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Synthesis of Propynyldifluorophosphine

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Prop-1-ynyldifluorophosphine has been prepared by the reaction of LiC_3H_3 and PF_2Br. $PF_2C_3H_3$ slowly decomposes *in vacuo* at room temperature and combines with B_2H_6 to form an adduct. Nuclear magnetic resonance, infrared, and mass spectral techniques have been used to demonstrate that the borane is attached to the phosphorus. Boron trifluoride reacts with $PF_2C_3H_3$ to yield the phosphorane, $PF_4C_3H_3$. Propynyltetrafluorophosphorane is also produced by the fluorination of $PF_2C_3H_3$ with SbF_3 and catalytic amounts of $SbCl_5$.

Introduction

The preparation and characterization of several acetylenic phosphines have previously been reported,[1-6] with the most common method of preparation consisting of condensing an organophosphorus halide with an acetylide

$$n\mathrm{RC{\equiv}CM} + R'_{3-n}\mathrm{PX}_n \xrightarrow{\text{solvent}} (\mathrm{RC{\equiv}C})_n\mathrm{PR}'_{3-n} + n\mathrm{MX}$$

where M = MgX, Hg; R = alkyl, aryl, alkenyl, etc.; R′ = alkyl, aryl; and X = halide. More recently Carty and others[6] have prepared various acetylenic phosphines by the reaction of organophosphorus halides with alkynyllithium compounds. We report here the preparation of the first alkynylfluorophosphine, prop-1-ynyldifluorophosphine, by the metathetic reaction of lithium propynyl on bromodifluorophosphine.

Experimental Section

General Techniques. Standard high-vacuum techniques were used throughout.[7] 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 spectra were obtained on a Varian M66 (70 eV), while ^{19}F nmr spectra were recorded on a Jeol JNM-C-60 HL operating at 56.4 MHz. Proton nmr spectra were determined with a Varian Associates A-60 nmr instrument at 60 MHz and a Jeol MH-100 operating at 100 MHz. ^{11}B and ^{31}P spectra were recorded with a Varian Associates HR-100 nmr spectrophotometer at 32.1 and 40.4 MHz, respectively. Internal TMS and external $CFCl_3$, $(C_2H_5)_2OBF_3$, and 85% H_3PO_4 served as references for ^1H, ^{19}F, ^{11}B, and ^{31}P spectra, respectively, unless stated otherwise.

Material. Commercial BF_3 (Matheson), $LiC{\equiv}CCH_3$ (Research Organic Chemicals/Research Inorganic Chemicals), SbF_3 (Allied Chemicals), and $SbCl_5$ (Alfa Organics) were used without further purification. PF_2Br,[8] B_2H_6,[9] $PF_2N(CH_3)_2$,[10] $PF_2N(CH_3)_2BH_3$,[10] and PF_2HBH_3[11] were prepared by literature methods.

Synthesis of $PF_2C_3H_3$. A 20.0-mmol (0.92 g) sample of LiC_3H_3 was weighed and placed in a 500-cm^3 reaction bulb with a removable tube. The bulb was evacuated for 3 hr; then a 15.0-mmol sample of PF_2Br was frozen at −196° on the LiC_3H_3. The reaction mixture was allowed to warm to −78° in a Dry Ice–acetone slush and sit for 12 hr. The reaction bulb was then placed in a petroleum ether slush at −80° which warmed to −45° in approximately 4 hr. The mixture was cooled to −196°, allowed to warm slowly, and distilled through traps held at −60, −98, −135, and −196°. The −60° trap contained traces of an unidentified volatile solid which was discarded along with small amounts of PF_3 in the −196° trap. A 6.0-mmol amount of unreacted PF_2Br was found in the −135° trap, and 2.0 mmol of $PF_2C_3H_3$ was isolated in the −98° trap. PF_3 and PF_2Br were identified by infrared spectra. The per cent yield based on consumed PF_2Br was 22.2%.

