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Chemistry of 1,2-Bis(difluorophosphino)ethane. Preparation of 2,5-Difluoro-1-methyl-1,2,5-azadiphospholidine and 1-Dimethylaminofluorophosphino-2-difluorophosphinoethane

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The gas-phase reaction of methylamine with $F_2PCH_2CH_2PF_2$ has resulted in ring closure and the formation of 2,5-difluoro-1-methyl-1,2,5-azadiphosphilidine, $F\overline{PCH_2CH_2PFN}CH_3$. Under similar conditions, ammonia apparently reacts to give ring closure also but in much lower yield and with lower product stability. Dimethylamine reacts to give 1-dimethylaminofluorophosphino-2-difluorophosphinoethane, a potentially useful bidentate ligand.

Introduction

The formation of nitrogen–phosphorus bonds by means of the metathesis reaction of a nontertiary amine and a phosphorus–halogen bond is a well-established reaction.[1] The chemistry of the resultant aminophosphine compounds has been of interest in terms of both the competition for Lewis acids[1a,2] between the two sites (N and P) and the extent of π bonding between the two atoms.[1a,3] In this work, we have studied the reactions of the bidentate fluorophosphine ligand, $F_2PCH_2CH_2PF_2$, with ammonia, methylamine, and dimethylamine because of the probability of formation of a new heteroring system and/or of unusual new bidentate ligands.

Experimental Section

General Information. Standard high-vacuum techniques were used throughout. Ammonia, methylamine, and dimethylamine were obtained from Matheson Gas Products and were used without further purification. $F_2PCH_2CH_2PF_2$ was prepared as previously described.[4] All nmr data were obtained with neat liquids using a Varian XL-100-12 nmr spectrometer. Chemical shifts were determined by tube interchange. Ir data were recorded on a Beckman IR-20-A spectrometer, and mass spectra, on a Hitachi Perkin-Elmer RMU-6E spectrometer at 70 eV.

Preparation of 1,1-Dimethylaminofluorophosphino-2-difluorophosphinoethane, $(CH_3)_2NPFCH_2CH_2PF_2$. In a typical reaction, 0.70 mmol of dimethylamine was condensed at −196° into a 200-ml reaction bulb connected *via* a stopcock to a 500-ml reaction bulb in which 0.45 mmol of $PF_2CH_2CH_2PF_2$ was condensed. The reactants were allowed to warm to room temperature (both reactants completely vaporized) and the connecting stopcock was opened. The immediate formation of a cloud of white solids and droplets of liquid on the sides of the reaction vessel were observed. The reaction was allowed to proceed for 15 sec and then condensed at −196°. The volatile products were distilled through traps held at −45, −95, and −196°. The trap held at −196° contained 0.06 mmol of PF_3 with a trace of $PF_2N(CH_3)_2$ (ir). The trap held at −95° contained 0.22 mmol of $PF_2CH_2CH_2PF_2$ (ir). The trap held at −45° contained 0.16 mmol of a colorless liquid (vp $\lesssim$1 mm at 23°) which was subsequently identified as $PF_2CH_2CH_2PFN(CH_3)_2$. This new compound decomposes to a yellow liquid upon standing at room temperature under vacuum for periods longer than a few minutes. Unidentified nonvolatile solids remained in the original reaction vessel. The yield of product based on $F_2PCH_2CH_2PF_2$ consumed was 70%. In a similar reaction containing higher ratio of amine to phosphine (1.51 mmol of $HN(CH_3)_2$ to 0.50 mmol of $F_2PCH_2CH_2PF_2$), similar cloud formation was observed. In this case, the principal volatile product recovered was 0.07 mmol of $F_2PN(CH_3)_2$ (ir and mass spectra). A trace of $F_2PCH_2CH_2PFN(CH_3)_2$ was also observed (mass spectrum).

