THE INTERACTION OF THE [B$_{10}$H$_{10}$]$^{2-}$ CAGE WITH LEWIS ACIDS AND THE FORMATION OF DECABORANE DERIVATIVES BY CAGE-OPENING REACTIONS

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Dedicated to Professor Jaromir Plesek on the occasion of his 70th birthday in recognition of his outstanding contributions to organic, borane and carborane chemistry. We had several times the advantage of working with him and would like to express our gratitude to the great chemist and the humanist that he is.

The interaction of hydroborates M$_2$[B$_{10}$H$_{10}$] (M = NH$_4$, Et$_4$N, Bu$_4$N, *etc.*) or Et$_4$N[B$_{10}$H$_9$-NH$_2$COCH$_3$] with Lewis acids AlX$_3$ (X = Cl, Br, I) in the solid state is sufficiently strong to produce an increase of more than 85 cm^{-1} of the BH stretching vibrations. A similar interaction was not observed for the hydroborate (NH$_4$)$_2$[B$_{10}$H$_9$I] owing to the electronegativity of the iodine substituent which hampers the electron donor properties of the cage. Hydrolysis of (AlX$_3$)$_n$–[B$_{10}$H$_{10}$]$^{2-}$ adducts under mild conditions results in opening of the boron cage with the formation of halodecaboranes 6-B$_{10}$H$_{13}$X. It seems that this reaction proceeds only when the above adducts can form in a preliminary step. Pure hexane solutions of 6-B$_{10}$H$_{13}$X were easily obtained with a 45% yield for X = Cl or Br and a 30% yield when X = I.
Key words: Decaborane; Halodecaboranes; *closo*-Decahydrodecaborate(2–); *closo*-Hydroborate anions.

Aluminium trichloride reacts with the hydroborates M$_2$[B$_{10}$H$_{10}$] (M = Et$_4$N, Bu$_4$N, K or Na) in the solid state[1] and the products obtained are dissociated by THF by complexation and dissolution of the AlCl$_3$. The formation of these products resulted in an increase of more than 100 cm^{-1} of the BH stretching vibrations. A possible interpretation supposed a disproportionation of AlCl$_3$ leading to the formation of [AlCl$_4$]$^-$ and its cationic counterpart [AlCl$_2$]$^+$ or Al^{3+} which would associate with the cage. Such scheme is comparable to those proposed for the formation of AlCl$_3$ complexes with various Lewis

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bases including CH_3COCCl_3 (ref.[2]), Et_2O (ref.[3]), Me_2O, $MeCN$, HCO_2Me (ref.[4]) and THF (refs[5,6]) but is not consistent with IR and ^{27}Al NMR data. A more probable interpretation consists in the coordination of $AlCl_3$ to a boron–boron bond with a charge redistribution leading to the localization of a negative charge on the $AlCl_3$ group (Fig. 1). The number of $AlCl_3$ groups attached to the cage in this manner should be one or two and each of them should be capable of coordinating another aluminium chloride group similarly to $[AlCl_4]^-$ when $[Al_2Cl_7]^-$ forms.

Hydrolysis of the complexes formed from $[B_{10}H_{10}]^{2-}$ and $AlCl_3$ or reaction of $(R_4N)_2[B_{10}H_{10}]$ (R = H, Me, Et, *etc.*) with hydrated $[B_{10}H_{10}]^{2-}$ results in opening of the $[B_{10}H_{10}]^{2-}$ cage. $6\text{-}B_{10}H_{13}Cl$ is the only chloroborane obtained[7]; the reaction has to be carried out without water excess and in presence of an organic solvent dissolving the chloroborane as soon as it forms. The opening of the $[B_{10}H_{10}]^{2-}$ cage can occur without preliminary adduct formation with a Lewis acid but a few number of such reactions have been described in the literature. They concern the formation of bis(dialkylsulfide)decaborane $B_{10}H_{12}(Et_2S)_2$ (refs[8,9]), decaborane $B_{10}H_{14}$ (ref.[10]), $B_{10}H_{13}OH$ and $B_{10}H_{13}OB_{10}H_{13}$ (ref.[11]). The formation of these compounds requires the addition of two protons and two neutral moieties to the cage as depicted in Fig. 2. This process is the reverse to the conversion of decaborane $B_{10}H_{14}$ to $[B_{10}H_{10}]^{2-}$ in basic medium[12–14]. In the present work we have investigated some of the possibilities to extend to other halodecaborane derivatives the method of preparation based on the hydrolysis of $[B_{10}H_{10}]^{2-}$–Lewis acid adducts. $AlCl_3$, $AlBr_3$ and AlI_3 were used as Lewis acids. We have also attempted to convert $[B_{10}H_9I]^{2-}$ and $[B_{10}H_9\text{-}NH_2COCH_3]^-$ to decaborane derivatives using the same process as for $[B_{10}H_{10}]^{2-}$.
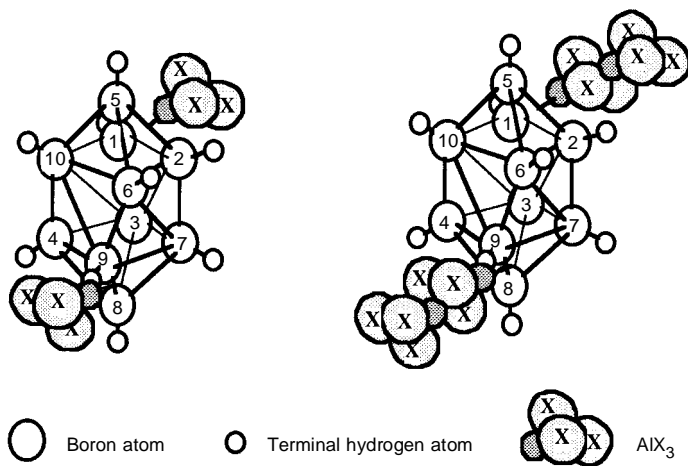
F$_{IG}$. 1
Possible structure for $[B_{10}H_{10}(AlX_3)_2]^{2-}$ and $[B_{10}H_{10}(Al_2X_6)_2]^{2-}$

