CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN 48104

Fluorophosphine Ligands. VII. Difluorophosphine Adducts with Tetraborane-8

BY L. F. CENTOFANTI, G. KODAMA, AND R. W. PARRY

Received April 1, 1969

The compound HF_2P is a strong base toward B_4H_8, forming a 1:1 adduct. The adduct is significantly more stable than COB_4H_8 or $F_3PB_4H_8$. The ^{11}B nmr spectrum can be explained in terms of a boron cage structure similar to that found in $(CH_3)_2NPF_2B_4H_8$. Investigation of the ^{19}F nmr of the previously reported compound $(CH_3)_2NPF_2B_4H_8$ suggests the existence of isomers for this compound, but no isomers were found for $F_2PHB_4H_8$.

Several Lewis base adducts of B_4H_8 have been prepared from B_4H_8CO by a simple base-displacement reaction of the general form

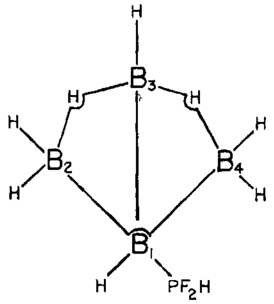
$$\text{base} + B_4H_8CO \longrightarrow B_4H_8(\text{base}) + CO$$

Both $F_3PB_4H_8$ and $F_2PN(CH_3)_2B_4H_8$ have been prepared by this process.[1,2] In the current study, $F_2HPB_4H_8$ has also been prepared by the displacement of CO.

$$B_4H_8CO + PF_2H \longrightarrow PF_2HB_4H_8 + CO$$

The reaction occurs readily at 25° to give yields of about 80% based on the B_4H_8CO consumed. $F_2HPB_4H_8$ is significantly more stable than B_4H_8CO and $F_3PB_4H_8$. The liquid compound showed no decomposition after standing at 25° for 9 days. In contrast, $F_3PB_4H_8$ undergoes complete decomposition under these conditions in less than 3 days.[1]

On the basis of nmr data, the structure assigned to $F_2HPB_4H_8$ is very similar to that obtained by La Prade and Nordman[3] for $F_2PN(CH_3)_2B_4H_8$ using X-ray methods. The structure can be represented as



The boron nmr (Figure 1) of the neat liquid resembles the $F_3PB_4H_8$ spectrum.[4] It consists of an overlapping low-field doublet and triplet and a high-field triplet. The low-field triplet may be assigned to borons 2 and 4 (J_{BH} = 123 cps, δ(relative to $(C_2H_5)_2OBF_3$) 8.7 ppm), while the low-field doublet can be assigned to boron 3 (J_{BH} = 120 ± 10 cps, δ(relative to $(C_2H_5)_2OBF_3$) 2.9 ppm). The numbering system of the boron cage is shown above. The high-field triplet is the result of boron coupling with both the attached proton and phosphorus, where $J_{BH} = J_{BP}$ ($J_{BH} = J_{BP}$ = 140 cps, δ(relative to $(C_2H_5)_2OBF_3$) 56 ppm). The small peak on the upfield side of the low-field signal can be attributed to B_5H_9 which could not be removed by repeated fractionation. From the data available, it could not be determined whether the splitting (about 20 cps) seen in Figure 1 for the low-field doublet (assigned to boron 3) was caused by an impurity or from coupling with another atom such as H or P on boron 1.

The 100-MHz proton nmr spectrum shows clearly that the F_2PH unit is still intact and is coordinated to the B_4H_8 framework. The tracing for the proton in PF_2H consists of a doublet due to P–H spin–spin coupling (J_{PH} = 651 cps, δ(relative to TMS) −7.8 ppm). Each member of the doublet is split into a 1:2:1 triplet by coupling with two equivalent fluorines (J_{HPF} = 60 cps), thus establishing the integrity of the HPF_2 unit. Each member of the triplet was split into a quintet which can only be due to coupling of the phosphorus proton with the B_4H_8 framework. A quintet of the type observed would result if each member of an initial doublet due to HBPH coupling were split into a 1:1:1:1 quartet by BPH coupling (B has spin of $^3/_2$). If the coupling constants of HBPH and BPH were very close to the same value ($J_{HBPH} = J_{BPH}$ = 9.4 cps), overlapping peaks would give rise to the observed quintet. Coupling between boron of the B_4H_8 unit and protons on the phosphorus in PF_2H is of interest here, since in alkylphosphine–boranes coupling between boron and protons on phosphorus is not observed. The BH portion of the proton spectrum could not be resolved.