The gas-phase ir spectrum of $PF_2CH_2CH_2PFN(CH_3)_2$ shows the following absorption bands (relative intensity and tentative assignment in parentheses) (cm^{-1}): 2292 (vw, ν(CH)), 2902 (w, ν(CH)), 2858 (vw, ν(CH)), 1450 (vw, $\delta(CH_2)$), 1408 (w), 1282 (w), 1186 (w), 1060 (w), 980 (m, ν(PN–C)), 816 (s, ν(PF)), 731 (m, ν(P–NC)), 695 (m, ν(PC)). The mass spectrum included the following *m/e* peaks (relative intensity and assignment in parentheses): 192 (0.7, isotope peak of 191), 191 (12, $(CH_3)_2NPFCH_2CH_2PF_2^+$), 147 (4.1 (4.1, $PFCH_2CH_2PF_2^+$), 115 (4.1, $(CH_3)_2NPFCHCH^+$), 97 (7.3, $PF_2CH_2CH_2^+$), 94 (100, $PFN(CH_3)_2^+$), 78 (7, $CH_2CH_2PF^+$), 69 (46, PF_2^+), 60 (9, $PNCH_3^+$), 59 (10.2, $CH_2CH_2P^+$ or $PNCH_2^+$), 50 (5, PF^+), 45 (1.3 PN^+). Other peaks, omitted for brevity, were consistent with these assignments. Nmr data: ^1H (100.1 MHz, +10°), δ 2.1 ppm (TMS, area 2), δ 3.2 ppm (TMS, area 3); ^{19}F (94.1 MHz, +10°), δ 98.7 ppm (upfield from $CFCl_3$, doublet, area 2, J_{PF} = 1157 Hz), δ +120.3 ppm (doublet, area 1, J_{PF} = 940 Hz); ^{31}P (40.5 MHz, +10°), δ −221.9 ppm (downfield from 85% H_3PO_4, OPA, triplet, area 1, J_{PF} = 1150 Hz), δ −169.4 ppm (doublet, area 1, J_{PF} = 933 Hz).

Preparation of 2,5-Difluoro-1-methyl-1,2,5-azadiphospholidine. The compound $F\overline{PCH_2CH_2PFN}CH_3$ results from the low-pressure gas-phase reaction of H_2NCH_3 and 1,2-bis(difluorophosphino)ethane, $PF_2CH_2CH_2PF_2$. In a typical reaction 0.284 mmol of H_2NCH_3 and 0.226 mmol of $PF_2CH_2CH_2PF_2$ were allowed to react in a manner analogous to that described for the $PF_2CH_2CH_2PF_2$–$HN(CH_3)_2$ reaction. The formation of a white solid on the walls of the reaction bulb was immediately apparent. After the reaction had proceeded for 15 sec, the reaction mixture was condensed at −196° and then allowed to warm to room temperature and stand for 2 min. The volatile products were distilled through traps held at −23, −45, and −196°. No material was recovered from the trap held at −23°. The trap held at −196° held 0.064 mmol of $PF_2CH_2CH_2PF_2$. The trap held at −45° contained 0.085 mmol of a colorless liquid of low volatility (vp ~4.5 mm at 26°) which was subsequently identified as $\overline{PFCH_2CH_2PFN}CH_3$. This colorless liquid attains increasing yellow coloration on standing at room temperature under vacuum indicating fairly rapid decomposition. The yield of $\overline{PFCH_2CH_2PFN}CH_3$ was 60% based on the amount of H_2NCH_3 and a balanced equation.