RESULTS AND DISCUSSION

As described above, $AlCl_3$ interacts in the solid state with the $[B_{10}H_{10}]^{2-}$ cage of deca-hydroborates and, as expected, we observed the same effect when $AlBr_3$ or AlI_3 were used instead of $AlCl_3$ (Table I). The behaviour of $[B_{10}H_9I]^{2-}$ and $[B_{10}H_9\text{-}NH_2COCH_3]^-$ in presence of AlX_3 was less predictable, no interaction was detected with the former whereas an increase of 87.4 cm^{-1} in the BH stretching frequency indicated that an ad-duct had been formed with the latter. The adduct formation was attributed to the ability of the B_{10} cage to release electrons[1]. In this regard iodine appears as sufficiently eletron attractive to prevent the cage from donating electrons whereas this property is preserved when $[B_{10}H_{10}]^{2-}$ is converted to the monoanion $[B_{10}H_9\text{-}NH_2COCH_3]^-$.

Hydrolysis of $AlX_3–[B_{10}H_{10}]^{2-}$ adducts leads to the formation of pure $6\text{-}B_{10}H_{13}X$ with 45% yields when X = Cl, Br or a 30% yield when X = I. The ^{11}B NMR and IR data obtained for these compounds (Tables II and III) are consistent with those already

TABLE I
Effect of the adduct formation on the BH stretching vibrations and the B–B skeletal stretching vibrations of $[B_{10}H_{10}]^{2-}$ (the $AlX_3/[B_{10}H_{10}]^{2-}$ ratio was ≥ 4)

Compound	γ(B–H), cm^{-1}	γ(B–B), cm^{-1}
$(NH_4)_2[B_{10}H_{10}]$	2 444	1 034–1 008
$(NH_4)_2[B_{10}H_{10}]–(Al_2Cl_6)_2$	2 563	1 033–1 000
$(NH_4)_2[B_{10}H_{10}]–(Al_2Br_6)_2$	2 575	1 031–999
$(NH_4)_2[B_{10}H_{10}]–(Al_2I_6)_2$	2 560	1 031–1 003
$(NH_4)_2[B_{10}H_9–NH_2COCH_3]–(Al_2Cl_6)_2$	2 531	–

○ Boron atom　　◯ Terminal hydrogen atom　　● Bridging hydrogen atom
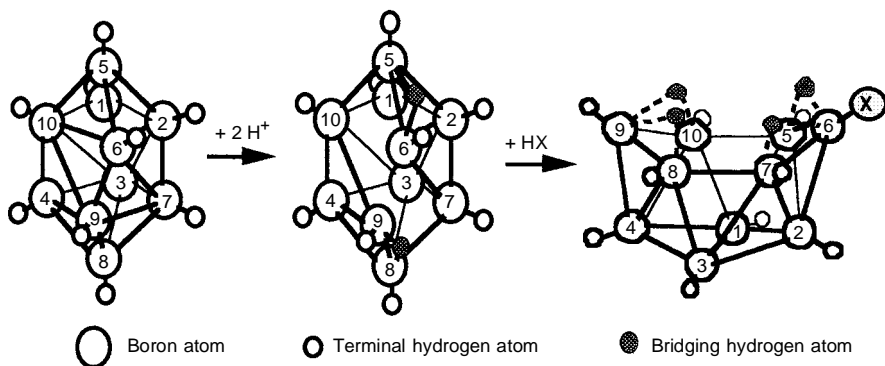
FIG. 2
Proposed scheme for the opening of the $[B_{10}H_{10}]^{2-}$ cage