The fluorine spectrum of $HF_2PB_4H_8$ obtained at 94.1 MHz shows the expected pair of doublets. The fluorine signal is first split into a doublet by the phosphorus (J_{PF} = 1120 cps, δ(relative to trifluoroacetic acid, TFA) 41.8 ppm); each member is then further split into doublets by the proton (J_{FPH} = 54 cps). The phosphorus nmr showed only a very broad peak at about δ −118 ppm relative to orthophosphoric acid. It could not be resolved.

It is interesting that J_{BH} and J_{PB} for these molecules and also for $PF_3B_4H_8$,[4] $(CH_3)_2PB_5H_8$, and $(CF_3)(CH_3)PB_5H_8$ (both isomers)[5] are equivalent. No explanation can be given for this equality.

The Nmr Spectrum of $(CH_3)_2NPF_2B_4H_8$.—$(CH_3)_2NPF_2B_4H_8$ was first reported to be stable up to 55°.[2]

---

[1] J. R. Spielman and A. B. Burg, *Inorg. Chem.*, **2**, 1139 (1963).

[2] G. TerHaar, M. A. Fleming, and R. W. Parry, *J. Am. Chem. Soc.*, **84**, 1767 (1962).

[3] M. D. La Prade and C. E. Nordman, *Inorg. Chem.*, **8**, 1669 (1969).

[4] A. D. Norman and R. Schaeffer, *J. Am. Chem. Soc.*, **88**, 1143 (1966).

[5] A. B. Burg, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, No. M205.

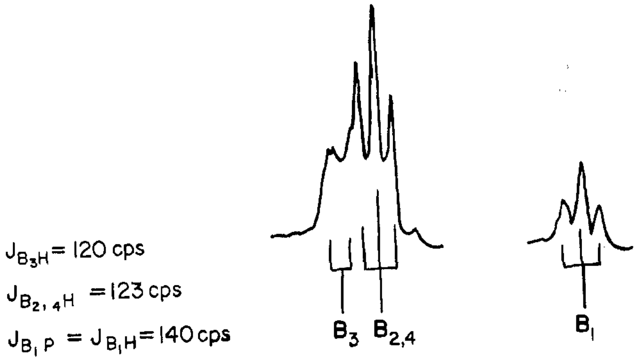


Figure 1.—The 32.1-Mc ^{11}B nmr spectrum of $PF_2HB_4H_8$ at 0°.

The B–P bond, originally suggested by nmr data, was later confirmed by the X-ray diffraction work of La Prade and Nordman.[3] Recent investigation of the nmr spectrum of $(CH_3)_2NF_2PB_4H_8$ has resulted in several interesting observations.

The B^{11} nmr spectrum of $(CH_3)_2NPF_2B_4H_8$ is similar to that of $PF_2HB_4H_8$. The spectrum consists of a high-field triplet with an area of 1 unit and a low-field group of peaks with an area of 3 units. As before, the high-field triplet can be assigned to B_1, the H–B_1 and the P–B_1 coupling (J_{BH} = J_{PB} = 136 cps, $\delta(R_2OBF_3)$ 53.5 ppm) being equivalent, so that a triplet results. Overlapping of the doublet from the B_3 with the low-field triplet occurs to an even greater extent in $F_2PN(CH_3)_2B_4H_8$ than in $F_2HPB_4H_8$. The triplet is the result of B_2 and B_4 coupling (J_{BH} = 121 cps, $\delta(R_2OBF_3)$ 4.1 ppm) with the attached protons. The coupling constant and chemical shift of the underlying doublet could not be determined because of overlap, but the coupling constant must be in the region of 120 cps.

