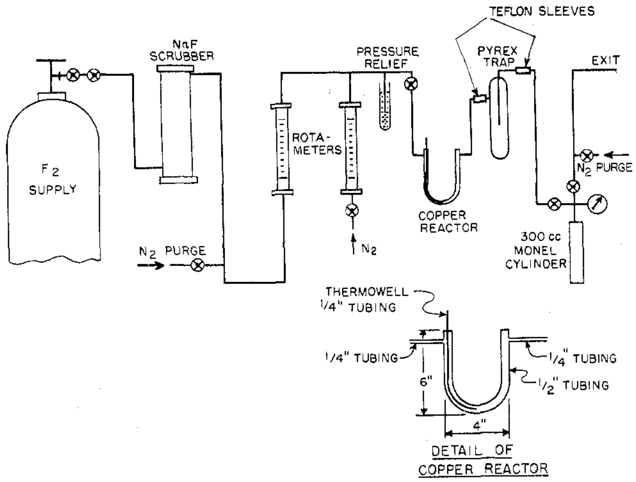


Fig. 1.—Apparatus for preparation of NF_2Cl.

temperature rise. The fluorine flow rate then was increased to 25 ml./min. and maintained at that rate until product ceased to be formed (about 2 hr. for the charge given above). The reaction was monitored continuously by running the product gas through an infrared cell before it was condensed in the Monel cylinder. At the completion, the excess fluorine was flushed from the system with nitrogen, the valves on the Monel cylinder closed, and the cylinder permitted to warm to room temperature. The cylinder contained about 8–10 g. of product which consisted of about 50% NF_2Cl and 50% Cl_2. The Cl_2 can be easily removed by bubbling the gas through 5% NaOH solution. After purification, the NF_2Cl appears to be unstable to storage in metal cylinders under pressure. On standing for a few hours, the NF_2Cl was found to decrease significantly and NF_3 to appear (infrared analysis). Therefore, it is recommended that if the product must be stored for a length of time before use, it be kept as a crude material contaminated with Cl_2, and then be used directly after purification.

According to reactions 4 and 5, ClN_3 should be a useful starting material for NF_2Cl. Chlorine azide was generated by dropping dilute phosphoric acid into a solution of NaOCl and NaN_3. By means of a slow nitrogen stream the ClN_3 was swept into a copper tube reactor cooled to $-20°$. A 1:1 fluorine and nitrogen mixture contacted the ClN_3 in the reactor. Then, the gases were passed through an infrared cell. The only gas detected was NF_2Cl. The reaction was found to be somewhat erratic, a second run yielding no NF_2Cl, but, presumably, only N_2, Cl_2, and F_2.

Acknowledgment.—We wish to thank Professor Robert West and Dr. Abe Maxwell for helpful discussions.

CONTRIBUTION NO. 824 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY, WILMINGTON 98, DELAWARE

Chemistry of Boranes. VI.[1] Preparation and Structure of $B_{10}H_{14}^{-2}$

BY E. L. MUETTERTIES

Received November 24, 1962

We previously[2] have characterized the $B_{10}H_{13}^-$ anion as an acceptor structure by demonstrating the addition of both neutral and charged donor species to yield $B_{10}H_{14}^{-2}$ derivatives.

$$B_{10}H_{13}^- + S(CH_3)_2 \longrightarrow B_{10}H_{13}S(CH_3)_2^- \qquad (A)$$

$$B_{10}H_{13}^- + CN^- \longrightarrow B_{10}H_{13}CN^{-2} \qquad (B)$$

The generality of reaction A to neutral donors, *e.g.*, R_3N and R_3P, has been reported recently.[3] We now have found that the parent structure $B_{10}H_{14}^{-2}$ can be prepared in aqueous solution by effective hydride ion transfer from BH_4^- to $B_{10}H_{13}^-$. The reaction simply comprises addition of decaborane to aqueous potassium borohydride, and the reaction sequence may be visualized as

$$B_{10}H_{14} + H_2O \rightleftharpoons B_{10}H_{13}^- + H_3O^+ \qquad (C)$$

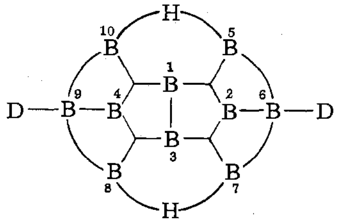
$$B_{10}H_{13}^- + BH_4^- \rightleftharpoons B_{10}H_{14}^{-2} + [BH_3] \qquad (D)$$

$$[BH_3] + 3H_2O \xrightarrow{\text{fast}} B(OH)_3 + 3H_2 \qquad (E)$$

A competing reaction that destroys borohydride ion is its acid-catalyzed hydrolysis. However, use of an excess of borohydride ion provides a simple, rapid, and high-yield synthesis of $B_{10}H_{14}^{-2}$ which is superior from a laboratory standpoint to $Na_2B_{10}H_{14}$ synthesis from decaborane and sodium in liquid ammonia.[4]

The $B_{10}H_{14}^{-2}$ anion has moderate stability with respect to hydrolysis in neutral or basic solutions. Saturated aqueous solutions of $Rb_2B_{10}H_{14}$ degrade slowly to boric acid; the conversion in a period of 4 weeks at 25° is about 10–20%. In acid (pH 1–3) solutions of $B_{10}H_{14}^{-2}$, decomposition as evidenced by hydrogen evolution is quite rapid.