published[15,16]. The hydrolysis has to take place in presence of hexane in order to dissolve the haloborane as soon as it is formed. The hydrolysis has also to be carried out under mild conditions to prevent formation of $6\text{-}B_{10}H_{13}OH$; this product is present as an impurity in all cage-opening reactions of $[B_{10}H_{10}]^{2-}$ whenever H_2O may interfere in the formation process of the product. In the present case that means that the H_2O concentration in the reaction medium must be just sufficient to produce some hydrolysis of the more reactive aluminium halide part of the adduct. The above process is the most convenient route to 6-halodecaboranes especially in the case of bromo and iodo derivatives. Mixtures of decaborane isomers halogenated at the 5 and 6 boron atoms have been obtained for the first time by Stibr, Plesek and Hermanek from the reaction of the anhydrous halogen halide with a decaborane dialkyl sulfide diligand[17,18], $B_{10}H_{12}(R_2S)_2$ (R = CH_3, C_2H_5). Preparative thin layer chromatography was used in the purification of halodecarborane isomers[19]. The method that we have used for the preparation of 6-halodecaborane could not be successfully applied to the preparation of dihalo derivatives of decaborane from $[B_{10}H_9I]^{2-}$. This should be due to the absence of any interaction of this anion with $AlCl_3$ or AlI_3. Our failure in obtaining a borane by hydrolysis of $[B_{10}H_9\text{-}NH_2COCH_3]^-\text{-}AlCl_3$ adducts was due to the instability of the borane formed as indicated by the presence of boric acid.

Opening of the $[B_{10}H_{10}]^{2-}$ cage requires the addition of two protons (Fig. 2) explaining that this reaction has been shown to occur when the cage was in contact either with

TABLE II
^{11}B Chemical shifts (δ, ppm) for halogen substituted $6\text{-}B_{10}H_{13}X$

X	B(1)	B(2)	B(3)	B(4)	B(5)	B(6)	B(7)	B(8)	B(9)	B(10)
Cl	9.6	–32.0	9.6	–39.7	–2.5	18.8	–2.5	2.5	9.6	2.5
Br	10.7	–32.4	10.7	–38.3	–0.4	9.8	–0.4	2.1	10.7	2.1
I	12.2	–32.1	12.2	–36.7	2.1	–5.7	2.1	2.1	10.3	2.1

TABLE III
Infrared data (cm^{-1}) for halogen substituted $6\text{-}B_{10}H_{13}X$

X	γ(B–H) terminal	γ(B–H) bridging	δ(B–H) bridging	δ(B–H) terminal or γ(B–B)	γ(B–X)
Cl	2 584	1 902	1 499–1 413	1 046–990	1 064–1 046
Br	2 589	1 897	1 499–1 459	1 102–1 021	868–807
I	2 589	1 900	1 510–1 413	1 102–1 026	863–807

a liquid containing a strong acid in high concentration or with a Lewis acid releasing protons by hydrolysis. All these reactions probably obey similar mechanisms since the proton addition is always accompanied by the addition of neutral moieties at the 6 and 9 positions. When aluminium halides are used, the preliminary formation of an adduct with the cage seems to be a necessary step of the cage-opening process: the formation of haloboranes in appreciable concentrations has never been observed when the hydroborates were not able to interact with the aluminium halide. Another argument for this assumption is that hydrogen chloride does not react when bubbled through a hexane suspension of $(NEt_4)_2[B_{10}H_{10}]$. A favourable effect on the haloborane formation due to the adduct may consist in maintain a proton source close to the cage when the hydrolysis takes place. The adduct may also act in a further step of the process: after addition of two protons (Fig. 2), the next step is probably a nucleophilic attack of the neutral $B_{10}H_{12}$ species. This attack may be favoured owing to the transfer of electrons from the cage to the aluminium part of the adduct.

EXPERIMENTAL

^{11}B NMR spectra were recorded on a Bruker AM 300 instrument at 96.28 MHz with $Et_2O \cdot BF_3$ as an external reference. The IR spectra of the solid adducts were obtained from Nujol mulls and those of the boranes as concentrated hexane solutions in a hermetic cell with CsI windows on a 550 Nicolet spectrometer.

