

New method of synthesis of 6-hydroxy-nido-decaborane 6-(OH)B₁₀H₁₃ by cage opening of closo-[B₁₀H₁₀]²⁻

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Abstract

6-hydroxy-nido-decaborane 6-(OH)B₁₀H₁₃ was prepared by opening the cage [B₁₀H₁₀]²⁻ in strong acidic medium. The reaction must be carried out in the presence of an inert solvent such as hexane. 6-(OH)B₁₀H₁₃ is obtained with a 30% yield and characterized by ¹¹B NMR and I.R. Boric acid was also detected. Attempts to reproduce the opening of the [B₁₀H₁₀]²⁻ cage in basic or neutral media have been unsuccessful.

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Closo-decahydrodecaborate anion [B₁₀H₁₀]²⁻ [1] and nido-decaborane B₁₀H₁₄ [2–4] are two different types of compounds of great importance in boron chemistry. [B₁₀H₁₀]²⁻ is a bi-capped Archimedean square antiprismatic structure, where as B₁₀H₁₄ is a nido compound, the structure of which can be described as a fragment of an icosahedron with boron atoms at ten of the twelve vertices (Fig. 1).

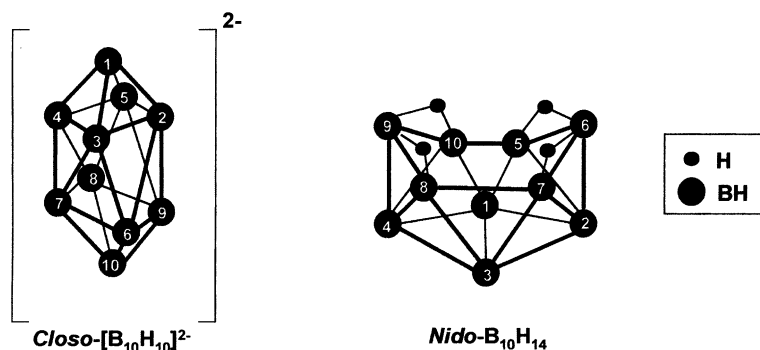
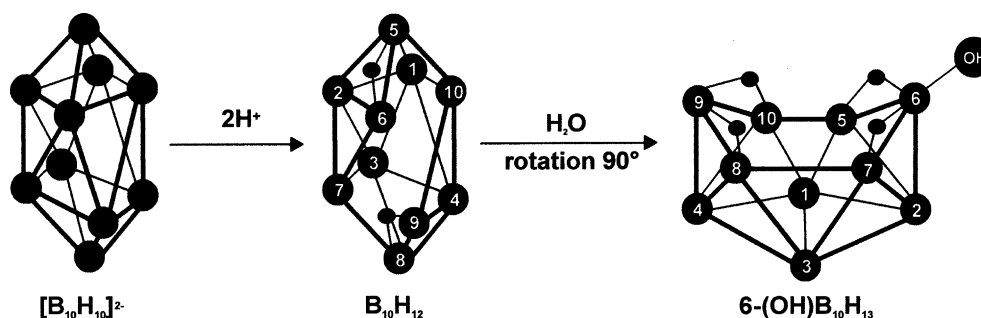
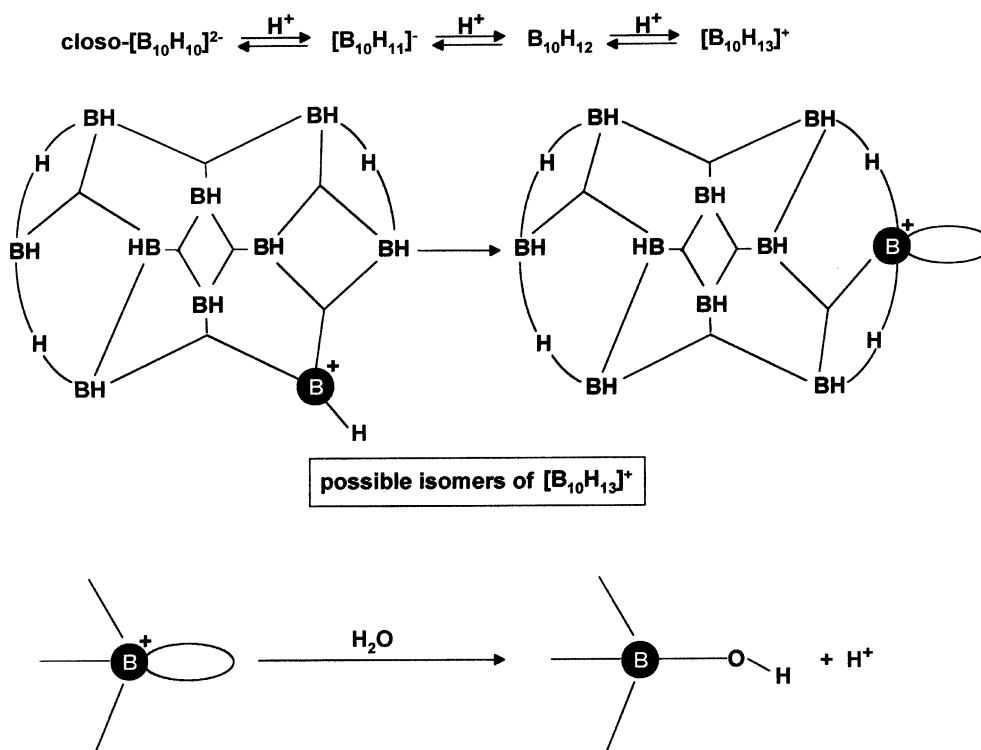
[B₁₀H₁₀]²⁻ is the starting material from which [LB₁₀H₉]⁻ derivatives are prepared [5]. These derivatives are used in boron neutron capture therapy while B₁₀H₁₄ is used to prepare the decaborane derivatives, 6,9-L₂B₁₀H₁₂ and 6-LB₁₀H₁₃ [6]. 6,9-L₂B₁₀H₁₂ is the starting product in the synthesis of carboranes C₂B₁₀H₁₂. 6-LB₁₀H₁₃ serves as important intermediates in the synthesis of new derivatives of B₁₀H₁₄ [7].

