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Reactions of Pentaboranes with Dimethylaminodifluorophosphine and Difluorophosphine[1]

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The base $PF_2N(CH_3)_2$ attacked B_5H_9 to give a solid adduct of variable composition from which $[PF_2N(CH_3)_2]_2B_2H_4$ was vaporized. A solid remained which emitted the little volatile $PF_2N(CH_3)_2B_6H_{10}$ and from which $PF_2N(CH_3)_2B_4H_8$ and $PF_2N(CH_3)_2BH_3$ were obtained from treatment with diborane(6). Presumably the solid was an adduct of triborane(5).

Pentaborane(9) has been reported to react with trimethylamine[3,4] and with trimethylphosphine[5] to give bis adducts, which with extra base give borane adducts. Certainly in the first case, and possibly in the second, adducts of tetraborane(6) were obtained also. Pyrolysis of that final trimethylphosphine adduct yielded bis(trimethylphosphine)-diborane(4).[5]

According to the information reported here, dimethylaminodifluorophosphine gives different products with pentaborane(9). The stoichiometry of any adduct was obscured by the variability in composition found for the solid phase as shown in Table I. The results are best understood as describing an adduct slowly formed and itself subject to attack by the base. From the latter event bis(dimethylaminodifluorophosphine)-diborane(4) was a definitely identifiable product.[6] Only a negligible amount of borane adduct was observed. Because the other substances could not be isolated by vacuum techniques, their presence was determined by indirect means. There appeared good mass spectrometric evidence for the formation of hexaborane(10) mono adduct, presumably from the condensation of a triborane(5) adduct not volatile at 0°. A component of the solid phase reacted with boron-10 labeled diborane(6) to give borane adduct and dimethylaminodifluorophosphine-tetraborane(8)[7] that contained three boron atoms from the alleged triborane(5) adduct and one boron atom from the diborane (see Tables II and III). Approximately, the principal processes appeared concordant with the following equations, where b represents $(CH_3)_2NPF_2$

$$B_5H_9 + 4b \longrightarrow B_3H_5b_2 + B_2H_4b_2$$

$$2B_3H_5b_2 \longrightarrow B_6H_{10}b + 3b$$

$$B_3H_5b_2 + B_2H_6 \longrightarrow B_4H_8b + BH_3b$$

TABLE I

STOICHIOMETRY OF THE REACTION OF PENTABORANE(9) AND DIMETHYLAMINODIFLUOROPHOSPHINE

Reactant ratio, base/B_5H_9	Reaction time, days	Ratio in solid products, base/B_5H_9	% conversion of B_5H_9
2.7	0.66	4.16	39
2.92	1	3.42	57
3.00	3	3.60	76
2.96	3	4.19	77
2.19	3	3.23	64
2.09	3	3.28	58
2.16	5	2.76	72
2.14	14	2.96	97
1.00	3	2.22	40

TABLE II

PRODUCTION OF DIMETHYLAMINODIFLUOROPHOSPHINE-TETRABORANE(8)

Ratio of reactants,[a] $PF_2N(CH_3)_2/B_5H_9$	Reaction period,[b] days	Product ratio,[c] $PF_2N(CH_3)_2B_4H_8/B_5H_9$
2.7	$^2/_3$	0.43
3	1	0.34
3	3	0.23
2	3	0.0
2	14	0.0

[a] Ratio of starting materials present in solid material. [b] Time employed to prepare the solid adduct from pentaborane(9). [c] Ratio of the tetraborane(8) adduct produced to pentaborane(9) consumed in the reaction to produce the solid material.

TABLE III

MASS SPECTROMETRIC RESULTS FROM BORON-10-LABELED DIMETHYLAMINODIFLUOROPHOSPHINE-TETRABORANE(8)

		Ratio, intensities	
	Sample	Calcd	Obsd[b]
1	Natural abundance	2.66[a]	2.71 ± 0.14
2	Solid product and labeled diborane	1.38[b] 1.08[c]	1.15 ± 0.05
3	Exchange experiment		2.42 ± 0.08

[a] Ratio of the coefficients of the terms, $^{11}B_3{}^{10}B:{}^{11}B_2{}^{10}B_2$ as calculated by expansion of $(a + b)^4$. [b] Ratio of observed intensities, $^{11}B_3{}^{10}BH_6L^+:{}^{11}B_2{}^{10}B_2H_6L^+$ as calculated by expansion of $(a + b)^3(a' + b')$ without correction for exchange. [c] Ratio in *b*, corrected for exchange using the result from sample 3 in a three-halves order process.

