

### Preliminary communication

## AN UNUSUAL HALOGEN EXCHANGE IN A *closo*-CARBORANE SYSTEM\*

KEITH FULLER and THOMAS ONAK\*

*Department of Chemistry, California State University, Los Angeles, California 90032 (U.S.A.)*

(Received January 12th, 1983)

### Summary

The 1/1 amine/bromocarborane adduct  $(\text{CH}_3)_3\text{N} \cdot 5\text{-BrC}_2\text{B}_5\text{H}_6$  undergoes quantitative Br/Cl exchange with  $\text{CH}_2\text{Cl}_2$ , forming  $5\text{-ClC}_2\text{B}_5\text{H}_6$  and  $[(\text{CH}_3)_3\text{NCH}_2\text{Cl}]^+ \text{Br}^-$ . From the results of control experiments it is suggested that a  $[5\text{-(CH}_3)_3\text{N-2,4-C}_2\text{B}_5\text{H}_6]^+$  intermediate plays an important role in this exchange reaction.

Recently we reported that all three *B-Cl-closo-2,4-C}\_2\text{B}\_5\text{H}\_6* isomers react with  $(\text{CH}_3)_3\text{N}$  to form 1/1 adducts which can be converted, upon adding  $\text{BCl}_3$ , to  $[B\text{-(CH}_3)_3\text{N-closo-2,4-C}_2\text{B}_5\text{H}_6] \text{BCl}_4^-$  [1]. An effort to carry out similar chemistry on  $5\text{-Br-closo-2,4-C}_2\text{B}_5\text{H}_6$  has resulted in the observation of an unusual halogen exchange reaction with the solvent,  $\text{CH}_2\text{Cl}_2$ .

The desired starting material in this sequence  $5\text{-Br-closo-2,4-C}_2\text{B}_5\text{H}_6$ , was prepared in a manner similar to that described earlier [2] except that the use of  $\text{CS}_2$  was found to be unnecessary;  $^{11}\text{B}$  NMR (160.44 MHz):  $-20.1$  ppm (d, 2B, B(1,7),  $J(\text{BH})$  185 Hz),  $+2.2$  ppm (d, 1B, B(6),  $J(\text{BH})$  173 Hz),  $+5.9$  ppm (d, 1B, B(3),  $J(\text{BH})$  189 Hz),  $+7.7$  ppm (s, 1B, B(5));  $^1\text{H}$  NMR: 0.50 ppm (1/1/1/1 q, 2H, H(1,7),  $J(\text{HB})$  184 Hz), 3.99 ppm (1/1/1/1 q, 1H, H(6),  $J(\text{HB})$  175 Hz), 4.79 ppm (1/1/1/1 q, 1H, H(3),  $J(\text{HB})$  188 Hz), 5.50 ppm (s, 1H, H(2 or 4)), 5.61 (s, 1H, H(4 or 2)). The conversion of  $5\text{-Br-closo-2,4-C}_2\text{B}_5\text{H}_6$  to the 1/1 adduct with  $(\text{CH}_3)_3\text{N}$  was accomplished in  $\text{CDCl}_3$ . Clear colorless crystals of  $(\text{CH}_3)_3\text{N} \cdot 5\text{-BrC}_2\text{B}_5\text{H}_6$  separated from the solution within 2 days; these crystals, soluble in  $\text{CH}_2\text{Cl}_2$  and slightly soluble in  $\text{CHCl}_3$ , were characterized by  $^{11}\text{B}$  NMR:  $-19.9$  ppm (d, 2B, B(1,7),  $J(\text{BH})$  186 Hz),  $+0.8$  ppm (d, 1B, B(6),  $J(\text{BH})$  176 Hz),  $+6.1$  ppm (d, 1B, B(3),  $J(\text{BH})$  ca. 180 Hz),  $+16.9$  ppm (s, 1B, B(5));  $^1\text{H}$  NMR: 0.30 ppm (1/1/1/1 q, 2H, H(1,7),  $J(\text{HB})$  184 Hz), 3.74 ppm (1/1/1/1 q, 1H, H(6),  $J(\text{HB})$  ca. 173 Hz), 4.49 ppm (1/1/1/1 q, 1H, H(3),  $J(\text{HB})$  ca. 187 Hz), 5.26 (s, 1H, H(2 or 4)), 7.18 ppm (s, 1H, H(4 or 2)), 3.40 ppm (s, 9H,  $\text{CH}_3\text{N}$ ).