In the proton nmr spectrum, only the methyl protons were assigned. It consisted of a doublet (J_{HCNP} = 10.8 cps, δ(TMS) 2.71 ppm) caused by coupling with phosphorus, each member of which was further split into a triplet (J_{FPNCH} = 3.0 cps) from coupling with the two fluorine atoms.

The fluorine nmr (Figure 2) indicates two isomers. Two *doublets* were observed at 25°, each resulting from PF coupling (J_{PF} = 1110 cps, δ(TFA) -8 ppm and J_{PF} = 1150 cps, δ(TFA) -7.0 ppm). At $-65°$ (lowest temperature of instrument), the signal broadened but two doublets could still be detected. The doublet at δ -8.0 ppm was broader than its companion doublet (δ -7.0 ppm). At temperatures above 25° the two doublets began to coalesce to give a single doublet. The changes were reversible. In Figure 3 the coalescence of the high-field members of each doublet is shown. Since the relative areas of the two peaks change with temperature, the possibility that the spectrum is the result of two fluorines in the same molecule with different electronic environments is highly improbable.

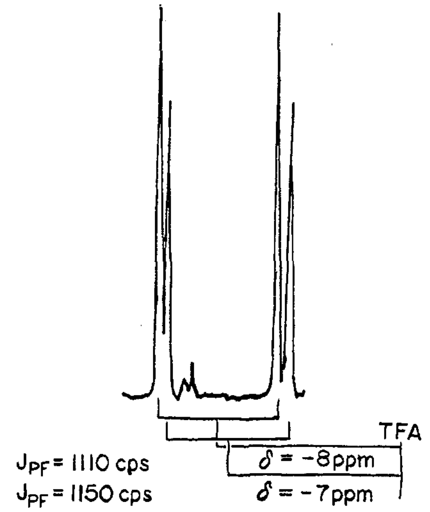


Figure 2.—The 94.1-Mc ^{19}F nmr spectrum of $F_2PN(CH_3)_2B_4H_8$.

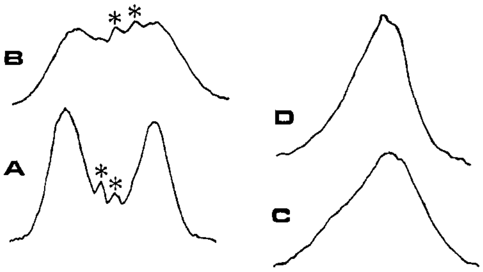
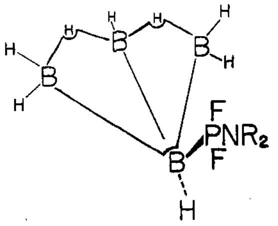
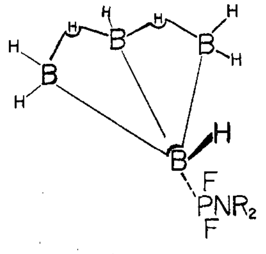


Figure 3.—Temperature dependence of the ^{19}F nmr spectrum of $(CH_3)_2NPF_2B_4H_8$. High-field member of each doublet is shown: A, 60°; B, 80°; C, 90°; D, 100°. The two small peaks marked with asterisks result from impurities.

The existence of geometric isomers for $(CH_3)_2NPF_2B_4H_8$ is the most reasonable interpretation of the data. The known structure[3] of one form of $(CH_3)_2NPF_2B_4H_8$ was used earlier as the basis of the structure indicated for $F_2HPB_4H_8$. The known isomer has the phosphorus up and the B–H proton down (I). A second isomer can be drawn with the proton up and the phosphorus down (II). In considering these possibilities, it is significant that no evidence was obtained for isomers of $F_2HPB_4H_8$. The $-NR_2$ moiety may be playing a specific role in isomer stabilization. The conversion process between isomers is now being studied in a more quantitative manner in this laboratory.



I



II

Experimental Section

Apparatus.—Standard high-vacuum techniques were used throughout. Mass spectra were obtained on a Consolidated Electrodynamics Model 21-103B mass spectrometer at 70 eV.