Following are the mass numbers (species) and relative abundances of the ions in the mass spectrum of $F_2PC_3H_3$: 109 ($PF_2C_3H_4^+$), 3.8; 108 ($PF_2C_3H_3^+$), 100.0; 107 ($PF_2C_3H_2^+$), 4.3; 89 ($PFC_3H_3^+$), 1.9; 88 (PF_3^+, $PFC_3H_2^+$), 1.7; 87 (PFC_3H^+), 1.9; 69 (PF_2^+), 63.5; 68 (PC_3H^+), 3.3; 67 (PC_3^+), 1.0; 57 ($PC_2H_2^+$), 2.6; 55 (PC_2^+), 1.0; 50 (PF^+), 2.6; 42 ($C_3H_6^+$), 1.0; 41 ($C_3H_5^+$), 1.5; 40 ($C_3H_4^+$), 1.4; 39 ($C_3H_3^+$), 28.7; 38 ($C_3H_2^+$), 6.2; 37 (C_3H^+), 4.2; 32 (PH^+, CFH^+), 3.1; 29 ($C_2H_5^+$), 1.0; 28 ($C_2H_4^+$), 5.8. The vapor pressure values (−45.3°, 1.7 mm; −35.7°, 3.2 mm; −22.8°, 7.7 mm; −6.6°, 19.9 mm; 0.0°, 29.4 mm; 5.2°, 38.1 mm) can be expressed by the equation

$$\log P(\mathrm{mm}) = -1710/T + 7.718$$

where T is in degrees Kelvin. The entropy of vaporization at the normal boiling point is 22.1 cal/mol deg. Little association is apparent. The extrapolated boiling point is 80.2°; mp −64.0 ± 1.0°.

Decomposition of $PF_2C_3H_3$. A 7.39-mmol sample of $PF_2C_3H_3$ was frozen at −196° in a 50-cm^3 bulb and then allowed to warm to ambient temperature. After 86 hr we distilled the products through traps held at −56, −100, −162, and −196°. Yellow solids remained in the bulb. A trace of an unidentified oil in the −56° trap was discarded along with traces of SiF_4 and PF_3, identified by ir, in the −162 and −196° traps, respectively. The −100° trap contained $PF_2C_3H_3$ and a trace of $PF_4C_3H_3$, identified by ir. The two compounds could not be separated by trap to trap distillation. The −100° trap (mixture) contained approximately 5.8 mmol of $PF_2C_3H_3$ indicating 28% decomposition.

Reaction of $PF_2C_3H_3$ and H_2O. A 3.17-mmol sample of $PF_2C_3H_3$ was condensed at −196° with the same amount of H_2O in a 50-cm^3 bulb and allowed to warm to room temperature. After 132 hr the mixture was distilled from −35° through a −196° trap. A 0.24-mmol amount of SiF_4, identified by ir, was found in the −196° trap while the bulb contained an unidentified oil and white solid. Further attempts at characterization of the mixture failed.

Reaction of $PF_2C_3H_3$ and B_2H_6. A 1.27-mmol sample of B_2H_6 and a 2.25-mmol sample of $PF_2C_3H_3$ were frozen in a 50-cm^3 bulb open to a manometer and allowed to warm to room temperature. The mixture was alternately warmed and frozen until the pressure above the reaction was constant. The mixture was then distilled through traps held at −70, −105, and −196°. An unidentified oil remained in the bulb, while a trace of B_2H_6 was found at −196°. A 0.22-mmol sample of $PF_2C_3H_3$ was recovered from the −105° trap while 1.93 mmol of $PF_2C_3H_3BH_3$ was isolated in the −70° trap for a per cent yield based on consumed ligand of 95.1%. B_2H_6 and $PF_2C_3H_3$ were identified by ir. The principal ions (^{11}B only) in the mass spectrum are given below. Fragmentation was quite extensive and the mass peak of the molecular ion was small. Several peaks appear which are either the result of addition of a hydrogen atom to an observed fragment[12] or the result of a fluorine migration from