The structure of $B_{10}H_{14}^{-2}$ has not yet been determined; however, investigations of $B_{10}H_{14}^{-2}$ derivatives such as $B_{10}H_{12}(NCCH_3)_2$[5] and $B_{10}H_{12}[S(CH_3)_2]_2$[6] have established the stereochemistry as depicted topologically below



where D is the donor ligand and each boron atom has a terminal hydrogen atom which is not shown in the structure. Representation of $B_{10}H_{14}^{-2}$ simply involves replacement of D by H^-. We have examined the B^{11} n.m.r. spectra of aqueous solutions of $Rb_2B_{10}H_{14}$ and find the results consistent with such a structure. In Fig. 1, the B^{11} resonance is reproduced and tentative assignments of peaks are made. On a sweep with a

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(1) Paper V: V. D. Aftandilian, H. C. Miller, G. W. Parshall, and E. L. Muetterties, *Inorg. Chem.*, **1**, 734 (1962).

(2) W. H. Knoth and E. L. Muetterties, *J. Inorg. Nucl. Chem.*, **20**, 66 (1961).

(3) B. M. Graybill, A. R. Pitochelli, and M. F. Hawthorne, *Inorg. Chem.*, **1**, 622 (1962).

(4) R. H. Toeniskoetter, G. W. Schaeffer, E. C. Evers, R. E. Hughes, and G. E. Bagley, Abstracts, 134th National Meeting, American Chemical Society, Chicago, September 7–11, 1958, p. 23-N.

(5) J. M. Reddy and W. N. Lipscomb, *J. Chem. Phys.*, **31**, 616 (1959).

(6) D. E. Sand and A. Zalkin, *Acta Cryst.*, **15**, 410 (1962).

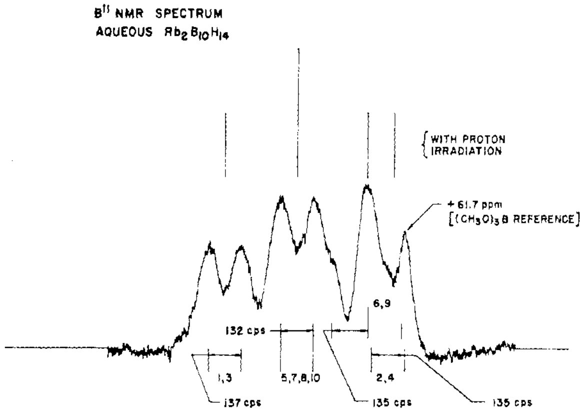

Fig. 1.—B^{11} magnetic resonance spectrum (19.2 Mc.) of aqueous $Rb_2B_{10}H_{14}$ externally referenced to trimethyl borate. Possible assignments of peaks to specific boron environments of predicted $B_{10}H_{14}^{-2}$ structure are noted along with the BH spin–spin coupling constants. Position of collapse of individual boron resonance doublets and triplet on irradiation of H^1 at 60 Mc. is indicated at the top. As noted by a referee, an alternative scheme is simply the assignment of the 1,3 and 2,4 boron atoms to the high and low field doublets, respectively.

saturating 60 Mc. field, the multiplets of the B^{11} spectrum successively collapsed as noted in Fig. 1. Acidified solutions of $B_{10}H_{14}^{-2}$ have a B^{11} spectrum that consists of three peaks (146 c.p.s. separations at 19.2 Mc.) of unequal intensity. Exchange of hydrogen atoms may be rapid under these conditions. In any case, the spectrum sheds no light on the $B_{10}H_{14}^{-2}$–$B_{10}H_{15}^-$ equilibrium[7] nor on the $B_{10}H_{15}^-$ structure.

Experimental

Reagents and Equipment.—See paper V.[1]

Synthesis of $B_{10}H_{14}^{-2}$.—To a stirred solution of 0.04 mole of KBH_4 in 200 ml. of distilled water was added 0.02 mole of decaborane. The outlet of the flask was connected to a wet test meter, and within 15–30 min. about 3–4 l. (~0.15 mole) of hydrogen evolved. At this stage, essentially all of the decaborane had dissolved. The solution was filtered, and saturated aqueous CsCl solution was added until no further precipitation was evident. The yield of crude $Cs_2B_{10}H_{14}\cdot CsCl$ (*vide infra*) averaged 0.144 mole (72%). Yields up to 90% were obtained by using 0.08 mole of KBH_4 instead of 0.04 mole.