B₁₀H₁₄ or its 6,9-arachno-L₂B₁₀H₁₂ derivatives were converted to [B₁₀H₁₀]²⁻ by the action of amines [8,9] or NH₃ [10]. The reverse conversion requires the opening of the very stable [B₁₀H₁₀]²⁻ cage. In strong acidic medium and in the presence of chelating and not highly polar solvent L, the cage [B₁₀H₁₀]²⁻ is opened and 6,9-L₂B₁₀H₁₂ is produced [11–13]. When the solvent L is non polar and not chelating as C₆H₆ and in presence of the very strong acid CF₃SO₃H, the conversion products are 6-(C₆H₅)B₁₀H₁₃ and 6-(OSO₃H)B₁₀H₁₃ [13]. In highly polar solvents such as amines or nitriles, L₂B₁₀H₁₂, [LB₁₀H₁₁]⁻ and [B₁₀H₁₁]⁻ are produced [14]. We reported [15] that LB₉H₁₃, an important starting material in the synthesis of carboranes, heterocarboranes and metallaboranes, is produced.

In the present work, we report the opening reaction of the [B₁₀H₁₀]²⁻ cage in acidic medium and in absence of ligand L. We prove that this reaction produces 6-(OH)B₁₀H₁₃ and not B₁₀H₁₄ as it was mentioned in the literature [19]. Since 6-(OH)B₁₀H₁₃ has been detected

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Fig. 1. Structures of closo-[B₁₀H₁₀]²⁻ and nido-B₁₀H₁₄.Fig. 2. Possible mechanism of 6-(OH)B₁₀H₁₃ formation by [B₁₀H₁₀]²⁻ cage opening. Numbering of boron atoms is as for decaborane derivatives.Fig. 3. Possible mechanism of formation of 6-(OH)B₁₀H₁₃ by [B₁₀H₁₀]²⁻ cage opening.

as by product in all reactions of [B₁₀H₁₀]²⁻ cage opening, we are sure that this formation is due to the pres-

ence of water molecules which act as chelating ligand in this reaction.