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phosphorus to carbon or boron.[13,14] Following are the mass numbers (species) and relative abundances of the mass spectrum of $PF_2C_3H_3BH_3$: 122 ($PF_2C_3H_3{}^{11}BH_3{}^+$), 1.0; 121 ($PF_2C_3H_3{}^{11}BH_2{}^+$), 12.8; 120 ($PF_2C_3H_3{}^{11}BH^+$), 5.2; 119 ($PF_2C_3H_3{}^{11}B^+$), 2.6; 109 ($PF_2C_3H_4{}^+$), 5.3; 108 ($PF_2C_3H_3{}^+$), 59.2; 107 ($PF_2C_3H_2{}^+$), 16.2; 106 ($PF_2C_3H^+$), 4.6; 105 ($PF_2C_3{}^+$) 4.8; 104 ($PFHC_3H_3{}^{11}BH_3{}^+$), 1.7; 97 ($PF_2C_2H_4{}^+$, $PF_2CH^{11}BH_3{}^+$), 1.7; 94 ($PF_2C_2H^+$), 1.0; 93 ($PF_2C_2{}^+$), 8.5; 92 ($PFC_3H_6{}^+$), 2.7; 90 ($PFC_3H_4{}^+$), 1.8; 89 ($PFC_3H_3{}^+$), 9.7; 88 ($PF_3{}^+$, $PFC_3H_2{}^+$), 2.4; 87 (PFC_3H^+), 2.4; 77 ($PFC_2H_3{}^+$), 1.6; 75 (PFC_2H^+), 2.9; 74 ($PFC_2{}^+$), 1.6; 73 ($PC_3H_6{}^+$), 2.7; 72 ($PF_2H_3{}^+$, $PC_3H_5{}^+$), 2.6; 71 ($PF_2H_2{}^+$, $PC_3H_4{}^+$), 10.7; 70 (PF_2H^+), 6.4; 69 ($PF_2{}^+$, $PC_3H_2{}^+$), 56.2; 68 (PC_3H^+, $^{11}BF_3{}^+$), 6.3; 67 ($PC_3{}^+$), 1.0; 65 ($PFH_4{}^{11}B^+$, $PFCH_3{}^+$), 2.7; 64 ($PF^{11}BH_3{}^+$, $PFCH_2{}^+$), 1.0; 63 ($PFCH^+$, $PF^{11}BH_2{}^+$), 1.0; 62 ($PFH^{11}B^+$, PFC^+), 1.0; 58 ($PC_2H_3{}^+$, $PCH^{11}BH_3{}^+$), 8.7; 57 ($PC_2H_2{}^+$, $P^{11}BH_3C^+$), 9.7; 56 (PC_2H^+, $P^{11}BH_2C^+$), 1.5; 55 ($PC_2{}^+$, $P^{11}BHC^+$), 2.2; 54 ($P^{11}BC^+$), 1.0; 53 ($PFH_3{}^+$, $C_3{}^{11}BH_6{}^+$), 9.9; 52 ($PFH_2{}^+$, $C_3{}^{11}BH_5{}^+$), 9.0; 51 (PFH^+, $C_3{}^{11}BH_4{}^+$), 100.0; 50 (PF^+, $C_3{}^{11}BH_3{}^+$), 39.0; 49 ($C_3{}^{11}BH_2{}^+$, $^{11}BF_2{}^+$), 10.9; 48 ($C_3{}^{11}BH^+$), 2.7; 47 ($C_3{}^{11}B^+$), 2.8; 46 ($PCH_3{}^+$, $P^{11}BH_4{}^+$), 1.0; 45 ($PCH_2{}^+$, $P^{11}BH_3{}^+$), 14.3; 44 ($PCH_2{}^+$), 2.5; 41 ($C_3H_5{}^+$), 1.4; 40 ($C_3H_4{}^+$), 1.2; 39 ($C_3H_3{}^+$), 27.2; 38 ($C_3H_2{}^+$), 5.7; 37 (C_3H^+), 4.8; 36 ($C_3{}^+$), 1.1; 32 (PH^+, CFH^+), 2.0; 31 (P^+, CF^+), 3.1; 30 ($C_2H_6{}^+$), 1.0; 29 ($C_2H_5{}^+$), 6.7; 28 ($C_2H_4{}^+$, $^{11}B_2H_5{}^+$), 3.2; 26 ($C_2H_2{}^+$), 1.1; 18 (H_2O^+), 1.1; 13 ($^{11}BH_2{}^+$, CH^+), 2.0; 12 ($^{11}BH^+$), 1.0; 11 ($^{11}B^+$), 1.7. Nmr spectra: ^1H (neat): δ_{CH_3} 2.28 ppm[15] (t, $J_{FCH} = 4.6$ Hz); each member of a triplet is a doublet ($J_{PCH} = 2.0$ Hz); each member of a doublet is a quartet ($J_{^1HBCH} = {\sim}0.5$ Hz ($-10°$)); δ_{BH_3} 0.99 ppm (q, $J_{BH} = 104$ Hz ($-10°$), 99.5 Hz ($-50°$)); each member of a quartet is a quartet (q, $J_{PBH} = 20.6$ Hz $= J_{FBH} = 20.6$ Hz ($-10°$)); ^{19}F: δ_F 74.9 ppm (d, $J_{PF} = 1177$ Hz ($-10°$)); each member of a doublet is a quartet (q, $J_{FBH} = 20.2$ Hz); each member of a quartet is a quartet (q, $J_{FCH} = 4.6$ Hz) [s = singlet, d = doublet, t = triplet, q = quartet].