Characterization of $B_{10}H_{14}^{-2}$ Salts.—The simple cesium and rubidium salts were prepared by adding a saturated cesium or rubidium fluoride solution to the reaction solution obtained from decaborane and KBH_4. The tetraaminozinc salt was prepared in a similar fashion employing a concentrated solution of zinc chloride in ammonium hydroxide. The zinc salt was recrystallized from hot aqueous ammonium hydroxide, and the other salts were recrystallized from hot water.

Anal. Calcd. for $Cs_2B_{10}H_{14}\cdot 0.5H_2O$: Cs, 66.8; B, 27.2; H, 3.79. Found: Cs, 65.1; B, 27.7; H, 3.81.

Anal. Calcd. for $Cs_2B_{10}H_{14}\cdot CsCl$: Cs, 71.7; B, 19.5; H, 2.52; Cl, 6.37. Found: Cs, 70.6; B, 19.5; H, 2.87; Cl, 6.63.

Anal. Calcd. for $Zn(NH_3)_4B_{10}H_{14}$: Zn, 25.6; N, 21.9; B, 42.4; H, 10.3. Found: Zn, 25.2; N, 21.5; B, 42.1; H, 9.65.

Anal. Calcd. for $Rb_2B_{10}H_{14}\cdot 1.5H_2O$: Rb, 53.3; B, 33.7. Found: Rb, 53.7; B, 33.5.

Infrared Spectra.—The infrared spectra of Nujol mulls of the $B_{10}H_{14}^{-2}$ salts show the following major characteristics attributable to the anion: 2460 cm.$^{-1}$ (vs), 2400 cm.$^{-1}$ (m), 2330 cm.$^{-1}$ (m), ~2000 cm.$^{-1}$ (vw), and 1200 cm.$^{-1}$ (s). From 1200 cm.$^{-1}$ down, the spectral details vary from salt to salt. In the case of $Cs_2B_{10}H_{14}\cdot 0.5H_2O$ and $Rb_2B_{10}H_{14}\cdot 1.5H_2O$, there are major absorptions at 1070 cm.$^{-1}$ (m), 1030 cm.$^{-1}$ (s), 775 cm.$^{-1}$ (m), and 726 cm.$^{-1}$ (m). Solutions of $Rb_2B_{10}H_{14}$ in water show the same BH stretching frequencies at 2460, 2400, and 2330 cm.$^{-1}$ as a mull of the solid. The absorptions at 2400 and 2330 cm.$^{-1}$ suggest that a BH_2 group is present, and the broad weak absorption at 2000 cm.$^{-1}$ may reflect a B–H–B grouping.

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[7] J. A. Dupont and M. F. Hawthorne have reported the preparation of the $B_{10}H_{15}^-$ ion by reaction of $B_{10}H_{14}^{-2}$ and HCl in alcohol [*Chem. Ind.* (London), 405 (1962)].

Contribution from Peninsular ChemResearch, Inc.,
Gainesville, Florida

The Synthesis of Difluoraminosulfur Pentafluoride[1]

By Eugene C. Stump, Jr., Calvin D. Padgett,
and Wallace S. Brey, Jr.

Received November 17, 1962

Several monosubstituted derivatives of sulfur hexafluoride are known. These include SF_5Cl, SF_5OF, SF_5OSF_5, SF_5OOSF_5, and RSF_5, where R is an alkyl, substituted alkyl, aryl, or perfluoroalkyl radical.[2] We wish to report the synthesis of difluoraminosulfur pentafluoride, SF_5NF_2, a derivative of sulfur hexafluoride containing the previously unreported SF_5–N bond.

This compound has been obtained in a number of reactions, but the best method of preparation is the reaction of disulfur decafluoride with tetrafluorohydrazine at 150° in a stainless steel autoclave.

Difluoraminosulfur pentafluoride is a white solid at −186° and a colorless liquid below its boiling point, which is roughly estimated from vapor pressure data as −17°. It has been recovered unchanged after storage at room temperature for periods in excess of 1 month.

The structural assignment of this compound is based on molecular weight determinations, nuclear magnetic resonance, and infrared analysis, all of which are consistent with the structure SF_5NF_2. The infrared spectrum is shown in Fig. 1. Attempts at obtaining consistent elemental analyses were not successful.

Besides SF_5NF_2, the major product, several other compounds are isolated from the reaction mixture. These include SF_6, SiF_4, SOF_2, SF_5OSF_5, and a compound whose infrared spectrum is nearly identical with that of $SF_4(SO_3F)_2$.[3] The oxygen- and silicon-containing compounds, however, are formed during transfer in the glass vacuum system. The last two compounds are present in only trace amounts.

Optimum conversions are obtained at a reaction temperature of 150° after 3 hr. This was determined by

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[1] This work was supported by the Department of the Navy under Contract NOrd 16640, Subcontract No. 16 with Allegany Ballistics Laboratory.

[2] H. L. Roberts, *Quart. Rev.* (London), **16**, 30 (1961).

[3] J. M. Shreeve and G. H. Cady, *J. Am. Chem. Soc.*, **83**, 4521 (1961).