Proton, boron, fluorine, and phosphorus nmr spectra were determined with a Varian Associates HR-100 nmr spectrometer at 100, 32.1, 94.4, and 40.4 MHz, respectively. Chemical shifts were obtained by tube interchange.

The infrared spectrum was determined with a Beckman IR-12 in a 75-mm gas cell equipped with CsI windows.

Material.—PF_2H was prepared by the reaction of PF_2I, PH_3, and Hg.[6] B_4H_{10} and B_2H_6 were kindly supplied by Callery Chemical Co. B_4H_8CO was prepared by the reaction of B_5H_{11} and CO. $(CH_3)_2NPF_2\cdot B_4H_8$ was prepared by the reaction of B_4H_8CO and $(CH_3)_2NPF_2$[2] and also by the reaction of $(CH_3)_2NPF_2$ with B_5H_{11}.

Preparation of $PF_2HB_4H_8$.—In a typical reaction, 0.981 mmol of PF_2H and 0.919 mmol of B_4H_8CO were placed in a 100-ml reaction vessel. The reactants were warmed to 25°, were allowed to stand for 15 min, and then were frozen with liquid nitrogen. The trap was opened to the Toepler system through two −196° traps. The material stopping in the −196° traps was recondensed into the reaction vessel after all of the CO had been removed. This procedure was continued until, upon freezing at −196°, no noncondensable gas was recovered from the reactants. The products were then passed through traps cooled to −63, −85, and −196°. A 0.608-mmol sample of $PF_2HB_4H_8$ was found in the trap at −63°. The −85° trap contained 0.148 mmol of B_4H_8CO; the −196° trap contained 0.410 mmol of mostly PF_2H. The amount of CO released was found to be 0.652 mmol. The distillation should not be carried out over too long a period of time, because $PF_2HB_4H_8$ will pass slowly through −63° to a colder trap. The vapor density molecular weight was found to be 123 g/mol (calculated for $HF_2PB_4H_8$: 121.4) at 23° (20 mm). The mass spectrum gave a parent peak at 121 and a fragmentation pattern expected for a B_4 species. The identification of $PF_2HB_4H_8$ was established unequivocally by the ^1H, ^{19}F, ^{11}B, and ^{31}P nmr spectra (see above). Although no elemental analysis was run, the identification and analysis by nmr were unequivocal.

Reaction of B_5H_{11} with $(CH_3)_2NPF_2$.—A 0.551-mmol sample of B_5H_{11} and a 1.10-mmol sample of $(CH_3)_2NPF_2$ were condensed in a 20-ml reaction bulb at −196°. The mixture was allowed to warm to room temperature and then was cooled to 0° and was allowed to set for 4 hr. The products were then distilled through traps cooled to −25, −35, and −196°. The −25° trap contained a trace of unidentified solid, and pure $(CH_3)_2NPF_2B_4H_8$ was found at −35°, while $(CH_3)_2NPF_2BH_3$ and $(CH_3)_2NPF_2$ were found at −196°. The product weighed 81.8 mg (0.50 mmol of $(CH_3)_2NPF_2.B_4H_8$) for 91% yield.

Properties of $F_2HPB_4H_8$.—The vapor pressure data for $F_2HPB_4H_8$ are: −54.6° (1.0 mm), −24.8° (5.5 mm), −0.1° (23.1 mm), 11.1° (40.0 mm), 22.7° (67.5 mm); extrapolated bp 90.2°; mp −80.4 to −79.3° in a sealed tube; Trouton's constant 20.98 cal/deg mol. The vapor pressure data can be summarized by the equation

$$\log P(\text{mm}) = -\frac{1667}{T} + 7.463$$

The infrared spectrum is similar to that for other B_4H_8 species.[7]

Assignments for $F_2HPB_4H_8$ are based on the assignments given earlier for these molecules. Absorptions and assignments are as follows: 2592 (m) [ν_{as}(B–H)]; 2559 (s) [ν_s(B–H)]; 2530 (w); 2505 (w); 2432 (s) [ν_s(P–H)]; 2332 (w); 1920 (m), 1612 (m), 1504 (s) (H bridge modes); 1169 (m); 1082 (s) [δ,(P–H)]; 1031 (w); 983 (m); 898 (s) [ν_s, $\nu_{as}(PF)_2$]; 822 (m); 757 (w); 565 (s) [ν(PB)]; 412 (m); 324 (s) [δ,(PF_2)]. (The symbols used above are defined as: ν, stretch; δ, deformation; s, strong; m, moderate; w, weak; v, very. All values are in cm^{-1}.)