Decomposition of $PF_2C_3H_3BH_3$. A 1.94-mmol sample of $PF_2C_3H_3BH_3$ was condensed in a 50-cm^3 reaction tube and allowed to warm to room temperature. After 132 hr the products were distilled through traps held at −95 and −196°. A 0.03-mmol amount of $PF_2C_3H_3BH_3$ was found at −95°, while 0.10 mmol of BF_3 was trapped at −196°. A yellow-white solid remained in the tube. After 980 hr at room temperature, a 2.87-mmol sample of $PF_2C_3H_3BH_3$ was 100% decomposed. Distillation through −196° yielded approximately 0.05 mmol of SiF_4 contaminated by a trace of PF_3. A yellow-white crystalline solid remained in the tube. No BF_3 was found. All products were identified by ir and no noncondensables were ever present.

Base-Exchange Reactions. Equimolar quantities of the reactants were frozen together in a 50-cm^3 reaction bulb and allowed to warm to −10° for 24 hr. In each case side products were noted by ir. The reactants were then warmed to ambient temperature for 48 hr. Ir indicated mixtures of the ligands and their borane adducts and various side products. Solids were visible in each reaction.

Reaction of $PF_2C_3H_3$ and BF_3. An 11.2-mmol sample of BF_3 and a 5.08-mmol sample of $PF_2C_3H_3$ were frozen in a 50-cm^3 bulb at −196° and allowed to warm to room temperature. The mixture was then warmed and frozen until no peaks of $PF_2C_3H_3$ were visible in the infrared spectrum. The products were distilled through traps at −120 and −196°. An unidentified brown solid remained in the reaction bulb. A 5.92-mmol amount of BF_3 was recovered from the −196° trap, while 1.22 mmol of $PF_4C_3H_3$ was isolated at −120°. The per cent yield based on $PF_2C_3H_3$ was 22.0%. Following are the mass numbers (species) and relative abundances of the mass spectrum of $PF_4C{\equiv}CCH_3$: 147 ($PF_4C_3H_4{}^+$), 2.9; 146 ($PF_4C_3H_3{}^+$), 78.5; 131 ($PF_4C_2{}^+$), 1.9; 128 ($PF_3C_3H_4{}^+$), 2.1; 127 ($PF_3C_3H_3{}^+$), 48.0; 126 ($PF_3C_3H_2{}^+$), 5.0; 124 ($PF_3C_3{}^+$), 9.0; 108 ($PF_2C_3H_3{}^+$), 1.0; 107 ($PF_4{}^+$), 100; 104 ($PF_3CH_4{}^+$, $SiF_4{}^+$, $POF_3{}^+$), 5.6; 96 ($PF_2C_2H_3{}^+$), 2.1; 88 ($PF_3{}^+$), 4.6; 69 ($PF_2{}^+$), 12.5; 58 ($PC_2H_3{}^+$), 6.3; 57 ($PC_2H_2{}^+$), 20.0; 56 (PC_2H^+), 4.8; 50 (PF^+), 2.1; 41 ($C_3H_5{}^+$), 1.7; 40 ($C_3H_4{}^+$), 8.8; 39 ($C_3H_3{}^+$), 28.4; 38 ($C_3H_2{}^+$), 17.3; 37 (C_3H^+), 13.0; 36 ($C_3{}^+$), 3.6; 32 (PH^+), 2.9; 31 (P^+), 4.0; 29 ($C_2H_5{}^+$), 2.1; 28 ($C_2H_4{}^+$), 6.9; 27 ($C_2H_3{}^+$), 2.5; 20 (HF^+), 4.2; 18 (H_2O^+), 3.7.