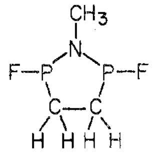
The infrared spectrum of gaseous $\overline{PFCH_2CH_2PFN}CH_3$ displayed the following absorption bands (cm^{-1}): 3002 (vw, ν(CH)), 2943 (m, ν(CH)), 2920 (m, ν(CH)), 2910 (m, ν(CH)), 1481 (vw, $\delta(CH_3)$), 1404 (w), 1187 (m), 1131 (ms), 857 (s), 820 (w), 775 (ms), 743 (s, ν(PF)), 674 (m), 635 (vw), 575 (vw), 520 (w, ρ(PF)). The mass spectrum (75 eV) displayed the following principal peaks (relative intensities and assignments in parentheses): 157 (26, $\overline{PFCH_2CH_2PFN}CH_3^+$), 129 (27, $PFNCH_3PF^+$), 114 (24, $FPNPF^+$), 110 (4, $PNCH_3PF^+$), 106 (0.5, metastable), 95 (1.5, $PNPF^+$), 78 (12, CH_2PFN^+ or $FPCH_2CH_2^+$), 60 (100, $PNCH_3^+$), 50 (12, PF^+), 43 (8, PC^+). Nmr data: ^1H (100.1 MHz, +10°), δ 1.15 ppm (br, unresolved, area 4), δ 2.44 ppm (br, unresolved, area 3); ^{19}F (94.1 MHz, +10°), δ +125.7 ppm (doublet, J_{PF} = 993 Hz); ^{31}P (40.5 MHz, +10°), δ −185.6 ppm (doublet, J_{PF} = 985 Hz).

Reaction of $F_2PCH_2CH_2PF_2$ with NH_3. A typical reaction mixture of 0.29 mmol of NH_3 and 0.21 mmol of $F_2PCH_2CH_2PF_2$ was prepared in a manner analogous to that described for the previous systems. The reaction was allowed to proceed for 20 sec (immediate formation of solid particles on the sides of the reaction vessel was observed) and then was frozen at −196° and allowed to warm again for ~2 min. Volatile products were then distilled through traps held at −45, −63, and −196°. The reaction vessel held unidentified solids. The trap held at −196° contained 0.01 mmol of unidentified material. The trap held at −63° contained 0.10 mmol of $PF_2CH_2CH_2PF_2$ (mass spectrum). The trap held at −45° contained 3 small drops of material which was tentatively identified as a mixture of $PF_2CH_2CH_2PF_2$ and $HN\overline{PFCH_2CH_2P}F$. The mass spectrum of the −45° fraction showed in addition to peaks due to $PF_2CH_2CH_2PF_2$ the following *m/e* values (assignment and relative intensity in parentheses): 143 (1.5, $HNPFCH_2CH_2PF^+$), 129 (2.9, $PFNHPFCH_2^+$), 115 (2.0, $PFNHPF^+$), 114 (3.0, $PFNPF^+$), 110 (0.5, $PNHPFCH_2^+$), 78 (2.2, $FPCH_2CH_2^+$), 60 (9, CH_2PNH^+), 50 (6.5, PF^+), 46 (5, PNH^+). Peaks of low mass numbers were omitted for brevity.