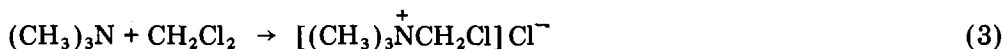
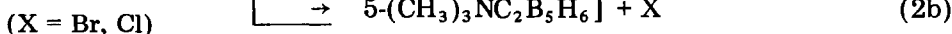
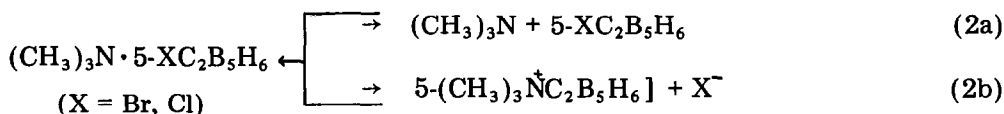
\*Dedicated to Professor H.J. Emeléus on the occasion of his 80th birthday on 22nd June 1983.

After dissolution of the adduct,  $(\text{CH}_3)_3\text{N} \cdot 5\text{-BrC}_2\text{B}_5\text{H}_6$ , in  $\text{CH}_2\text{Cl}_2$  a slow but quantitative conversion to 5-Cl-*closo*-2,4- $\text{C}_2\text{B}_5\text{H}_6$  ensues according to eq. 1, as monitored by  $^{11}\text{B}$  and  $^1\text{H}$  NMR.



After completion of the reaction cold column fractionation of the volatile portion removes the excess  $\text{CH}_2\text{Cl}_2$  and gives pure 5- $\text{ClC}_2\text{B}_5\text{H}_6$  identified by both  $^{11}\text{B}$  and  $^1\text{H}$  NMR [3]. The  $^{11}\text{B}$  NMR of the nonvolatile crystalline solids (dissolved in  $\text{CD}_3\text{OD}$ ) from the reaction mixture shows no evidence of a boron containing compound, and the  $^1\text{H}$  NMR is consistent with  $[(\text{CH}_3)_3\text{NCH}_2\text{Cl}]\text{Br}$ .

It is to be noted that a control experiment indicated that no reaction takes place between 5- $\text{BrC}_2\text{B}_5\text{H}_6$  and  $\text{CH}_2\text{Cl}_2$ . This observation and other considerations mentioned below suggest that the following steps, eq. 2 and 3, may account for the halogen exchange involving the adduct.



In solution it is anticipated that a very small equilibrium amount of free trimethylamine is available from the adduct, eq. 2a [1]; and the free amine is expected to quantitatively react with  $\text{CH}_2\text{Cl}_2$  to form  $[(\text{CH}_3)_3\overset{+}{\text{N}}\text{CH}_2\text{Cl}]\text{Cl}^-$ , eq. 3 [4]. Formal interchange of halide ions between  $[(\text{CH}_3)_3\overset{+}{\text{N}}\text{CH}_2\text{Cl}]\text{Cl}^-$  and  $[5\text{-}(\text{CH}_3)_3\overset{\dot{\text{N}}}{\text{C}}\text{-}closo\text{-}2,4\text{-C}_2\text{B}_5\text{H}_6]\text{Br}^-$  (present in small quantity from eq. 2b) gives access to  $(\text{CH}_3)_3\text{N} \cdot 5\text{-Cl-}2,4\text{-C}_2\text{B}_5\text{H}_6$  via the reverse of eq. 2b,  $\text{X} = \text{Cl}$ . Once  $(\text{CH}_3)_3\text{N} \cdot 5\text{-ClC}_2\text{B}_5\text{H}_6$  is formed, subsequent removal of  $(\text{CH}_3)_3\text{N}$  by way of eq. 3 drives eq. 2a ( $\text{X} = \text{Cl}$ ) to the right, giving the observed carborane product, 5- $\text{ClC}_2\text{B}_5\text{H}_6$ , and producing more  $[(\text{CH}_3)_3\overset{+}{\text{N}}\text{CH}_2\text{Cl}]\text{Cl}^-$  for further halide exchange. In an independent experiment it indeed has been found that a mixture of  $(\text{CH}_3)_3\text{N} \cdot 5\text{-ClC}_2\text{B}_5\text{H}_6$  and  $\text{CH}_2\text{Cl}_2$  converts quantitatively to 5- $\text{ClC}_2\text{B}_5\text{H}_6$  and the salt  $[(\text{CH}_3)_3\overset{+}{\text{N}}\text{CH}_2\text{Cl}]\text{Cl}^-$  [5].

