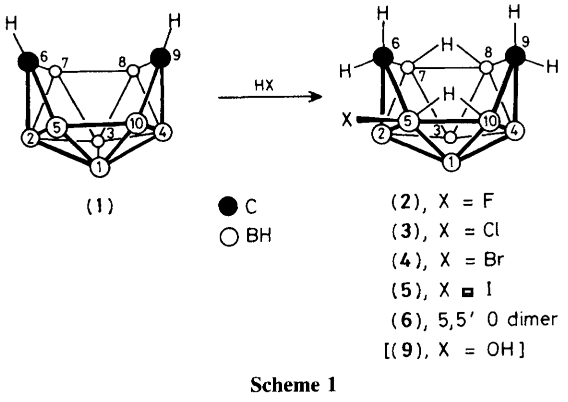
We have reported the preparation[1] and structure[2] of the *nido*-[6,9-$C_2B_8H_{10}$]$^{2-}$ anion (**1**) and some reactions leading to its metallaborane complexes.[2] Reaction of (**1**) with hydrochloric acid[1] produced the *arachno*-4,6-$C_2B_7H_{13}$ carbaborane[3] as a product of the degradation of one boron atom. We report now an unusual addition reaction of the dianion (**1**) with anhydrous hydrogen halides.

A series of *arachno*-5-X-6,9-$C_2B_8H_{13}$ [(**2**), X = F; (**3**), X = Cl; (**4**), X = Br; and (**5**), X = I] derivatives† can be obtained by the reaction of the disodium salt of (**1**) with anhydrous hydrogen halides in benzene at room temperature (Scheme 1), the overall process being represented by equation (1). When *ca.* 96% hydrogen fluoride is used, 5,5′-O-(6,9-$C_2B_8H_{13}$)$_2$ (**6**) is the main product, together with the fluoro-derivative (**2**).

$$\underset{(\mathbf{1})}{nido\text{-}[6,9\text{-}C_2B_8H_{10}]^{2-}} + 3\,HX \rightarrow arachno\text{-}5\text{-}X\text{-}6,\,9\text{-}C_2B_8H_{13} + 2\,X^- \quad (1)$$

Deuterium chloride and the anion (**1**) yield the trideuterio-derivative 5-Cl-[$^2H_3$]6,9-$C_2B_8H_{10}$ (**7**), the ^1H n.m.r. spectrum of which clearly indicates almost quantitative deuteriation at both axial CH sites and *ca.* 50% deuteriation at the bridging positions.

We therefore postulate that the reaction is a consequence of unsaturated character of the dianion (**1**) whose electronic structure can be expressed in terms of the only possible 0660 topological formula. As shown in Scheme 2, the proposed mechanism consists in the stereoselective addition of DCl to the B(5)–C(6) bond, having partial double bond character. The intermediate *arachno*-[5-Cl-6-D-6,9-$C_2B_8H_{10}$]$^{2-}$ (**8**) dianion thus formed adds subsequently two more deuterons, one at the bridging site and the other at the C(9) atom, to generate species (**7**) with two axial C–D bonds and one



Scheme 1

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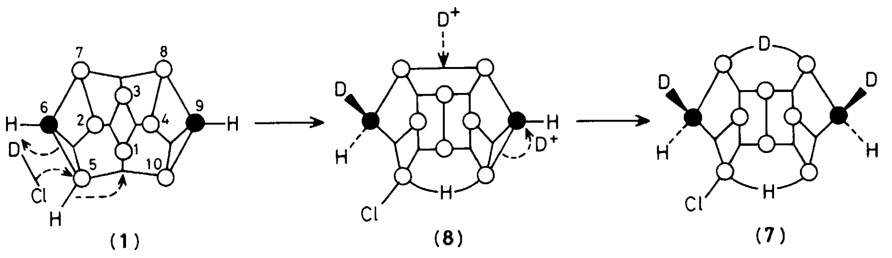
† Spectral data and yields for (**2**)—(**6**); ^1H n.m.r., 200 MHz, $CDCl_3$; ^{11}B n.m.r., 64.18 MHz, $CDCl_3$, +ve shifts in p.p.m. downfield from external $BF_3 \cdot OEt_2$, $J(^{11}B—^1H)$ values in Hz, μ-H couplings in parentheses: Compound (**2**), yield 10%; m.p. 142—144 °C; M^+, m/z 144; ^1H n.m.r.: δ 0.94 [2 H, s, CH(*eq*)], −0.50 [2 H, s, CH(*ax*)], and −2.91 (2 H, br.s, μ-H); ^{11}B n.m.r.: δ 3.26 [1 B, d, *J* 145, B(2)], 0.71 [1 B, d, *J* 156, B(4)], 4.55 [1 B, s, B(5)], −19.44 [1 B, d, *J* 135 (51), B(10)], −21.45 [1 B, d, *J* 145 (51), B(8)], −23.66 [1 B, d, *J* 140 (49), B(7)], −39.26 [1 B, d, *J* 154, B(1)], and −39.26 [1 B, d, *J* 154, B(3)].