Reaction of $PF_2C_3H_3$ and SbF_3. A 2.34-mmol amount of $PF_2C_3H_3$ was condensed at −196° on an excess of SbF_3 and then allowed to warm to room temperature. The reaction was alternately warmed and frozen to ensure good contact between the reactants. No formation of $PF_4C_3H_3$ was seen in the ir spectrum.

Reaction of $PF_2C_3H_3$ and SbF_3 and $SbCl_5$. A 4.77-mmol sample of $PF_2C_3H_3$ was condensed on an excess of SbF_3 (catalytic amount of $SbCl_5$ added). The mixture was alternately warmed and frozen to ensure good contact. The products were led through traps held at −60, −100, and −196°. A trace of solid at −60° was discarded along with a mixture of PF_5, PF_3, and POF_3 at −196°. A 0.91-mol amount of $PF_4C_3H_3$ was isolated at −100° for a per cent yield based on consumed $PF_2C_3H_3$ of 19%. PF_5, PF_3, and POF_3 were identified by ir.

Results and Discussion

1. Preparation and Characterization of $PF_2C_3H_3$. In the reaction

$$PF_2Br + LiC{\equiv}CCH_3 \rightarrow PF_2C{\equiv}CCH_3 + \text{solids}$$

$PF_2C_3H_3$ was produced in yields of 20–25%. The compound is a clear volatile liquid which decomposes (28% in 84 hr) *in vacuo* at room temperature to solids and traces of $PF_4C_3H_3$, PF_3, and SiF_4. Hydrolysis yields small amounts of SiF_4 and an unidentified oil and white solid. Vapor density measurements were repeatedly high due to decomposition but the formulation $PF_2C_3H_3$ is shown unequivocally by mass, ir, and ^{19}F, ^1H, and ^{31}P nmr spectra.

Since propargylic rearrangements involving the conversion of an alkyne to an allene or to another alkyne are not uncommon,[16,17] the structure of the difluorophosphine was somewhat uncertain; however, spectroscopic analysis indicates the prop-1-ynyl moiety and not an allenic or prop-2-ynyl group. The gas-phase infrared spectrum shows a very strong peak at 2193 cm^{-1} characteristic of a carbon-carbon triple bond stretching frequency, while no stretch attributable to C=C=C asymmetric stretch, a $=CH_2$ wagging, or a C≡C–H stretch was evident in the spectrum.[18,19] This triple bond stretching frequency is very similar to those found in other prop-1-ynyl phosphines,[3] for example, $(C_6H_5)_2PC{\equiv}CCH_3$ at 2190 cm^{-1} and $(C_2H_5)_2PC{\equiv}CCH_3$ at 2180 cm^{-1}.[20] The ir spectrum of $PF_2C_3H_3$ with tentative assignments is listed in Table I.

The nmr spectra are consistent with the $C{\equiv}CCH_3$ structure. In the proton spectrum, a triplet of doublets, the CH_3 group was first split into a triplet from coupling with two equivalent fluorines ($J_{FH} = 7.2$ Hz, δ(relative to internal tetramethylsilane) 1.93 ppm); each member of the triplet was then further split by the phosphorus into doublets ($J_{PH} = 3.7$ Hz). The appearance of only a single type of proton confirms the $C{\equiv}CCH_3$ functionality rather than the $HC{=}C{=}CH_2$ or $CH_2C{\equiv}CH$ structure for $PF_2C_3H_3$.[21-26] No peaks indicative of an allenic or a terminal acetylenic group were observed in the proton spectra. Both the chemical shift of

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(20) These compounds have been isolated as the prop-1-ynyl derivatives. No rearrangements of the prop-1-ynyl moiety to the prop-2-ynyl or the allenic structure have been observed for these phosphines. See ref 16 and 17.

