Journal of Fluorine Chemistry, *27* (1985) 119–122

Received: August 29, 1984; accepted: October 16, 1984

PRELIMINARY NOTE

The Preparation of B-Fluoro Derivatives of the Pentagonal Bipyramidal Closo-2,4-dicarbaheptaborane Carborane System

BRADFORD NG and THOMAS ONAK*

Chemistry Department, California State University, Los Angeles, 90032 (USA)

SUMMARY

The B-Halo-closo-carboranes, 5-Br-2,4-$C_2B_5H_6$ and 3,5-I_2-2,4-$C_2B_5H_5$, are quantitatively converted to the corresponding B-fluoro closed cage derivatives, 5-F-2,4-$C_2B_5H_6$, and 3,5-F_2-2,4-$C_2B_5H_5$. These reactions, accomplished with the use of fluoride ion in a nonaqueous solvent, amount to a net front-side displacement of the cage bonded halogen.

Although numerous carboranes [1,2] are now known, very few fluoro derivatives of these cage compounds of carbon and boron have been prepared. It is believed that B-fluoro derivatives of many small carboranes could well play an important part in promoting partial, or complete, cage opening. This is based on (a) conclusions derived from MO calculations on small closo-carborane derivatives [3,4] and (b) the observation that both the parent nido-2,3,4,5-$C_4B_2H_6$ [5–7] and a peralkyl derivative [8,9] are known to have pentagonal pyramidal geometry whereas the skeletal C_4B_2 unit of the related B,B'-difluoro derivative, $(R)_4C_4B_2F_2$ (prepared from the highly reactive BF species and various acetylenes), is arranged in a 'classical' planar 1,4-diboracyclohexa-2,5-diene configuration [10].

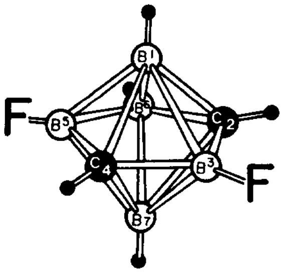
The possibility that B-fluoro derivatives of small closo polyboranes and carboranes may be prone to cage distortions, or cage fluxional behavior, makes it highly desirable to find good yield routes to these unique systems. In a previous study it was observed that treatment of

0022-1139/85/$3.30

the pentagonal bipyramidal closo-2,4-$C_2B_5H_7$ with F_2 results in extensive cage decomposition with only very small yields of desired B-fluoro carboranes realized [11]. We have recently discovered a facile high-yield halogen/halogen displacement reaction that is expected to provide a general pathway to B-fluoro compounds of the carboranes and perhaps other polyhedral systems as well. Although fluoride ion is known to be a poor nucleophile in hydroxylic solvents, the results of several investigations indicate that it is capable of displacing higher halogens in the absence of solvents which hydrogen bond to F^- [12,13]. Displacement reactions at skeletal cage-atom sites of closo carboranes are unknown and would be considered unfeasible via a back-side attack mechanism. It was then unexpected when we found that F^-/X^- (X = Cl, Br, I) exchange occurs rather readily with B-X- derivatives of the pentagonal bipyramidal closo-2,4-$C_2B_5H_7$. Examples are given as follows:

A sample of 5-Br-$C_2B_5H_6$ (0.3 mmoles) was combined with tetrabutylammonium fluoride (0.5 mmoles) in 0.5 mL of tetrahydrofuran and sealed into an NMR tube. After allowing the mixture to stand at room temperature for 2 days, B-11 NMR (160.44 MHz) analysis indicated that approximately half of the starting 5-Br-$C_2B_5H_6$ had disappeared with concurrent appearance of the B-11 pattern [11] of 5-F-$C_2B_5H_6$. The sample was allowed to stand at room temperature for another 14 days after which time 5-F-$C_2B_5H_6$ was observed in the B-11 NMR [resonances at δ = -20.77 ppm, area 2, d, 176 Hz, B(1,7); -6.02, area 1, d, 160 Hz, B(6); +2.74, area 1, d, 175 Hz, B(3); +17.18, area 1, s, B(5)] as the only boron containing component of the reaction mixture. The 5-F-2,4-$C_2B_5H_6$ can also be obtained from a reaction between $(CH_3)_3N$:5-Br-2,4-$C_2B_5H_6$ and $[(C_4H_9)_4N]F$ in CH_2Cl_2 solution. Cold column vacuum fractionation [14] of the volatile portion gives the 5-F-$C_2B_5H_6$ in the -90°C fraction.