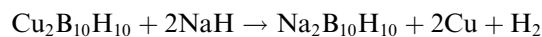
6,6'-bis(nido-decaboranyl) oxide, $(\text{B}_{10}\text{H}_{13})\text{O}(\text{B}_{10}\text{H}_{13})$, was prepared by the reaction of concentrated sulfuric acid with the decaborane(14) derivative, 6,9-(R_2S) $_2$ - $\text{B}_{10}\text{H}_{12}$ ($\text{R} = \text{Et}, \text{Me}$) [16]. It was mentioned [17] that this reaction produces the $\text{B}_{10}\text{H}_{14}$ derivative, 6-(OH) $\text{B}_{10}\text{H}_{13}$. This method of preparation proceeds via $\text{B}_{10}\text{H}_{14}$ or its derivatives which are considered to be toxic. 6-(OH) $\text{B}_{10}\text{H}_{13}$ has also been detected as by product in the dehydration reaction of an aqueous solution of $(\text{H}_3\text{O})_2[\text{B}_{10}\text{H}_{10}]$ [18].

We report its simple synthesis by reaction of $(\text{NH}_4)_2[\text{B}_{10}\text{H}_{10}]$ salt with very concentrated acids (i.e., H_2SO_4 or H_3PO_4). Our reaction occurs readily at room temperature, when pure acid is added drop wise to a suspension of $(\text{NH}_4)_2[\text{B}_{10}\text{H}_{10}]$ salt in an inert solvent such as hexane. 6-(OH) $\text{B}_{10}\text{H}_{13}$ dissolves as it is formed, with a 30% yield, and thus, is not decomposed. A part of the starting material also reacts with the acid to give boric acid. To know the role of H_2O molecules, the above reaction is carried out in a more diluted acidic medium. The reaction does not proceed and only cationic exchange takes place to produce $(\text{H}_3\text{O})_2[\text{B}_{10}\text{H}_{10}]$.

The mechanism of the reaction between $[\text{B}_{10}\text{H}_{10}]^{2-}$ and concentrated acids would be very similar to that between strong acid and a $[\text{B}_{10}\text{H}_{10}]^{2-}$ anion salt in diethylsulphide suspension, from which $(\text{Et}_2\text{S})_2\text{B}_{10}\text{H}_{12}$ is obtained [12,13]; the first step is the fixation of one proton on each of the apical positions. Cage opening occurs when hydrogen-bridge bonds form between (B-5 and B-6), (B-8 and B-9) and boron–boron bonds are destroyed (Fig. 2).

The formation of 6-(OH) $\text{B}_{10}\text{H}_{13}$ by the $[\text{B}_{10}\text{H}_{10}]^{2-}$ cage could be explained by another mechanism which possibly involves the reactive intermediate open cage species $[\text{B}_{10}\text{H}_{13}]^+$ formed by the addition of three protons to $[\text{B}_{10}\text{H}_{10}]^{2-}$ [20] (Fig. 3); $[\text{B}_{10}\text{H}_{13}]^+$ rearranges into an isomer by the conversion of an empty localized skeletal orbital to an empty terminal boron orbital by an internal hydride migration. The cationic B-6 then attacks H_2O , an available electron source to give 6-(OH) $\text{B}_{10}\text{H}_{13}$.

Attempts to reproduce the opening of the $[\text{B}_{10}\text{H}_{10}]^{2-}$ cage in basic or neutral media have been unsuccessful. For instance, the reduction of the cuprous salt $\text{Cu}_2\text{B}_{10}\text{H}_{10}$ in solution in acetonitrile by NaH does not yield the expected compound $\text{Na}_2\text{B}_{10}\text{H}_{12}$. These results confirm the role played by acids in the opening of the $[\text{B}_{10}\text{H}_{10}]^{2-}$ cage.