The equilibrium between adduct and ion, eq. 2b, is suggested by other work [1] where it was unexpectedly found that  $\text{BCl}_3$  rapidly, and quantitatively, extracts  $\text{Cl}^-$  (rather than  $(\text{CH}_3)_3\text{N}$ ) from  $(\text{CH}_3)_3\text{N} \cdot 5\text{-ClC}_2\text{B}_5\text{H}_6$ . In support of the implied equilibrium direction of eq. 2b it has been observed that the treatment of  $[5\text{-}(\text{CH}_3)_3\overset{\dot{\text{N}}}{\text{C}}\text{-}closo\text{-}2,4\text{-C}_2\text{B}_5\text{H}_6]\text{BCl}_4^-$  with  $(\text{CH}_3)_3\text{N}$  results in the formation of the adduct  $(\text{CH}_3)_3\text{N} \cdot 5\text{-ClC}_2\text{B}_5\text{H}_6$  and  $(\text{CH}_3)_3\text{N} \cdot \text{BCl}_3$  [5]; the assumed carborane intermediate,  $[5\text{-}(\text{CH}_3)_3\overset{\dot{\text{N}}}{\text{C}}\text{-}closo\text{-}2,4\text{-C}_2\text{B}_5\text{H}_6]\text{Cl}^-$  is apparently unstable relative to the adduct.

Given the above results it may be reasonably questioned why 5-*Br-closo*-2,4- $\text{C}_2\text{B}_5\text{H}_6$  is not produced in substantial quantity when its trimethylamine adduct is treated with  $\text{CH}_2\text{Cl}_2$ . But if a route to the chlorocarborane is available within the proposed mechanistic scheme the nature of observed product, 5- $\text{XC}_2\text{B}_5\text{H}_6$  ( $\text{X} = \text{Cl}$  and/or  $\text{Br}$ ?), can then be decided by thermodynamic stability factors. It would follow that an important consideration would be the relative stability of the  $\text{Br-B}$  bond versus the  $\text{Cl-B}$  bond, the latter expected to be more energetically favored [6].

**Acknowledgements.** The authors wish to thank the National Science Foundation and the National Institutes of Health, MBRS program (K.F.) for partial support of this study. Some of the NMR data were obtained using a Bruker WM-500 at the Southern California Regional NMR facility at the California Institute of Technology, funded by NSF Grant CHE-7916324. In this regard, the collaboration of L. Müller and E. Krauss is appreciated.

## References

- 1 G. Siwapinyoyos and T. Onak, *Inorg. Chem.*, 21 (1982) 156.
- 2 R.R. Olsen and R.N. Grimes, *J. Am. Chem. Soc.*, 92 (1970) 5072.
- 3 C. Takimoto, G. Siwapinyoyos, K. Fuller, A.P. Fung, L. Liauw, W. Jarvis, G. Millhauser, and T. Onak, 19 (1980) 107.
- 4 H. Böhme, M. Hilp, L. Koch and E. Ritter, *Chem. Ber.*, 104 (1981) 2018.
- 5 G. Siwapinyoyos and T. Onak, unpublished results.
- 6 D.A. Johnson, *Some Thermodynamic Aspects of Inorganic Chemistry*, Cambridge University Press, Cambridge, 1968, page 159.