In contrast with pentaborane(9), pentaborane(11) reacts with bases as weak as ethers[8] to give hexaborane(10); with carbon monoxide[9] and trifluorophosphine[10] tetraborane(8) adducts are formed. Trimeth-

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[1] Research supported by National Science Foundation Grant GP-7888.

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ylamine[11] disrupts pentaborane(11) into the borane adduct, hydrogen, and unidentified solid products. This study has found that dimethylaminodifluorophosphine and difluorophosphine behave toward pentaborane(11) in essentially the way found for carbon monoxide and trifluorophosphine, but, owing to the vulnerability of the tetraborane(8) adducts to further attack, adducts of diborane(4) and of what is believed to be triborane(5) were finally formed.

Experimental Part

Starting Materials.—Pentaborane(11) was prepared from diborane in a hot–cold reactor (−80, 160°).[12] Dimethylaminodifluorophosphine and difluorophosphine were prepared by the methods of Cavell[13] and Rudolph,[14] respectively. Pentaborane(9) was supplied by Professor T. D. Parsons. The volatile materials were purified by a suitable combination of glpc[15] and fractional condensation. All reactions were conducted in heavy-wall glass tubes (volume 7 ml) fitted with Teflon-plug glass stopcocks.[16] As a caution it should be noted that the vapor pressure of difluorophosphine at 21.6° is 21.2 ± 0.3 atm.

Reactions. Pentaborane(9) **and Dimethylaminodifluorophosphine.**—B_5H_9 (1 mmol) and $PF_2N(CH_3)_3$ (1–4 mmol) were allowed to react with stirring for periods up to 14 days at 23° as shown in Table I. After 3–5 days a faint yellow color developed, darkening slowly as the reaction proceeded. At the end of the reaction only unreacted starting materials could be transferred from the tube kept at 0°. No noncondensable gas was observed. The material remaining in the tube was a slightly wet, white or yellow solid.

When the temperature of the solid was raised from 0 to 23°, $[PF_2N(CH_3)_3]_2B_2H_4$ was vaporized.[6] After bulk transfer of starting material had essentially stopped at 0°, enough substance still issued from the solid to be detected in the mass spectrometer.[17] A scan at low resolution (250 ppm) over the range *m/e* 10–500 showed no value larger than 252, parent peak for $[PF_2N(CH_3)_2]_2$-B_2H_4, and the complete spectrum of that substance was contained among the measured values.[6] After these were subtracted, there remained two envelopes, one that of pentaborane(9) and another with the values

m/e	188	187	186	185	184	183	182
Intensity	2	20	27	18.5	8	3	2

These were assigned to dimethylaminodifluorophosphine–hexaborane(10), $PF_2N(CH_3)_2B_6H_{10}$, on the following grounds: (1) the envelope gave a reduction to the ^{11}B monoisotopic representation in accordance with the statistics for a B_6 molecule;[18] (2) the spectrum contained the components assignable to the species $PF_2N(CH_3)_2{}^{11}B_6H_8{}^+$ and $PF_2N(CH_3)_2{}^{11}B_5{}^{10}BH_8{}^+$; (3) the ratio of the intensities of the two peaks was 1.45; calculated for a B_6 species, 1.50. To establish points (2) and (3) the mass spectrometer was adjusted to obtain a resolution of 130 ppm (10% peak overlap). The peak-matching facility was calibrated by examining the mass ratio for two perfluorotributylamine peaks (mass 180.989 (C_4F_7) and 187.993 (C_5F_6N)) with an uncertainty of 5 ppm. In the mass spectrum of the boron compound two peaks were found assignable to $PF_2N(CH_3)_2{}^{11}B_6H_8{}^+$ (mass: calcd, 187.137; obsd, 187.139 ± 0.004) and to $PF_2N(CH_3)_2$-$^{11}B_5{}^{10}BH_8{}^+$ (mass: calcd, 186.141; obsd, 186.143 ± 0.003). The intensities were estimated from the areas under the peaks.

The solid material, as processed at 0°, was treated with excess diborane(6) at 23° for 20 min to produce $PF_2H(CH_3)_2B_4H_8$[19] and $PF_2N(CH_3)_2BH_3$.[20] The yield of tetraborane(8) adduct varied inversely with the age of the solid material as is shown in Table II. In one case isotopically normal B_5H_9 (1.29 mmol) was caused to react with $PF_2N(CH_3)_2$ (4.81 mmol) giving a ratio 3.72 in terms of Table II. After the usual curing at 0° the solid was treated with diborane(6) (1.75 mmol) in which the ratio $^{11}B:{}^{10}B$ was 0.07:0.93. The resulting dimethylaminodifluorophosphine–tetraborane(8) was examined in the mass spectrometer to determine the intensity ratio between peaks assigned to $PF_2N(CH_3)_2$-$^{11}B_3{}^{10}BH_6{}^+$ and to $PF_2N(CH_3)_2{}^{11}B_2{}^{10}B_2H_6{}^+$. The attenuation scale of the peak-matching facility was used to determine the relative peak areas. Tetraborane(8) adduct with natural isotopic abundance was examined as a check on the method.