In another example, a solution of tetrabutylammonium fluoride (0.5 mmol) in 0.5 mL of tetrahydrofuran was syringed into a solution of 3,5-$I_2C_2B_5H_5$ (0.25 mmole) in 0.5 mL pentane; the mixture was allowed to stand at room temperature for a period of 13 days. Boron-11 NMR (160.44 MHz) analysis of the product showed a 100% conversion to the heretofore unknown 3,5-F_2-closo-2,4-$C_2B_5H_5$ [boron-11 resonances at δ = -17.04 ppm, area 2, d, 173 Hz, B(1,7); -10.58, area 1, d, 148 hz, B(6); +13.00, area 1, s, B(3); +15.33, area 1, s, B(5)].



$3,5\text{-}F_2\text{-closo-}2,4\text{-}C_2B_5H_5$

The mechanism for halogen displacement at a boron site of a closo carborane is not obvious at this time but may well involve partial ionic dissociation of the B-X bond in a first step. Contributing to the driving force for the reaction is the expected increase in bond energy for the conversion of a B-Br bond to a B-F bond [15,16]. This F^- displacement reaction, when coupled to the knowledge that chloro, bromo, and iodo derivatives of carboranes can generally be prepared in excellent yields [1,2], gives promise of an overall high-yield sequence to fluorocarboranes. Syntheses of appropriate per-B-fluoro small-cage carboranes for testing cage pliability arguments should now be practicable by extensions of such a scheme.

The authors wish to thank the National Science Foundation and the National Institutes of Health, MBRS program (B.N.), for partial support of this study. The boron-11 NMR data were obtained using a Brucker WM-500 instrument at the Regional Facility, California Institute of Technology, funded by NSF grant CHE-7916324.

1 R.N. Grimes, Carboranes, Academic Press, New York, 1970.

2 T. Onak, in G. Wilkinson, F.G.A. Stone, and E.W. Abel (Editors), Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, 1982, Vol. 1, Chap. 5.4, p.411.

3 G.D. Graham, D.S. Marynick and W.N. Lipscomb, J. Am. Chem. Soc., 102 (1980) 2939.

4 R.N. Camp, D.S. Marynick, G.D. Graham and W.N. Lipscomb, J. Am. Chem. Soc., 100 (1978) 6781.

5 T. Onak and G.T.F. Wong, J. Am. Chem. Soc., 92 (1970) 5226.

6 V.R. Miller and R.N. Grimes, Inorg. Chem., 11 (1972) 862.

7 J.P. Pasinski and R.A. Beaudet, J. Chem. Phys., 61 (1974) 683.

8 P. Binger, Tetrahedron Lett., (1966) 2675.

9 J. Hasse, Z. Naturforsch., 28a (1973) 785.

10 P.L. Timms, J. Am. Chem. Soc., 90 (1968) 4585; P.L. Timms, Acc. Chem Res., 6 (1973) 118.

11 N.J. Maraschin and R.J. Lagow, Inorg. Chem., 14 (1975) 1855.

12 S. Winstein, L.G. Savedoff, S. Smith, I.D.R. Stevens and J.S. Gall, Tetrahedron Lett., (1960) 24.

13 W.N. Olmstead and J.I. Brauman, J. Am. Chem. Soc., 99 (1977) 4219.

14 J. Dobson and R. Schaeffer, Inorg. Chem., 9 (1970) 2183.

15 R.T. Sanderson, Polar Covalence, Academic Press, New York, 1983, pg. 149.

16 D.A. Johnson, Some Thermodynamic Aspects in Inorganic Chemistry, Cambridge University Press, Cambridge, 2nd Ed., 1982, pg. 202.