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Synthesis of Difluorophosphine Azide

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The reaction of halophosphines with metal azides is a convenient route for the preparation of phosphorus azide compounds.[1-6] Several disubstituted phosphorus azides have been synthesized by this route including $(C_6H_5)_2PN_3$[5] and $(CF_3)_2PN_3$.[6] $(C_6H_5)_2PN_3$ is unstable at room temperature but can be examined at low temperature, while $(CF_3)_2PN_3$ is unpredictably explosive. We would like to report the preparation of a stable phosphorus azide, difluorophosphine azide, PF_2N_3.

Difluorophosphine azide was prepared by the reaction of PF_2X ($X = I, Br$) with MN_3 ($M = Na, Li$) which appears to be catalyzed by trace amounts of

$$PF_2X + MN_3 \xrightarrow[H_2O]{\text{trace}} MX + PF_2N_3$$

water. If the metal azide was carefully dried, no reaction occurred. The best results (60% yield) were obtained with the bromide and LiN_3, using a slight excess of PF_2Br to inhibit the formation of the more highly substituted azides which are explosive.[7] PF_2N_3 is purified by condensing on ZnF_2 and then distilling.

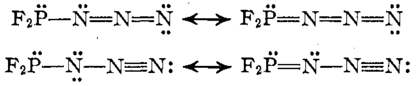
Spectroscopic analysis indicates an acyclic structural formulation for PF_2N_3.[8] The gas-phase infrared spectrum[9] shows a very strong peak at 2155 cm^{-1} which can be assigned to the asymmetric azide stretching vibration. Medium peaks at 1262 and 1225 cm^{-1} result from the azide symmetrical stretching vibration. Other medium bands observed include 850 and 827 (PF sym and asym) and 740 cm^{-1} (PN stretch).[10,11]

The ^{19}F nuclear magnetic resonance spectrum supports the structure. The spectrum, determined at $-60°$, is a doublet, $J_{PF} = 1320$ cps, $\delta(CF_3COOH) = -19.4$ ppm. The chemical shift is similar for other PF_2N compounds) $\delta(PF_2N(CH_3)_2$ is -12.4 ppm).[12,13]

In the proposed structure the presence of a lone pair of electrons on the nitrogen adjacent to the phosphorus could produce enhanced basicity of the phosphorus *via* a dative p–dπ interaction.[14-18] This effect is graphically illustrated by the stereochemistry of nitrogen in F_2PNH_2 and $F_2PN(CH_3)_2$[17,18] where the nitrogen (P–N<) is planar and the PN bond is very short. The enhanced basicity is evident as aminodifluorophosphine is one of the strongest difluorophosphine bases toward borane.[19,20] In a similar manner delocalization of the lone pair on the nitrogen adjacent to the phosphorus in PF_2N_3 should produce a shorter PN bond and increase base strength at the phosphorus. The borane adduct of PF_2N_3 was prepared and found by infrared and molecular weight data to be undissociated in the gas phase (10–175 mm) at room temperature. Base exchange studies and a structural analysis should further confirm base strength and the extent of dative π bonding in PF_2N_3.

The adduct was prepared by the direct reaction of the ligand and B_2H_6 and was characterized by its molecular weight and infrared and mass spectra. We prepared and worked with the adduct on several occasions during which no problems were encountered; however, once during the transfer of a 6.0-mmol sample in a vacuum line a violent explosion occurred. Further characterization has not been undertaken because of the unpredictable nature of the compound or of impurities contained therein.

The ligand PF_2N_3 has three potential basic sites; however, we suggest that the borane is coordinated to the phosphorus atom. The gas-phase infrared spectrum[9] of $PF_2N_3 \cdot BH_3$ showed expected peaks which are listed with tentative assignments: 2533 vw; 2448 s; 2420 m (B–H str);[11,12] 2185 vs (NNN sym str); 1275 vs (NNN asym str);[10,11] 1110 m, 1060 m (BH_3 def);[12] 927 vs, 803 (PF str); 702 vw (NP str);[10,11] 605 w (PB str).[19,21] Upon coordination only one ligand vibration is both shifted and altered significantly in area. The area of the 740-cm^{-1} absorption of PF_2N_3, assigned as a symmetric PN stretch, decreases greatly in the adduct and shifts to 702 cm^{-1}. This area is dependent upon the magnitude of the change in dipole moment associated with the PN stretching vibration. Considering the following resonance structures for PF_2N_3,[22]