Exchange between the tetraborane(8) adduct and diborane(6) was determined by mixing isotopically normal dimethylaminodifluorophosphine–tetraborane(8) (0.20 mmol) and the isotopically biased diborane(6) (0.37 mmol) for 10 min at 23° in the same volume used for the tracer experiment. The intensity ratio for the peaks at *m/e* 162.119 and 161.112 was determined by peak matching. All of the results are found in Table III. The expectation values for the peak ratios were calculated from the statistics for isotopic mixing,[18] assuming that in the B_4 product species three boron atoms were from the solid, and the fourth boron atom was from diborane(6). The result recorded in Table III is consistent with the hypothesis, after correction has been made for the exchange of boron atoms between the tetraborane(8) and diborane(6). The rate equation for isotope exchange was used to calculate the correction for the tracer experiment.[21,22] When the mechanism selected for the exchange was half order respecting tetraborane(8) adduct and first order respecting diborane(6), the concordance between observed and calculated peak ratios was better than that found by assuming a process first order in each participant. When the observed peak ratio was assumed to be exactly correct, an exchange time of about 14 min could be calculated, which allowed about 6 min of reaction time between solid and diborane(6).

Pentaborane(9) **and Difluorophosphine.**—B_5H_9 (0.726 mmol) and PF_2H (3.00 mmol) were mixed during 65 min at 23°. Decomposition products of difluorophosphine, a very small amount of difluorophosphine-borane, and pentaborane(9) (0.703 mmol) were recovered. After removal of the volatile materials the tube contained a yellow solid. Apparently the base decomposed faster than it reacted with the hydride.

Pentaborane(11) **and Dimethylaminodifluorophosphine.**—The reaction of B_5H_{11} (1 mmol) with $PF_2N(CH_3)_2$ (2.5–4.0 mmol) for periods between 10 and 60 min at 23° produced $PF_2N(CH_3)_2$-B_4H_8[19] and $PF_2N(CH_3)_2BH_3$[20] in yields greater than 90%.[23] If a longer reaction period was allowed, the yield of tetraborane(8) adduct decreased and the production of the borane adduct increased as is shown in Table IV. The substances that could be removed by vaporization at 0° over a 2-day period were the unreacted starting materials and the adducts of borane and of tetraborane(8). A white solid remained in the reaction tube. At 23° $[PF_2N(CH_3)_2]_2B_2H_4$ was recovered from the solid,[5] and

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[21] Meyers and Prestwood, "Radio Activity Applied to Chemistry," A. C. Wahl and N. A. Bonner, Ed., Wiley, New York, N. Y., 1951, Chapter I.

[22] For the detailed calculations order Document No. NAPS-00969 from ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10001, remitting $2.00 for microfiche or $5.00 for photocopies. Advance payment is required. Make checks or money orders payable to: CCMIC–NAPS.

[23] See also (a) E. R. Lory and D. M. Ritter, Abstracts, Northwest Regional Meeting of the American Chemical Society, Portland, Ore., June 1968, paper 55-23; (b) L. Centofanti and R. W. Parry, *Inorg. Chem.*, **8**, 2074 (1969).

TABLE IV

REACTIONS OF PENTABORANE(11) AND OF DIMETHYLAMINODIFLUOROPHOSPHINE–TETRABORANE(8) WITH DIMETHYLAMINODIFLUOROPHOSPHINE

Reactant ratio base/B_5H_{11}	Reaction time,[a] hr	% reaction of B_4H_8L[b]	% borane deficiency[c]
3.55	1	0	...
4.37	26	78	14
4.55	44	100	13
base/B_4H_8L			
2.55	2	44	7
3.76	8	67	10

[a] At 23°. [b] Per cent of B_4H_8L reacting to produce BH_3L and solid material. [c] Per cent of borane adduct not recovered, assuming 1 mol of borane adduct was produced per mole of tetraborane(8) adduct consumed.

the remaining material became dark yellow. The mass spectrum of the solid, refined and observed at 0°, showed the presence of the diborane(4) and hexaborane(10) adducts.