Results and Discussion

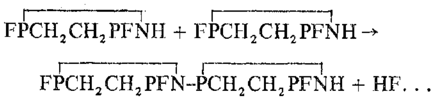
1-Dimethylaminofluorophosphino-2-difluorophosphinoethane. Identification of $(CH_3)_2NPFCH_2CH_2PF_2$ was made unequivocally by spectral data. The presence of the methyl group and of PF bonding was demonstrated by observation of the bonds characteristic of the features in the infrared spectra at 2800–3000 and 816 cm^{-1}, respectively. Other features of the infrared spectrum are similar to those of $F_2PN(CH_3)_2$[1a] and are consistent with the proposed structural assignment. The formulation is also supported by the mass spectrum (Experimental Section) both by the presence of the molecular ion peak (*m/e* 191) and by the presence of appropriate isotope and fragment ion peaks. The ratio of 191 and 192 peaks, 12:0.7, is reasonable for the ^{12}C to ^{13}C isotope ratio expected. The nmr data complete the characterization. The proton spectrum consisted of two signals in the 3:2 area ratio appropriate to the $(CH_3)_2$ and C_2H_4 proton ratio for $(CH_3)_2NPFCH_2CH_2PF_2$. Both signals appeared at chemical shift positions consistent with methyl and methylene protons, respectively. The methyl proton peak was quite broad as is normal for methyl protons bound to a nitrogen as a result of quadrupolar broadening. Unresolved splitting due to the proton–phosphorus coupling may also contribute to the breadth of the signal. The methylene signal was suggestive of unresolved splitting due to slight nonequivalence of the protons and to coupling with the phosphorus and/or fluorine nuclei. The fluorine nmr spectrum indicates the presence of nonequivalent fluorine nuclei in a ratio of 2:1. The two doublet signals are assignable to a PF and PF_2 group based on the area ratio and the following: the coupling constant of the doublet of area 1 (940 Hz) and its chemical shift (+120.3 ppm) are similar to those for $CH_3PFN(C_2H_5)_2$[5] (914 Hz and 110.2 ppm, respectively); the corresponding values for the doublet of area 2 (1157 Hz and 98.7 ppm) are consistent with those of the parent $F_2PCH_2CH_2PF_2$[4] (1168 Hz and 98.7 ppm, respectively). The phosphorus spectrum consists of a triplet and a doublet of equal areas arising from the ^{19}F coupling of the PF_2 group and the ^{19}F coupling in the $PFN(CH_3)_2$ group, respectively. The coupling constants are in excellent agreement with those obtained from the ^{19}F spectrum for the same functional groups. The ^{31}P chemical shifts agree well with those of similar fluorophosphine compounds: the triplet due to the PF_2 group occurs at −222 ppm and the doublet due to the $FPN(CH_3)_2$ group occurs at −169 ppm in $(CH_3)_2NPFCH_2CH_2PF_2$ compared with −234 ppm for the F_2P group in $F_2PCH_2CH_2PF_2$[4] and −167 ppm for the PF group in $CH_3PFN(C_2H_5)_2$.[5] Further confirmation of this assignment arises from the observation that the doublet ^{31}P signal of $(CH_3)_2NPFCH_2CH_2PF_2$ is clearly broader than the triplet signal as a result of quadrupolar broadening by the attached nitrogen. The spectral data then confirm the presence of each of the functional groups in the correct ratios for the proposed molecule; in addition, the sum of these gives the molecular weight determined by mass spectrometry so that the proposed formula is well established.

2,5′-Difluoro-1-methyl-1,2,5-azodiphospholidine. Characterization based on spectral data is again unequivocal. The presence of characteristic CH_3 and PF stretching bands is observed in the ir spectrum. The mass spectrum exhibits a strong molecular ion peak at *m/e* 157. Support for the ring structure comes from the presence of a peak at *m/e* 129, which is the molecular ion less C_2H_4. A metastable peak at *m/e* 106 is consistent with the transition from *m/e* 157 to *m/e* 129 *via* loss of a neutral fragment. It is difficult to conceive of a likely open-chain structure which could undergo loss of only the C_2H_4 fragment. The ^1H nmr spectrum displays peaks in the appropriate position and area ratios to correspond to the CH_3 and $-CH_2CH_2-$ portions of the compound. That both signals are broad with unresolved multiplicity is consistent with our observation in all other compounds of this type.[4,6] The ^{19}F nmr spectrum consists of a 1:1 doublet corresponding to a single fluorine environment coupled directly to the phosphorus to which it is bound. The ^{31}P nmr spectrum consists of a 1:1 doublet as well, with coupling in good agreement with that of the ^{19}F spectrum. The ^{19}F and ^{31}P chemical shift values and coupling constants (δ_F +126 ppm, δ_P −186 ppm, J_{PF} = 989 Hz) are in good agreement with the values found for similar magnetic environments, *e.g.*: $CH_3PFN(C_2H_5)_2$,[5] δ_F +110 ppm, δ_P −165 ppm, J_{PF} = 914 Hz; $H_3CNCH_2CH_2(CH_3)NPF$,[7] δ_F +90 ppm, δ_P −138 ppm, J_{PF} = 1055 Hz. All of these data confirm the structure I.