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Table I[a]

$PF_2C_3H_3$	$(BH_3)PF_2C_3H_3$	$PF_4C_3H_3$	Tentative assignment
2965 vw, sh	2965 w	2972 vw	
2935 w	2935 w	2940 vw	C–H str
2860 vw			
	2431 ms		
			B–H str
	2410 m, sh		
2193 vs	2220 vs	2240 vs	C≡C str
2050 mw	2100 vw	2144 w	Hot C≡C[18]
	1102 m		BH_3 def
1030 ms	1043 ms	1080 vs	?
	897 vvs		BH_3 rock
820 vvs	823 m		
	728 s		
		980 vs	P–F str
		882 vs	
593 s	645 ms	672 m	P–C str
	600 ms		P–B str
		571 s	?

[a] 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; sh, shoulder.

the CH_3 group and the $^{31}P-^1H$ coupling constant of $PF_2C_3H_3$ are similar to those reported for $(C_6H_5)_2PC_3H_3$ (δ(relative to tetramethylsilane) 2.09 ppm, $J_{PH} = 1.7$ Hz) and $(C_2H_5)_2PC_3H_3$ (δ(relative to tetramethylsilane) 1.93 ppm, $J_{PH} = 0.9$ Hz).[3]

The fluorine nmr showed the expected doublet of quartets (δ(relative to external $CFCl_3$) 79.8 ppm; $J_{PF} = 1199$ Hz, $J_{FH} = 7.2$ Hz). The J_{PF} is comparable to values for other trivalent organofluorophosphines (PF_2CH_3, δ(relative to $CFCl_3$) 92.9 ppm, $J_{PF} = 1157$ Hz; F_2PCCl_3, δ(relative to $CFCl_3$) 88.0 ppm, $J_{PF} = 1285$ Hz; $F_2PC_2H_5$, δ(relative to $CFCl_3$) +104.5 ppm, $J_{PF} = 1114$ Hz).[27] The phosphorus nmr spectrum confirms the proton and fluorine spectra. A triplet of quartets was observed for the phosphorus spectrum (δ(relative to external orthophosphoric acid) −177 ppm, $J_{PF} = 1199$ Hz; $J_{PH} = 3.7$ Hz). The simplicity of the nmr spectral data and the infrared spectrum[21-26] leaves no doubt that the structure is $F_2PC{\equiv}CCH_3$.

The mass spectrum is relatively simple and can be fitted very nicely to the compound. A complete mass spectrum and vapor pressure data appear in the Experimental Section.

2. Chemistry of $PF_2C_3H_3$. A. The Borane Addition Compound. Since hydroboration of acetylenic compounds occurs fairly readily,[28-30] it was not clear whether borane would add across the triple bond or form a phosphine-borane adduct;[31] however, infrared, nmr, and mass spectral evidence indicate that the initial reaction product is a borane adduct. Vapor density molecular weights were repeatedly high due to decomposition.

The adduct was obtained in 95% yields by the direct reaction of B_2H_6 and $PF_2C_3H_3$ in a 1:2 ratio. The gas-phase infrared spectrum is included in Table I where it can be compared with that of the free ligand.

Since the triple bond stretching frequency remains intact in the infrared spectrum of the adduct, undergoing only a minor shift in frequency (2193 to 2220 cm^{-1}) from that of the free ligand and no peaks appear which are assignable to a hydroboration product, *i.e.*, C=C[18,19] stretching frequencies, then hydroboration evidently does not occur under the conditions employed. The triple bond stretch in the spectrum of the adduct has undergone no gross changes when compared to that of the ligand; thus a π complex[18,19,32] involving the triple bond is also ruled out. The tentative assignment of a P-B[33] stretch in the infrared spectrum indicates that the molecule contains a phosphorus-boron bond.

The ^{11}B nmr spectrum provides confirmation of a P-B bond. At −50° the ^{11}B spectrum of a neat sample consists of a quartet of doublets with $J_{BH} = 99.5$ Hz and $J_{PB} = 68.0$ Hz; δ(relative to external boron trifluoride-ethyl etherate) +18.3 ppm.

