

THE SYNTHESIS AND CHARACTERIZATION OF SOME NEW DIFLUOROPHOSPHINE DERIVATIVES

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Abstract—The heretofore unknown chelating fluorophosphine ligands, $F_2PCH_2PF_2$ and $F_2PCH_2CH=CH_2$ have been prepared and characterized. The reagent F_2PCH_2I has been prepared and used in the synthesis of $F_2PCH_2PF_2$. NMR data are given.

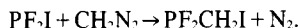
INTRODUCTION

A NUMBER of fluorophosphines with the general formula PF_2X (where $X = F, Cl, Br, I, NR_2, OR,$ etc.) have been studied extensively as ligands in coordination chemistry. Several such studies conducted in this laboratory suggested that new chelating fluorophosphines would have interesting and significant coordination properties. This report describes the synthesis of two of these new ligands, $F_2PCH_2PF_2$ and $F_2PCH_2-CH=CH_2$, both of which are capable of chelate ring formation. The unstable compound F_2PCH_2I was used as an intermediate in these syntheses. Its synthesis and characterization are also described.

The compound difluorophosphinoiodomethane, PF_2CH_2I

Synthesis. The reaction of commercial iodomethylmercury (II) iodide with difluoroiodophosphine[2], gave PF_2CH_2I in 50 per cent yield. The general reaction of organomercury compounds with halophosphines is well known[3] and is usually visualized as a simple metathesis reaction in which the halogen of the halophosphine is transferred to the mercury. Another reasonable but unproved possibility would involve insertion of a carbene into the P-I bond. This would be analogous to the well known insertion of CH_2 into the C-H bond[4].

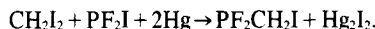
Another synthesis of PF_2CH_2I was patterned more directly after the reaction. Diazomethane was allowed to react with difluoroiodophosphine:



The desired product was obtained in only 10 per cent yield even though the theoretical yield of N_2 was obtained. This observation supports a previous generalization[5] to the effect that a carbene insertion reaction is useful for pentavalent phosphorus compounds, but is poor for

trivalent phosphorus species because of the possibility of addition reactions. These observations argue against the carbene insertion reaction in the more successful process.

A third method of synthesis was patterned after the coupling reaction used earlier in this laboratory[6] to prepare F_2PH from PF_2I and HI . The equation used in the present study is:

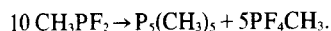


Yields were only 5 per cent or less and requisite reaction times ran from 12 to 15 hr.

Characterization and properties

The ^{19}F NMR spectrum of neat PF_2CH_2I at -15° gives the expected doublet ($\delta = +86.6$ from $CFCl_3$, $J_{PF} = 1197$ Hz), each member of which is split into a 1:2:1 triplet ($J = 13.9$ Hz). The 1H NMR shows two overlapping 1:2:1 triplets centered at $\delta = -2.96$ ppm from TMS ($J_{PCH} = 11.0$; $J_{FPCH} = 14.1$ HZ). The ^{31}P spectrum is a 1:2:1 triplet at -200 ppm from 85 per cent orthophosphoric acid. $J_{FP} = 1187$. Each member of the triplet is split into a 1:2:1 triplet ($J_{HCP} = 10.2$ Hz). The foregoing patterns clearly establish the identity of the species. Other characterization data are in the experimental section.

The compound F_2PCH_2I is a clear liquid which decomposes quite rapidly above $0^\circ C$. A sample of liquid held at $10^\circ C$ for 4 hr decomposed completely to red-brown solids. In the gas phase only 30 per cent decomposition occurred in 24 hr at 25° . No volatile products were obtained, but free iodine was identified. The resulting solid mass was not easily dissolved. Related compounds F_2PCH_3 and F_2PCH_2Cl are also unstable at room temperature. In independent studies Kulapova, Zinovév and Soborovskii[7] and Seel, Rudolph and Budenz[8] showed that CH_3PF_2 undergoes rapid disproportionation at 35° to 40° as defined by the equation:



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Further, PF_2CH_2Cl seems to undergo a similar reaction to

propene-1 spectrum[12]

$$[J_{(1)HCCCH} = 6.4, J_{(2)HCCCH} = -1.33, J_{(3)HCCCH} = 1.75]$$

The ^{31}P spectrum consists of a triplet ($\delta = -220$ ppm from H_3PO_4 , $J_{\text{FP}} = 1160$ Hz), each member of which is split into a 1:2:1 triplet ($J_{\text{HOP}} = 8.7$ Hz) of approximate quartets ($J_{(1-3)\text{HPCCCH}} \approx 3-4$ Hz). Again the NMR data provide strong evidence for the structure assigned. Additional characterization data are found in the experimental section.

A preliminary investigation[14] of the reaction of $\text{F}_2\text{P}-\text{CH}_2\text{CH}=\text{CH}_2$ with $\text{Ni}(\text{CO})_4$ at 0° revealed that some CO is displaced but the products were not defined. The expected coordination properties of these chelating π -ligands is worthy of further study.