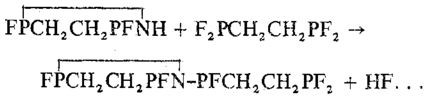
I

The Reaction of $F_2PCH_2CH_2PF_2$ with Ammonia. The mass spectrum of the volatile products of this reaction strongly suggests the formation of the product analogous to that of the reaction with CH_3NH_2. The molecular ion appropriate to $FPCH_2CH_2PFNH$ (*m/e* 143) is present as is the peak at *m/e* 115 corresponding to loss of C_2H_4 from the molecule. All peaks which are not attributable to this product in the spectrum are attributable to $F_2PCH_2CH_2PF_2$ present as impurity. There were clearly complications relative to the case of the reaction with CH_3NH_2, however. The yield of recoverable product was much poorer and the product which was recovered, after standing as a liquid for any length of time, left a white solid residue even after repeated distillations. This is consistent with the presence of a reactive hydrogen on the nitrogen atom which could react further with another like molecule or with $F_2PCH_2CH_2PF_2$ to give a nitrogen–phosphorus bond



$$FPCH_2CH_2PFNH + FPCH_2CH_2PFNH \rightarrow FPCH_2CH_2PFN\text{-}PCH_2CH_2PFNH + HF\ldots$$

or



$$FPCH_2CH_2PFNH + F_2PCH_2CH_2PF_2 \rightarrow FPCH_2CH_2PFN\text{-}PFCH_2CH_2PF_2 + HF\ldots$$

The HF formed in this manner would be likely to react with remaining NH bonds to form saltlike materials.

General Information. The nonobservance of clearly defined multiplets beyond the P–F coupling in the nmr spectra of these compounds implies fairly complex patterns with small coupling constants. As the fluorine nuclei are in each case separated from protons by three bonds and from the phosphorus by two (F–P–C–H), these coupling constants are expected to be small given the rapid falloff in phosphorus–proton coupling with intervening bonds and the greater bond separation for fluorine. In fact, they might be expected to be similar in magnitude and to contribute to the lack of resolution through second-order effects. The phenomenon is at least consistent with our other experience with similar compounds.[6]

The reactions and products described here confirm our expectation that the FP bond of $F_2PCH_2CH_2PF_2$ would be susceptible to cleavage by nontertiary amines to give N–P bonds and what are thought to be largely amine hydrogen difluoride salts.[1b,8] The reaction resulted in the formation of a new heterocyclic system in good yield in the one case. It is possible that a polymeric material also resulted, though the reaction in this case was run to optimize ring formation by limiting the quantity of methylamine available. When dimethylamine is used, the second methyl group effectively blocks ring or polymer formation and the observed singly substituted straight-chain product was formed. Surprisingly, no disubstituted product was recovered when higher amine:ligand ratios were used. Instead, increasing quantities of $(CH_3)_2NPF_2$ were observed suggesting that the formation of $(CH_3)_2NPFCH_2CH_2PFN(CH_3)_2$ is at least accompanied by P–C bond breakage. It is possible that $(CH_3)_2NPFCH_2CH_2PFN(CH_3)_2$ is sufficiently nonvolatile to have remained with the hydrogen difluoride salts in the solid residue where its presence would be very difficult to confirm. The unexpected observation of $(CH_3)_2NPF_2$ at higher stoichiometric ratio may be due to a kinetic effect; *i.e.*, formation of $(CH_3)_2NPF_2$ may be higher order in $HN(CH_3)_2$ than is formation of $(CH_3)_2NPFCH_2CH_2PF_2$. Alternately, the initial formation of $F_2PCH_2CH_2PFN(CH_3)_2$ could affect the opposite difluorophosphino group such that the P–C bond becomes susceptible to bond cleavage by $HN(CH_3)_2$. The product isolated should be of interest in its coordinating properties as either five- or six-membered chelate rings may form depending on whether the bonding is through the two phosphorus atoms or through phosphorus and the nitrogen atom. Further, the PF_2 group is expected to be a better π-acceptor site than is the PFN group while the PFN site is expected to be a better σ donor. We are, at present, investigating these possibilities.