Acknowledgment.—Support of this work by the National Cancer Institute through Grant CA 0798904 is gratefully acknowledged.

---

[6] R. W. Rudolph and H. W. Schiller, *J. Am. Chem. Soc.*, **90**, 3581 (1968).

[7] G. L. TerHaar, Doctoral Dissertation, University of Michigan, 1962.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF KANSAS, LAWRENCE, KANSAS 66044

Electrochemical Preparation and Halogenation of 1,1′-μ-Hydro-bis(undecahydro-*closo*-dodecaborate)(3−), $B_{24}H_{23}^{3-}$ [1]

BY R. J. WIERSEMA AND R. L. MIDDAUGH[2]

Received April 14, 1969

The product of the one-electron electrochemical oxidation of $B_{12}H_{12}^{2-}$ in acetonitrile is $B_{24}H_{23}^{3-}$. Halogenation reactions of $B_{24}H_{23}^{3-}$ yield compounds of the type $B_{24}X_nH_{23-n}^{3-}$ ($X = I$, $n = 2$; $X = Br$, $n = 7, 10, 11$) and $B_{24}X_nH_{22-n}^{4-}$ ($X = Br$, $n = 11, 14, 18$; $X = Cl$, $n = 18$). Sodium in liquid ammonia cleaves the $B_{24}H_{23}^{3-}$ ion and regenerates $B_{12}H_{12}^{2-}$. Under basic conditions, there is no H–D exchange; however, acidic deuteration gives almost complete H–D exchange in the $B_{24}H_{23}^{3-}$ ion. The proposed structure of the $B_{24}H_{23}^{3-}$ ion is two B_{12} units linked by a hydrogen-bridge bond, analogous to that of $B_{20}H_{19}^{3-}$ ion.

The aqueous chemical oxidation of $B_{10}H_{10}^{2-}$ produces $B_{20}H_{18}^{2-}$, the result of a two-electron oxidation per B_{10} unit.[3–7] Under milder conditions, it is also possible to isolate good yields of $B_{20}H_{19}^{3-}$, the result of a one-electron oxidation of $B_{10}H_{10}^{2-}$.[3,6,7] The electrochemical oxidation of $B_{10}H_{10}^{2-}$ has been characterized as an initial one-electron transfer, followed by a homogeneous chemical reaction, to yield $B_{20}H_{19}^{3-}$. The $B_{20}H_{19}^{3-}$ ion can undergo a further two-electron oxidation to give $B_{20}H_{18}^{2-}$.[8]

---

[1] (a) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. (b) Taken in part from the Ph.D. thesis of R. J. Wiersema, University of Kansas, 1969.

[2] Author to whom inquiries should be addressed.

[3] M. F. Hawthorne, R. L. Pilling, and P. F. Stokely, *J. Am. Chem. Soc.*, **87**, 1893 (1965).

[4] A. Kaczmarczyk, R. D. Dobrott, and W. N. Lipscomb, *Proc. Na'l. Acad. Sci. U. S.*, **48**, 729 (1962).

[5] A. R. Pitochelli, W. N. Lipscomb, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **84**, 3026 (1962).

[6] M. F. Hawthorne, R. L. Pilling, P. F. Stokely, and P. M. Garrett, *ibid.*, **85**, 3705 (1963).

[7] B. L. Chamberland and E. L. Muetterties, *Inorg. Chem.*, **3**, 1450 (1964).

[8] R. L. Middaugh and F. Farha, Jr., *J. Am. Chem. Soc.*, **88**, 4147 (1966).