EXPERIMENTAL

General procedures. All syntheses were carried out in a high vacuum system using standard high vacuum procedures. I.R. spectra were obtained with a Beckman IR-10 using polystyrene film for calibration. The spectrum of $\text{F}_2\text{PCH}_2\text{CH}=\text{CH}_2$ was also obtained with a Beckman ir-12. A gas cell with a 74 mm path length and CsI windows was used for all compounds. The NMR spectra were obtained using a Varian HR-100 or HA-60 spectrometer. Chemical shifts were by tube interchange. All samples were run in sealed, thin-wall tubes. Standards used were: ^1H , tetramethylsilane (TMS); ^{31}P , 85 per cent orthophosphoric acid (OPA); ^{19}F , fluoro-trichloromethane, CFCl_3 . Mass spectra were obtained on a Consolidated Electrodynamics Model 21-103 B Mass spectrometer operating at 70 eV.

Reagents. The ICH_2HgI used as a starting material was obtained from Alpha Inorganics, Inc. and used without further purification. Iodo-difluorophosphine F_2PI was prepared by literature methods[2]. Diiodomethane, H_2Cl_2 was obtained from Eastman Distillation Products and distilled before use. Diazomethane, CH_2N_2 , was prepared by the method of Moore and Reed[13], and the ether solvent was removed by fractional condensation. **Caution:** diazomethane is extremely explosive in concentrated form and extreme caution should be exercised in handling it! Allyl iodide was obtained from Eastman Distillation Products and purified by passing the vapors through a -37° trap before use.

Procedures for the preparation of $\text{F}_2\text{PCH}_2\text{I}$.

(1) *Metathesis between F_2PI and ICH_2HgI .* To an 11.2 mmole sample of ICH_2HgI in a thoroughly vacuum dried reaction flask was added a 10-15 ml sample of freshly distilled CH_2I_2 . The addition was done under N_2 and a Teflon stirring bar was added. At this point an 11.2 mmole sample of PF_2I was condensed into a 30 ml side arm-connected to the reactor through a stopcock. The PF_2I was allowed to warm to room temperature and distilled into the stirred solution of the mercury compound which was maintained at 7° . Formation of yellow Hg_2I_2 indicated a reaction. After 20 min the products were separated by fractional condensation using -45 , -78 , -122 and -196° traps. A 5.47 mmole quantity of $\text{F}_2\text{PCH}_2\text{I}$ was retained in the -78° trap. (49 per cent yield based on PF_2I). The -196° trap contained 1.17 mmole of PF_3 , while the -112° trap contained 0.53 mmole of unreacted PF_2I and an unidentified contaminant. Solvents were stopped at -45° .

(2) *The mercury coupling reaction for preparation of $\text{F}_2\text{PCH}_2\text{I}$ from CH_2I_2 and PF_2I .* A 4 ml quantity of mercury was placed in a 2 l. reaction bulb equipped with a stopcock. The bulb was evacuated and 20.1 mmole (5.39 g) of CH_2I_2 and 9.87 mmole

of PF_2I were condensed into the bulb. (The PF_2I must be completely free of HI or the desired products will not form). After the system warmed to room temperature, the mixture was shaken for 14 hr. A red-brown solid formed in the reactor. Products were separated by passage through traps held at -45 , -78 , -95 and -196° . A 0.47 mmole sample of $\text{F}_2\text{PCH}_2\text{I}$ was recovered from the -78° trap (5 per cent yield based on F_2PI). The -95° trap contained 0.08 mmole $\text{F}_2\text{PCH}_2\text{PF}_2$ (2 per cent yield); the -45° trap contained CH_2I_2 ; and the trap at -196° contained PF_3 and a still unidentified material.

(3) *The insertion reaction for preparing $\text{F}_2\text{PCH}_2\text{I}$ from F_2PI and CH_2N_2 .* **Caution:** CH_2N_2 is hazardous! A 1.68 mmole sample of CH_2N_2 and a 1.63 mmole sample of F_2PI were condensed into an evacuated 100 ml reaction tube connected to a manometer. As the tube warmed toward 25° a red-brown liquid formed in the tube; the pressure was constant after 0.5 hr. From the system at 25° a 1.64 mmole sample of N_2 (theoretical for 1.63 mmole sample of H_2CN_2) was pumped off by the Toepler pump. A 0.16 mmole sample of $\text{PF}_2\text{CH}_2\text{I}$ and another unidentified material remained at -78° ; at -45° some CH_2I_2 remained, and 1.62 mmole of a mixture containing PF_3 , F_2POPFF_2 , PF_2I and an unidentified material stopped at -196° .

Properties of $\text{F}_2\text{PCH}_2\text{I}$

(1) *Vapor pressure.* The vapor pressure is given by the equation:

$$\log P_{(\text{mm})} = -\frac{2093}{T} + 8.761$$

The normal boiling point is 83°C (extrapolated) and the entropy of vaporization at the normal boiling point is $26.9 \frac{\text{calories}}{\text{mole} \times \text{deg}}$.

(2) *Molecular weight.* The molecular weight by vapor density at 46.3 mm and 25°C is 205 ± 6 . Theory for $\text{F}_2\text{PCH}_2\text{I}$ is 209.9. The mass spectrum, given in detail elsewhere[14], shows the expected fragmentation pattern. The most intense peak and highest mass peak appear at the mass value of the molecular ion.