The ^1H and ^{19}F nmr spectra provide additional evidence for the borane adduct structure and the presence of a $C{\equiv}CCH_3$ group.[21-26] The data are summarized in the Experimental Section. The presence in the mass spectrum of fragments with the following mass numbers (species) and relative abundances also supports the presence of a P-B bond: 64 ($PH_3F^{11}B^+$, *et al.*), 1.0; 46 ($PH_4{}^{11}B^+$, *et al.*), 1.0; and 45 ($P^{11}BH_3{}^+$, *et al.*), 14.3. A complete mass spectrum appears in the Experimental Section.

$PF_2C_3H_3BH_3$ is found by ir to be undissociated in the gas phase; however, after 106 hr decomposition (98.5%) leads to a solid and small amounts of BF_3, identified by ir. In 980 hr the compound is 100% decomposed to a yellow-white crystalline solid (mp >300°), a small amount of SiF_4, and a trace of PF_3. The solid is soluble in CH_3CN but has not been further characterized. No BF_3 was isolated after 980 hr and no noncondensable was ever present.

An attempt to correlate the J_{PB} of $PF_2C_3H_3BH_3$ with base strength[34] of the ligand toward BH_3 on the basis of selected displacement reactions proved inconclusive because of the rapid decomposition of $PF_2C_3H_3BH_3$ and numerous side reactions. The following base displacements were attempted. Reacting species were identified by ir following trap to trap distillation.

$$PF_2C_3H_3 + PF_2HBH_3 \rightleftarrows PF_2HBH_3 + PF_2C_3H_3BH_3 + PF_2H + PF_2C_3H_3 + PF_3H_2 + SiF_4 + \text{solids} + \text{noncondensables}$$

$$PF_2N(CH_3)_2BH_3 + PF_2C_3H_3 \rightleftarrows PF_2C_3H_3BH_3 + PF_2C_3H_3 + PF_2N(CH_3)_2 + PF_2N(CH_3)_2BH_3 + \text{solids} + \text{noncondensables}$$

$$PF_2C_3H_3BH_3 + PF_2N(CH_3)_2 \rightleftarrows PF_2C_3H_3BH_3 + PF_2C_3H_3 + PF_2N(CH_3)_2 + PF_2N(CH_3)_2BH_3 + \text{solids} + PF_3$$

B. The Phosphorane $PF_4C_3H_3$. When $PF_2C_3H_3$ was reacted directly with BF_3 in an attempt to form the boron trifluoride adduct, a compound of the formula $PF_4C_3H_3$ was isolated in a 24% yield as the only volatile, while an uncharacterized oil remained behind. Further investigation of the reaction was not attempted.

$PF_4C_3H_3$ was characterized by vapor density molecular weight at 19.9° and 93 mm pressure (mol wt: found, 145.6; calcd, 146.0) and by infrared, ^{19}F and ^1H nmr, and mass spectra. The mass numbers (species) and relative abundances agree with the formulation $PF_4C_3H_3$. A complete mass spectrum is in the Experimental Section.

A very strong stretch in the gas-phase infrared spectrum of $PF_4C_3H_3$ at 2240 cm^{-1} is characteristic of a carbon-

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carbon triple bond and not an allenic group, and also as in the trivalent compound no stretches attributable to either $=CH_2$ wagging or a $C{\equiv}CH$ are present.[18,19] The infrared spectrum is listed in Table I.

The ^{19}F and ^1H nmr spectra support the prop-1-ynyl structure.[21-26] As in all RPF_4 compounds (R = alkyl) the fluorines appear to be equivalent over a wide range of temperatures. The ^{19}F nmr spectrum consists of a doublet of quartets ($J_{PF} = 896$ Hz, $J_{FH} = 2.6$ Hz) from -10 to $-80°$. The spectrum could not be taken any lower than $-80°$ as $PF_4C_3H_3$ began to freeze from the isopentane solution. J_{PF} and J_{FH} do not vary over this range of temperatures while the chemical shift from external $CFCl_3$ varies from +41.7 ppm ($-10°$, $CHCl_3$) to +40.7 ppm ($-80°$, isopentane). These spectra are typical of a tetrafluorophosphorane except that the chemical shift is slightly out of the range normally observed for these compounds ($\sim$+45 to +55 ppm).[35] No nmr spectra have been obtained on neat samples because of preparative difficulties.