$(NH_4)_2B_{10}H_{10}$ was provided by Katchem (Prague), $(NH_4)_2[B_{10}H_9I]$ was a mixture of 1- and 2-isomer[20] obtained by iodination of $(NH_4)_2[B_{10}H_{10}]$. $[B_{10}H_9-NH_2COCH_3]^-$ was prepared by substitution of acetonitrile for the diazo group of $[B_{10}H_9N_2]^-$ and subsequent hydrolysis of the product obtained[21–24]. The salts were dried at 0.05 Pa and 120 °C for at least 24 h before use. Aluminium halides were provided by Aldrich and were used as received.

The $(AlX_3)_n-[B_{10}H_{10}]^{2-}$ adducts were prepared in a dry box in an argon atmosphere. In a typical reaction $(NH_4)_2[B_{10}H_{10}]$ (0.6 g, 3.9 mmol) and an appropriate amount of aluminium halide were stirred in refluxing hexane (the hydroborate and the aluminium halide were usually taken in a 1/2 or 1/4 ratio in accordance with the type of adduct prepared). Hexane played the role of a heat transfer agent maintaining a homogeneous temperature in the reaction medium. After 12 h, the IR spectrum of the solid had ceased to change and all solid could be recovered by filtration. A side reaction was observed when AlI_3 was used: AlI_3 slowly decomposed releasing iodine which reacted with $[B_{10}H_{10}]^{2-}$ and so partly prevented formation of the adduct.

When the above adducts were converted to halodecaborane by slow hydrolysis, hexane was not separated from the solid and the reaction mixture was stirred for 12 h in contact with the atmosphere. The haloborane could be recovered as a solid after evaporation of the solvent at reduced pressure.

REFERENCES

1. Bonnetot B., Aboukhassib A., Mongeot H.: Inorg. Chim. Acta *156*, 183 (1989).
2. Cassimatis D., Bonnin J. P., Theophanides T.: Can. J. Chem. *48*, 3860 (1970).
3. Jones D. E. H., Wood J. L.: J. Chem. Soc., A *1966*, 1448.
4. Jones D. E. H., Wood J. L.: J. Chem. Soc., A *1972*, 3135.
5. Derouault J., Forel M. T.: Inorg. Chem. *16*, 3207 (1977).

6. Derouault J., Granger P., Forel M. T.: Inorg. Chem. *16*, 3214 (1977).
7. Mongeot H., Atchekzai J., Bonnetot B., Colombier M.: Bull. Soc. Chim. Fr. *1987*, 75.
8. Marshall H. D., Hunt R. M., Hefferan G. T., Adams R. M., Makhlouf J. M.: J. Am. Chem. Soc. *89*, 3361 (1967).
9. Guillevic G., Dazord J., Mongeot H., Cueilleron J.: J. Chem. Res. (S) *1978*, 402.
10. Mongeot H., Atchekzai H. R.: Z. Naturforsch. B *36*, 313 (1981).
11. Bonnetot B., Tangi A., Colombier M., Mongeot H.: Inorg. Chim. Acta *105*, L15 (1985).
12. Hawthorne M. F., Pilling R.: Inorg. Synth. *9*, 16 (1967).
13. Heying T. L., Naar-Colin C.: Inorg. Chem. *2*, 16 (1967).
14. Muetterties E. L., Balthis J. H., Chia Y. T., Knoth W. H., Miller H. C.: Inorg. Chem. *3*, 444 (1964).
15. Hermanek S.: Chem. Rev. *92*, 325 (1992).
16. Hanousek F., Stibr B., Hermanek S., Plesek J., Vitek A., Haruda F.: Collect. Czech. Chem. Commun. *37*, 3001 (1972).
17. Plesek J., Stibr B., Hermanek S.: Collect. Czech. Chem. Commun. *31*, 4744 (1966).
18. Stibr B., Plesek J., Hermanek S.: Collect. Czech. Chem. Commun. *34*, 194 (1969).
19. Sprecher R. F., Aufderheide B. E., Luther III G. W., Carter J. C.: J. Am. Chem. Soc. *96*, 4404 (1974).
20. Knoth W. H., Miller H. C., Sauer J. C., Balthis J. H., Chia Y. T., Muetterties E. L.: Inorg. Chem. *3*, 159 (1964).
21. Leyden R. N., Hawthorne F. M.: J. Am. Chem. Soc. *95*, 2032 (1973).
22. Leyden R. N., Hawthorne F. M.: Inorg. Chem. *14*, 2444 (1975).
23. Lai-Ling Ng, Shelly K., Cnobler C. B., Hawthorne F. M.: Inorg. Chem. *30*, 4278 (1991).
24. Knoth W. H.: J. Am. Chem. Soc. *88*, 935 (1966).