$$F_2\ddot{P}-\ddot{N}=N=\underset{\cdot\cdot}{\ddot{N}} \longleftrightarrow F_2\ddot{P}=N=N=\underset{\cdot\cdot}{\ddot{N}}$$

$$F_2\ddot{P}-\underset{\cdot\cdot}{\ddot{N}}-N\equiv N: \longleftrightarrow F_2\ddot{P}=\ddot{N}-N\equiv N:$$

coordination of the borane through the phosphorus atom would be expected to lessen the change in dipole moment associated with the PN stretching vibration and subsequently decrease the area of this absorption mode. Coordination of the borane moiety through the adjacent nitrogen may bring about the same effect; however, this is probably not the coordination site since the symmetric azide stretch appears not to change.

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[9] Vibrational frequencies are given in cm^{-1} followed by a tentative assignment in parentheses. Notation for intensities: v, very; s, strong; m, medium; w, weak.

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Bonding through the terminal nitrogen would not be expected to greatly alter the change in dipole moment of the PN absorption.[23–28] The observed decrease in area of the PN mode in the adduct and the tentative assignment of a PB stretch[21] indicate that the best representation of the adduct is attachment of the borane group to the phosphorus atom and not to one of the nitrogens; however, until a ^{11}B nmr can be obtained showing ^{31}P–^{11}B coupling the bonding site of the adduct is uncertain.

Experimental Section

Materials and General Techniques.—The PF_2Br, PF_2I,[29] and B_2H_6[30] were prepared by literature methods. NaN_3 and LiN_3 were obtained from Matheson Coleman and Bell and Eastman Organics.

High-vacuum techniques were used throughout.[31] Although no explosions occurred with PF_2N_3, secondary products are highly explosive (HN_3, $P(N_3)_3$, etc.)[7,32,33] and proper precautions should be followed. Several explosions have occurred in this laboratory during transfer and disposal of side products and a violent explosion occurred during transfer of $PF_2N_3BH_3$.

Infrared spectra were recorded at a sample pressure of 10 mm on a Perkin-Elmer 137 NaCl spectrophotometer and a Perkin-Elmer 421 grating spectrophotometer using a 10-cm gas cell with KBr windows. The mass spectrum was obtained on a Varian M60-6 (70 eV), while nmr spectra for ^{19}F were recorded on a Jeolco JNM-C-60 HL operating at 56.4 MHz. Chemical shifts refer to CF_3COOH by tube interchange.

Synthesis of PF_2N_3.—After allowing a 15.0-mmol sample of LiN_3 to sit at ambient temperature in moist air, we placed it in a 500-cm^3 reaction bulb and evacuated the bulb for several minutes. A slight excess of PF_2Br (16.0 mmol) was condensed on the LiN_3 at $-196°$. The reactants then were alternately warmed to room temperature and refrozen at $-196°$; this procedure was repeated several times. We cooled the reaction mixture to $-78°$ in a Dry Ice–acetone slush and allowed it to sit 18 hr. The material was then distilled through traps held at -110, -135, and $-196°$. The material at $-110°$, a mixture of PF_2HO[34] and several explosive azides (HN_3, etc.),[7,32,33] was identified by ir and then carefully discarded. Small amounts of PF_3 at $-196°$ were also discarded. The trap at $-135°$ contained PF_2N_3, very small amounts of F_2POPF_2,[35] and unreacted PF_2Br. This material was condensed on an excess of ZnF_2 and warmed and refrozen several times. The latter procedure converted the PF_2Br to PF_3 which could be removed by distillation. The products from this reaction were led through traps held at -110, -135, and $-196°$. Again the material at -110 and $-196°$ was discarded with care, while the $-135°$ trap contained 9.0 mmol of PF_2N_3, contaminated by very small amounts of F_2POPF_2. Separation of these two compounds was extremely difficult, but samples of PF_2N_3 could be obtained fairly pure by careful distillation through traps held at -112 and $-196°$ (see mass spectra). PF_2N_3 was trapped in the $-112°$ trap.

If the LiN_3 was very carefully dried, no reaction occurred. PF_2I could be substituted for PF_2Br and NaN_3 could be substituted for LiN_3.