As in $PF_2C_3H_3$, the simplicity of the ^1H spectra confirm the 1-alkynyl rather than the allenic or terminal acetylenic structure.[21-26] The spectrum is a doublet of pentets (J_{FH} = 2.6 Hz, J_{PH} = 2.6 Hz, δ(relative to internal tetramethylsilane) 1.98 ppm ($-10°$, $CHCl_3$)).

Prop-1-ynyltetrafluorophosphorane has also been obtained in the decomposition of $PF_2C{\equiv}CCH_3$ and from the reaction of SbF_3 (catalytic amount of $SbCl_5$[35]) with $PF_2C_3H_3$. No reaction occurs unless the catalyst is present. The infrared and ^{19}F and ^1H nmr spectra of the compound prepared from these reactions are identical with those of the compound prepared from the reaction of BF_3 and $PF_2C_3H_3$.

Registry No. $PF_2C_3H_3$, 37805-59-7; LiC_3H_3, 4529-04-8; PF_2Br, 15597-40-7; B_2H_6, 1928-74-57; $PF_2C_3H_3BH_3$, 37805-62-2; BF_3, 763-70-72; $PF_4C_3H_3$, 37805-63-3; SbF_3, 7783-56-4.

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Mass Spectra of Unsymmetrically B-Substituted Borazines

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The mass spectra of B-substituted derivatives of borazine and of *N*-trimethylborazine were recorded and analyzed in terms of the relative contribution of the parent ion and certain fragment ion intensities. A method of spectral analysis was developed to separate the observed distribution of mass peaks into overlapping distributions of parent and fragment ions. The results are discussed in terms of the relative stabilities of parent fragment ions arising from substituent effects. B-Substituents are more labile than the corresponding N-substituents, the six-membered ring fragments being stabilized by release of electron density from the adjacent nitrogen atoms. On the other hand, borazines containing *N*-methyl substituents lose a hydrogen atom to form immonium-like fragment ions.

Introduction

During the course of preparing a series of unsymmetrically B-substituted borazines for other purposes,[1,2] we became interested in the use of mass spectrometry as a method for establishing criteria of purity for these compounds. Such criteria were especially important for this series of borazines because the synthetic methods employed generally yield mixed substitution products; some of the pure compounds also undergo spontaneous redistribution reactions.[3] The results reported here verify the validity of our original interest in using mass spectrometry to characterize these compounds. In addition, the mass spectra contain features which can be related to the constitution of these compounds.

Experimental Section

The details of the preparation of the unsymmetrically B-substituted borazines used in this study are reported elsewhere.[1,2] Mass spectra were recorded with either a Consolidated Electrodynamics Corp. Type 21-1030 or a Bell and Howell 21491 mass spectrometer; both instruments operate with an ionization potential of 70 V and an ionizing current of 50 mA. The former instrument incorporated a heated inlet system; samples were introduced in capillary tubes that were broken either immediately prior to introduction or internally by a heat sensitive, bimetallic strip. The Bell and Howell spectrometer used a direct-probe system, solid samples being introduced in sealed capillary tubes opened immediately prior to introduction and liquid samples with a syringe. Experiments involving compounds with a *B*-halogeno moiety invariably yielded hydrolysis products when the capillary tube was broken immediately prior to introduction into the spectrometer.

The mass distribution of the molecular ion peak was calculated by a binomial expansion method described elsewhere[4] using a program available at the Mass Spectrometry Laboratory of the University of Texas. The following isotope abundances were used in the calculation: ^{10}B, 19.61%; ^{11}B, 80.39%; ^{12}C, 98.89%; ^{13}C, 1.11%; ^{35}Cl, 75.77%; ^{37}Cl, 24.23%; ^{79}Br, 50.54%; ^{81}Br, 49.46%.[5]

Discussion

General Features. Typical mass spectra observed for the borazines are shown in Figures 1 and 2. The lower mass range contains doubly charged species and fragment group

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