Dimethylaminodifluorophosphine (3.70 mmol) was used to treat $PF_2N(CH_3)_2B_4H_8$ (0.98 mmol) for 8 hr at 23°. Products were removed at 0° for 65 hr. $PF_2N(CH_3)_2B_4H_8$ (0.33 mmol) and $PF_2N(CH_3)_2BH_3$ (0.56 mmol) were found, and some free base (2.86 mmol) was recovered. The solid that remained gave the same mass spectrum as the one obtained from the solid adduct with pentaborane(9) except that the envelope attributed to pentaborane(9) was absent. At 23° $[PF_2N(CH_3)_2]_2B_2H_4$ was obtained, mp 43°.[5]

Pentaborane(11) with Difluorophosphine.—B_5H_{11} (1.295 mmol) reacted with the PF_2H (4.97 mmol) for 10 min at 23° to produce $PF_2HB_4H_8$ (1.23 mmol, 95% yield)[23] and PF_2HBH_3 (1.290 mmol).

$PF_2HB_4H_8$ (0.994 mmol) reacted with PF_2H (2.54 mmol) for 40 min at 23° to produce PF_2HBH_3 (0.384 mmol),[24] $(PF_2H)_2B_2H_4$ (0.102 mmol),[6] and a yellow solid. Some difluorophosphine–tetraborane(8) was recovered (0.558 mmol). In all of the reactions extensive decomposition of the base prevented a determination of the amount consumed. The difluorophosphine–borane recovered from the reaction between the tetraborane(8) adduct and the base corresponded to 1 mol of borane adduct per mole of tetraborane(8) adduct consumed.

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Ternary Nitrides of Calcium and Strontium with Molybdenum and Tungsten

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Ternary nitrides of molybdenum and tungsten with the alkaline earth metals calcium and strontium were formed by heating the transition metals with the alkaline earth nitrides in oxygen-free, dry nitrogen at atmospheric pressure. A hexagonal phase ($a = 11.40 \pm 0.01$ Å, $c = 7.45 \pm 0.01$ Å) has been assigned the tentative formula Ca_5MoN_5. A cubic phase is obtained in the Sr–Mo–N system at 750° which is isostructural with $Sr_{27}Re_5N_{28}$. Tungsten yields analogous compounds. At higher temperatures, the strontium compounds form other unidentified phases. Ca_5MoN_5 is an insulator with a temperature-independent paramagnetism similar to $Sr_{27}Re_5N_{28}$. $Sr_{27}W_5N_{28}$ and presumably $Sr_{27}Mo_5N_{28}$ are diamagnetic.

Introduction

The transition metals rhenium and osmium have been shown to yield ternary nitride phases when the metals are heated with strontium and barium nitrides in an atmosphere of nitrogen.[1] It was observed that molybdenum and tungsten also gave rise to new phases when treated in a similar manner. The pelleted mixtures of alkaline earth nitride and molybdenum crumbled to a fine yellow powder with phenomenal increase in bulk during the reaction. The product appeared to be a mixture which could not be resolved. In the present investigation it was found that this peculiar behavior was due to the inadvertent presence of small amounts of moisture or oxygen in the system. When suitable precautions were taken to eliminate these, ternary nitrides were obtained. This paper reports the preparation and some of the properties of the compounds obtained with molybdenum and tungsten.

There is a special interest in the fixation of nitrogen by molybdenum in view of the significant role played by molybdenum complexes in biological systems. The compounds described here are extremely reactive in protonic solvents, but no derivative chemistry has yet been developed.

Experimental Section

Materials.—The molybdenum and tungsten metals (200 mesh) were obtained from Alfa Inorganics Inc. The purity of each was 99.7% (99.9% based on metallic content only). Before use, these metals were heated at 900° in a stream of Extra Dry grade hydrogen for about 3 hr to remove any surface oxide. Pure nitrogen was obtained by decomposition of sodium azide by cautious heating in an evacuated round-bottomed flask directly attached to the vacuum line. The sodium produced in the reaction $2NaN_3(s) \rightarrow 2Na(s) + 3N_2(g)$ appears as a fine dispersion and serves as a useful getter for moisture and oxygen.

Calcium metal 99.9% pure with respect to other metals contains appreciable portions of oxide. It was distilled twice at 900° and 10^{-6} mm in a stainless steel container. The distilled metal collected on a metal plug at the cooler end of the container which was heated by induction. Strontium metal (98–99%) was similarly treated. The binary nitrides Ca_3N_2 and Sr_3N_2 were prepared by heating the distilled metals in 1 atm of nitrogen at 750° for several days.

The handling of all air- and moisture-sensitive materials was

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