Properties of PF_2N_3.—Difluorophosphine azide is a colorless spontaneously flammable gas at room temperature. No detonations were observed with the pure compound.

Difluorophosphine azide was characterized by its gas molecular weight at 23° (found, 111.6; calcd for PF_2N_3, 111.0) and the mass spectrum splitting pattern. Following are the mass numbers (species) and relative abundances of the ions in the mass spectrum of PF_2N_3: 154 ($PF_2OPF_2^+$), 2.2; 111 ($PF_2N_3^+$), 72.3; 92 (FPN_3^+), 8.2; 88 (PF_3^+), 1.6; 85 (PF_2O^+), 1.1; 83 (PF_2N^+), 30.4; 69 (PF_2^+), 100; 64 (PFN^+), 16.9; 50 (PF^+), 15.8; 47 (PO^+), 1.6; 45 (PN^+), 3.8; 43 (HN_3^+), 2.7; 42 (N_3^+), 6.0; 32 (PH^+), 2.7; 31 (P^+), 3.8; 28 (N_2^+), 11.4.

Synthesis of $PF_2N_3 \cdot BH_3$.—PF_2N_3 (6.53 mmol) was condensed with 14.0 mmol of B_2H_6 at $-196°$ in a 500-cm^3 reaction bulb. The mixture was allowed to warm and then sit for 6 hr at room temperature. The reaction mixture was distilled through traps held at -67, -110, -140, and 196°. The material at $-67°$ (small amounts of unidentified solids) and $-140°$ (0.1 mmol of PF_2N_3) was discarded. The $-196°$ trap held 10.9 mmol of unreacted B_2H_6, while the $-110°$ trap contained 6.02 mmol of $PF_2N_3 \cdot BH_3$. The yield of the adduct was 95% and PF_2N_3 and BH_3 combined in the ratio 0.99:1.0.

Properties of $PF_2N_3 \cdot BH_3$.—Difluorophosphine azide–borane is a colorless liquid at room temperature. A violent explosion was experienced on transferring this compound.

The borane was characterized by its infrared spectrum given earlier, mass spectrum, and its molecular weight at 20° and 175 mm (found, 125.3; calcd for $PF_2N_3BH_3$, 124.8). The following are the mass numbers (species) and relative abundances of the major ions in the mass spectrum of $PF_2N_3BH_3$: 125 ($PF_2N_3{}^{11}BH_3^+$), 2.81; 124 ($PF_2N_3{}^{11}BH_2^+$), 17.5; 123 (PF_2N_3-^{11}BH), 8.5; 112 ($PF_2N_3H^+$), 3.1; 111 (PF_2N_3), 48.3; 95 (PF_2N-$^{11}BH^+$), 2.44; 94 ($PF_2N^{11}B^+$), 20.8; 93 ($PF_2N^{10}B^+$), 5.3; 92 (PFN_3^+), 8.3; 83 (PF_2N^+), 12.2; 76 ($PFN^{11}BH^+$), 3.9; 64 (PF_2N^+), 72.1; 51 (PFH^+), 5.7; 50 (PF^+), 10.0; 49 (PNH_4^+), 7.8; 46 (PNH^+), 12.8; 33 (NF^+), 3.0; 32 (PH^+), 5.3; 31 (P^+), 8.6; 30 ($^{11}BH^+$), 2.8; 28 (N_2^+), 9.8; 18 (H_2O^+), 6.7; 13 ($^{11}BH_2^+$), 4.9.[36]

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(36) Note Added in Proof.—Since acceptance of this note a paper has appeared by S. R. O'Neill and J. M. Shreeve [*Inorg. Chem.*, **11**, 1629 (1972)] describing the preparation of PF_2N_3 by a similar route. Although we did not experience any explosions with PF_2N_3 their work suggests caution.

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A Novel and Improved Synthesis of $[IrCl(NO)(P(C_6H_5)_3)_2]^+$. A Nitrosyl Analog of Vaska's Compound

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There has been a great deal of interest lately, by ourselves[1] and others,[2] in the synthesis and properties of the complex $[IrCl(NO)(P(C_6H_5)_3)_2]^+$.

We report here a novel and greatly improved preparation for the complexes $[IrX(NO)(P(C_6H_5)_3)_2]^+$ (X = Cl, Br) beginning with the readily available com-

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