DIMETHYLAMIDODIFLUOROPHOSPHINE TETRABORANE-8—$F_2PN(CH_3)_2B_4H_8$—A STABLE ADDUCT OF B_4H_8

Sir:

In 1959 Burg and Spielman[1] found that CO under pressure removes a BH_3 group from B_5H_{11} to give the unstable compound B_4H_8CO. The liquid (v.p. 71 mm. at 0°) liberates up to 60% of its CO on standing for 12 hours at room temperature. The analogy between PF_3 and CO[2] suggested that PF_3 might displace CO to give a more stable $F_3PB_4H_8$. A displacement reaction did indeed occur, but the compound formed, presumably $F_3PB_4H_8$, was unstable under the conditions of the experiment and never could be purified in our vacuum system. The low basic strength of F_3P would appear to be a probable cause of compound instability. Attempts to stabilize the B_4H_8 complex by replacing CO with the stronger base $N(CH_3)_3$ were likewise unsuccessful.[1] In this research it was found that $N(CH_3)_3$ is such a strong base that it attacks the B_4H_8 group to give $(CH_3)_3NBH_3$ and other products.

Recently it has been found that the newly synthesized ligand[3] $F_2PN(CH_3)_2$ will form a *stable* adduct with B_4H_8. The reaction is $B_4H_8CO + F_2PN(CH_3)_2 \xrightarrow{-20°} (CH_3)_2NPF_2B_4H_8 + CO$. In a formal sense $F_2PN(CH_3)_2$ can be considered as a composite of F_3P and $N(CH_3)_3$ and seems to combine the required features of both. The clear liquid compound $F_2PN(CH_3)_2B_4H_8$ can be heated to 55° without significant decomposition, but above 55° a sudden break in the vapor pressure curve indicates decomposition. The compound melts at −18° and has been stored in a dry box at room temperature for more than a week. A slight yellow color developed on storage, but the infrared spectrum of the stored sample was identical with that of a fresh sample.

Although the ligand $(CH_3)_2NPF_2$ has two possible coördination sites, the preliminary spectroscopic and chemical evidence leads us to believe that the B_4H_8 group, with geometry comparable to the boron framework of B_4H_{10}, is coördinated only to the phosphorus. Structural and chemical studies are in progress.

Experimental.—A 1.8-millimole sample of B_4H_8CO was condensed into a reaction tube on the vacuum line; a 1.8-millimole sample of $F_2PN(CH_3)_2$ was frozen on top of the B_4H_8CO using liquid N_2. The tube was warmed slowly to −20° whereupon a gas came off over a 10-min. period. The system then was warmed to room temperature, and stirred in the vacuum line for 30 minutes with a magnetically operated "hopper type" stirrer. After the system was frozen with liquid N_2, the non-condensable gas was separated and recognized as CO (1.8 millimoles) by its molecular weight of 28 (vapor density). The condensable product was distilled from a trap at 0° into traps at −22° and −196°. The clear liquid product was found in the −22° trap; only a trace of material was found in the −196° unit. Analysis of the purified liquid product (m.p. −18°) showed: H, 8.52; N, 8.57; C, 15.15; hydridic hydrogen, 4.61. Theoretical for $F_2PN(CH_3)_2B_4H_8$ is: H, 8.58; N, 8.52; C, 14.61; hydridic hydrogen, 4.91. Although boron, fluorine, and phosphorus were not determined directly, the above results coupled with the stoichiometry of synthesis leave no reasonable alternative to the empirical formula $(CH_3)_2NPF_2B_4H_8$. The molecular weight of the sample, measured by freezing point depression in benzene, was 159 ± 8 as compared to a value of 165.4 expected for the above formula. The vapor pressure of the liquid over the temperature range 22 to 53.5 is represented by the equation

$$\log P = -1727/T + 6.128$$

VAPOR PRESSURE OF $(CH_3)_2NPF_2B_4H_8$

T, °K.	295.5	300.9	305.2	318.7	326.6
Obs. v.p. (mm. Hg)	1.9	2.5	2.9	4.9	7.4[a]
Calcd. v.p.	1.9	2.5	2.9	5.1	6.9[a]

[a] Decomposition rapid above 326.6.

The heat of vaporization over the temperature range studied is estimated as 8,000 cal. although the precision of the value is low in this region of very low vapor pressure. The molecular weight of the vapor, as estimated by gaseous effusion, was 160.

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[1] A. B. Burg and J. R. Spielman, *J. Am. Chem. Soc.*, **81**, 3479 (1959).

[2] R. W. Parry and T. C. Bissot, *ibid.*, **78**, 1524 (1956); R. W. Parry and L. J. Edwards, *ibid.*, **81**, 3544 (1959).

[3] Sr. M. A. Fleming and R. W. Parry, to be published.