1. Experimental

1.1. Synthesis

To a stirred suspension of 1.6 g (10.4 mmol) of $(\text{NH}_4)_2[\text{B}_{10}\text{H}_{10}]$ in 40 ml of hexane at room temperature

was added drop-wise 2 ml of pure sulfuric acid (2 ml in 30 min). A yellow, gummy material was formed and the solution was decanted and filtered. Hexane was removed under vacuum and yellowish-white needles of 6-(OH) $\text{B}_{10}\text{H}_{13}$ were recovered (0.43 g, 3.2 mmol, yield 30%).

1.2. Characterization

Boron (^{11}B) NMR spectra were obtained at 96.29 MHz on a Bruker WF-300 spectrometer and were, externally referenced to as $\text{Et}_2\text{O} \cdot \text{BF}_3$ (positive values downfield). (^{11}B) NMR spectra for 6-(OH) $\text{B}_{10}\text{H}_{13}$: $\{\delta(^{11}\text{B})/\text{ppm} : +26.72$ (1B, singlet), $+5.38$ (3B, doublet, 143 Hz), $+3.82$ (2B, doublet, 158 Hz), -13.35 (2B, doublet, 170 Hz), -31.56 (1B, doublet, 160 Hz), -43.80 (1B, doublet, 157 Hz) $\}$ were in complete agreement with published data [16,17]. IR spectra were recorded on a Nicolet Magna 550 FT spectrometer using KBr pressed discs. IR spectra of 6-(OH) $\text{B}_{10}\text{H}_{13}$ exhibited a band at 3570 cm^{-1} , assigned to the OH stretching vibration [17]. Mass spectroscopy measurements were realized on Fisons model (EI, 70 eV) at the Mass spectroscopy Laboratory, Analytical Central Service of the CNRS, Solaise (France). For 6-(OH) $\text{B}_{10}\text{H}_{13}$: $m/z = 133.2$, calculated 138. The difference between the experimental and calculated values of m/z could be due to the abstractions of hydrogen atoms. Such a difference was observed by Greenwood [21] for certain $\text{B}_{10}\text{H}_{14}$ derivatives.

References

- [1] R. Dobrott, W. Lipscomb, *J. Chem. Phys.* 37 (1962) 1779.
- [2] J. Kasper, C. Lucht, D. Harker, *J. Am. Chem. Soc.* 70 (1948) 881.
- [3] J. Kasper, C. Lucht, D. Harker, *Acta Cryst.* 3 (1950) 436.
- [4] E. Moore, R. Dickerson, W. Lipscomb, *J. Chem. Phys.* 27 (1957) 209.
- [5] D. Naoufal, B. Bonnetot, H. Mongeot, *Polyhedron* 18 (1999) 931.
- [6] R. Schaeffer, *J. Am. Chem. Soc.* 79 (1957) 1006.
- [7] R. Holtzmann, *Production of Boranes and Related Research*, Academic Press, New York, 1967.
- [8] M.F. Hawthorne, R. Pilling, *Inorg. Synth.* 9 (1967) 16.
- [9] T. Heying, C. Naar-Colin, *Inorg. Chem.* 2 (1964) 282.
- [10] E. Muettertis, J. Balthis, Y. Chia, *Inorg. Chem.* 3 (1964) 444.
- [11] M. Marshall, R. Hunt, G. Hefferan, US Patent 3489812, 1970.
- [12] M. Marshall, R. Hunt, G. Hefferan, *J. Am. Chem. Soc.* 89 (1967) 3361.
- [13] G. Guillevic, J. Dazort, H. Mongeot, *J. Chem. Res. (M)* (1978) 4864.
- [14] P. Wegner, D. Adams, F. Callabretta, *J. Am. Chem. Soc.* 95 (1973) 7513.
- [15] D. Naoufal, B. Gruner, B. Bonnetot, *Main Group Metal Chem.* 22 (1999) 127.
- [16] S. Hermanek, J. Plesek, B. Stibr, *Coll. Czech. Chem. Commun.* 33 (1968) 691.