Compound (**3**), yield 70%; m.p. 64—66 °C; M^+, m/z 122 ($^{12}C_2{}^{11}B_8{}^1H_{10}{}^+$); ^1H n.m.r.: δ 1.05 [2 H, s, CH(*eq*)], −0.09 [1 H, s, CH(*eq*)], −0.41 [1 H, s, CH(*ax*)], −0.92 (1H, br.s, μ-H), and −2.65 (1 H, br.s, μ-H); ^{11}B n.m.r.: δ 5.90 [1 B, d, *J* 164, B(2)], 1.90 [1B, d, *J* 162, B(4)], −5.50 [1 B, s, *J* (57), B(5)], −17.15 [1 B, d, 158 (55), B(10)], −18.20 [1 B, d, *J* 161 (54), B(8)], −20.55 [1 B, d, *J* 152 (49), B(7)], −37.50 [1 B, d, *J* 150, B(1)], −37.90 [1 B, d, *J* 151, B(3)].

Compound (**4**), yield 86%, m.p. 47—48 °C, M^+, m/z 122; ^1H n.m.r.: δ 1.17 [1 H, s, CH(*eq*)], 1.02 [1 H, s, CH(*eq*)], 0.03 [1 H, s, CH(*ax*)], −0.47 [1 H, s, CH(*ax*)], −1.01 (1 H, br.s, μ-H), and −2.54 (1 H, br.s, μ-H); ^{11}B n.m.r.: δ 6.55 [1 B, d, *J* 166, B(2)], 2.50 [1 B, d, *J* 164, B(4)], −13.02 [1 B, s, *J* (61), B(5)], −16.34 [1 B, d, *J* 157 (54), B(10)], −17.25 [1 B, d, *J* 157 (51), B(8)], −19.55 [1 B, d, *J* 150 (50), B(7)], −35.00 [1 B, d, *J* 154, B(1)], and −37.35 [1 B, d, *J* 153, B(3)].

Compound (**5**), yield 67%; m.p. 38—40 °C, M^+, m/z 122; ^1H n.m.r.: δ 1.23 [1 H, s, CH(*eq*)], 1.03 [1 H, s, CH(*eq*)], 0.09 [1 H, s, CH(*ax*)], −0.55 [1 H, s, CH(*ax*)], −1.22 (1 H, br.s, μ-H), and −2.52 (1 H, br.s, μ-H); ^{11}B n.m.r.: δ 7.20 [1 B, d, *J* 175, B(2)], 3.40 [1 B, d, *J* 173, B(4)], −15.75 [2 B, d, *J* 160 (5), B(8,10)], 18.05 [1 B, d, *J* 140 (50), B(7)], −30.00 [1 B, s, *J* (50), B(5)], −34.25 [1 B, d, *J* 157, B(1)], and −36.70 [1B, d, *J* 157, B(3)].

Compound (**6**), yield 35%; m.p. 200—220 °C; M^+, m/z 266; ^1H n.m.r.: δ 0.89 [2 H, s, CH(*eq*)], −0.84 [2 H, s, CH(*ax*)], and −2.92 (2 H, br.s, μ-H); ^{11}B n.m.r.: δ 1.97 [1 B, d, *J* 179, B(2)], 0.75 [1 B, d, *J* 173, B(4)], 3.25 [1 B, s, B(5)], −20.35 [1 B, d, *J* 154 (43), B(10)], −21.15 [1 B, d, *J* 157 (59), B(8)], −23.85 [1 B, d, *J* 173 (35), B(7)], −38.79 [1 B, d, *J* 155, B(1)], and −39.98 [1 B, d, *J* 144, B(3)].



Scheme 2

B–D–B bridge. Of course, the same mechanism is applicable to other hydrogen halides.

In the case of the reaction with hydrated hydrogen fluoride, one molecule of water is added to give an intermediate 5-HO-6,9-$C_2B_8H_{13}$ (**9**) species which is immediately dehydrated with excess of hydrogen fluoride to produce compound (**6**) containing two 6,9-$C_2B_8H_{13}$ moieties joined with one oxygen atom at the 5,5′-boron atoms. When more dilute acid is used, the intermediate (**9**) undergoes further degradation to give a high yield of 4,6-$C_2B_7H_{13}$, as demonstrated earlier[1] in the reaction of (**1**) with hydrochloric acid.

^{1}H N.m.r. spectra of all isolated derivatives† consist of four singlets, assigned to two $CH_{eq.}$ and $CH_{ax.}$ pairs, and two broad B–H–B signals, some signals being superimposed in a few cases. The corresponding ^{11}B n.m.r. spectra† exhibit one B(5) singlet and seven doublets of equal intensity. The n.m.r. data are in excellent agreement with the proposed unsymmetrical geometry of 5-substituted derivatives of *arachno*-6,9-$C_2B_8H_{14}$. The latter parent carbaborane was prepared earlier[4] in our laboratory.

The above reactions of the $[6,9\text{-}C_2B_8H_{10}]^{2-}$ dianion with hydrogen halides represent another example of a typical *nido–arachno* transformation.

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