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Registry No. $(CH_3)_2NPFCH_2CH_2PF_2$, 52810-60-3; $FPCH_2CH_2PFNCH_3$, 52810-61-4; $PF_2CH_2CH_2PF_2$, 50966-32-0; $HN(CH_3)_2$, 124-40-3; H_2NCH_3, 74-89-5; NH_3, 7664-41-7; ^{31}P, 7723-14-0.

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Reaction of Silicon Difluoride with Phosphine

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The cocondensation reaction of silicon difluoride and phosphine yields the new compounds difluorosilylphosphine, SiF_2HPH_2, and trifluorosilylphosphine, SiF_3PH_2. Proton and fluorine nmr parameters and mass spectroscopic data are presented. The reaction also yields pentafluorodisilane and higher molecular weight compounds which are thermally unstable. Improvement in the resolution of the ^{19}F nmr spectrum of Si_2F_5H is reported.

Introduction

Since 1965, the chemistry of the high-temperature species silicon difluoride, SiF_2, has been extensively studied[2] in numerous cocondensation reactions. Of the volatile main-group hydrides, the reactions of SiF_2 with diborane(6),[3] germane,[4] and ammonia[2] have been reported. Solan and Burg[3] found that the cocondensation of SiF_2 and B_2H_6 yielded nonvolatile materials and diborane derivatives of the 1,1-fluorosilylated type which were thermally unstable. Germane and SiF_2 react to give products of the type $GeH_3(SiF_2)_nH$ ($n = 1–3$) and the reaction of ammonia and SiF_2 apparently yields deeply colored polymeric material.[2] To date, the cocondensation reaction of SiF_2 with silane has not been reported.

The only phosphorus-containing compounds which have been cocondensed with SiF_2 are phosphorus trifluoride and phosphorus trichloride. The reaction of SiF_2 and PF_3 was reported[5] to yield a red polymer and a mixture of unstable compounds, presumably of the type $Si_nF_{2n+1}PF_2$, which readily decomposed to perfluorosilanes and black P–F polymers. The PCl_3 reaction[6] yielded a yellow-brown polymer and volatile products containing only silicon, fluorine, and chlorine. No volatile silicon–phosphorus compounds were detected.

Although no phosphorus-containing molecules have been isolated from cocondensation reactions with SiF_2, the phosphine molecule appeared to be a potential source of volatile silicon–phosphorus compounds. Reported herein are the results of our study of the SiF_2–PH_3 cocondensation reaction.

Experimental Section

Apparatus. All work was carried out in a conventional high-vacuum system employing greaseless stopcocks. Mass spectra were obtained on a Perkin-Elmer RMU-6 spectrometer. Exact mass measurements were obtained on an AEI MS 902. Infrared spectra in the range 4000–400 cm^{-1} were recorded with a Perkin-Elmer Model 337 on gaseous samples in a 10-cm cell fitted with KBr windows. Proton and fluorine nuclear magnetic resonance spectra were obtained at 100.1 and 94.1 MHz, respectively, on a Varian Associates XL-100-15 in the CW mode. Standard variable-temperature accessories were employed. The furnace for SiF_2 preparation was built in our laboratory from Transite pipe, insulation brick, and Kanthal heating wire. Mullite tubing was used in the furnace.

Materials. Silicon tetrafluoride was obtained commercially (Matheson, 99.6% stated minimum purity) and phosphine was prepared as described in the literature.[7] Silicon difluoride was prepared as described by Timms[8] and PH_3 was introduced into the SiF_2–SiF_4 stream as close to the cocondensation trap as possible. The furnace was maintained at approximately 1300° and a SiF_4 to SiF_2 conversion of about 70% was assumed.[8]

In a typical reaction 1.9 g (56 mmol) of PH_3 and 4.7 g (45 mmol) of SiF_4 were used over a period of 3 hr. After cocondensation was complete, the apparatus was allowed to warm to room temperature