(3) *I.R. spectrum.* The infrared spectrum is presented as: frequency of band, intensity of band, and probable assignment of band based on comparison to known structures. vw—very weak, w—weak, m—medium, s—strong, sh—shoulder, vs—very strong. ν —stretching frequency; δ —deformation; ρ —rocking; ω —wagging motion; τ —torsional; as—asymmetric; s—symmetric; 2950 (vw) νCH ; 1370 (w) δHCH ; 1005 (w) ρCH_2 ; 835 (vs) $\nu_s\text{PF}$; 815 (vs) $\nu_{\text{as}}\text{PF}$; 760 (s) νPF ; 700 (m)—; 680(m)—; 570 (w) νCl , 395 (w) δFPF ; 380 (w)—; 305 (w)—.

Procedures for preparation of $\text{F}_2\text{PCH}_2\text{PF}_2$

(1) *Photolytic decomposition of $\text{F}_2\text{PCH}_2\text{I}$ in the presence of Hg.* A 3 ml quantity of mercury was placed in a 500 ml reaction bulb equipped with a quartz window and stopcock. About a 1.14 mmole sample of $\text{F}_2\text{PCH}_2\text{I}$ was condensed into the evacuated bulb, warmed to 25°C , and irradiated while shaking for 5 hr. The light source was a 275 W G.E. sun lamp located 58 cm from the center of the reaction bulb. Products were fractionated through traps held at -78° , -100° and -196° . The -100° trap contained 0.18 mmole of $\text{F}_2\text{PCH}_2\text{PF}_2$ (32 per cent yield). The reaction is very sensitive to radiation intensity. Decomposition of $\text{F}_2\text{PCH}_2\text{PF}_2$ occurs at higher radiation levels.

(2) *The coupling $\text{F}_2\text{PCH}_2\text{I}$ and F_2PI in the presence of Hg.* A 3 ml quantity of mercury was placed in a 500 ml reaction bulb; after evacuation of the bulb a 0.69 mmole sample of $\text{F}_2\text{PCH}_2\text{I}$ and 0.83 mmole sample of F_2PI were condensed into the bulb. The reaction mixture was warmed to room temperature and shaken for 10 hr. Volatile products were passed through traps held at -78° .

-98°, -196°. The -98° trap retained 0.17 mmole of $F_2PCH_2PF_2$ (25 per cent yield based on F_2PCH_2I used). Yields were lower with longer reaction times suggesting decomposition of the $F_2PCH_2PF_2$ in the system.

Properties of $F_2PCH_2PF_2$

(1) *Vapor pressure.* Bis(difluorophosphino)methane has a vapor pressure of 88.3 mm at 0.2°C.

(2) *Mass spectrum.* The detailed mass spectrum (reported elsewhere)[14] displays the expected fragmentation pattern with one or two anomalous features. The most intense peak is not that of the molecular ion; instead it is at $m/e = 69$ corresponding to PF_2^+ . This behavior contrasts sharply with the behavior of F_2PCH_2I . The presence of two F_2P groups would increase the probability of the appearance of this group, but it does not explain the very low intensity of the parent ion. The C-PF₂ bond must be relatively weak. F_2PCH_2I was visible as an impurity at $m/e = 210$.

(3) *I.R. spectrum.* The data are tabulated as outlined for F_2PCH_2I . 2940 (vw) ν_{CH} ; 1355 (w) δ_{HCH} ; 1225 (m) ρ_{CH_2} ; 1095 (m)—; 835 (vs) ν_{PF} ; 820 (sh) ν_{PF} ; 795 (s) ν_{CP} ; 655 (w)—; 445 (w) δ_{FPF} ; 385 (w)—; 315 (w)—.

Synthesis of $F_2PCH_2CH=CH_2$

(1) *The reaction of $CH_2=CHCH_2I$ and PF_2I in the presence of Hg.* A 22.0 mmole sample of $CH_2=CHCH_2I$ and 22.0 mmole of PF_2I were frozen into an evacuated 1 l. reaction bulb containing 5 ml of mercury. The mixture was warmed to 25° and shaken for 3 hr. Volatile products were passed through traps held at -78°, -126° and -196°C. The desired $F_2PCH_2CH=CH_2$ (10⁻⁷ mmole, 49 per cent yield) was recovered from the -126° trap.

Properties of $F_2PCH_2CH=CH_2$

(1) *Vapor pressure.* Allyldifluorophosphine has a vapor pressure of 166 mm at 0.3°C.

(2) *Mass spectrum.* The mass spectrum shows the major peak at $m/e = 110$, which agrees with the expected value of 110.0 for $F_2PCH_2CH=CH_2$. The fragmentation pattern, given in detail elsewhere[14], is exactly that expected for this compound with a definite pattern of the allyl group at $m/e = 41$. The vapor density molecular weight measured at a pressure of 14 mm at 25°C was 112 ± 4 .

(3) *I.R. spectrum.* The observed spectrum and proposed vibrational assignments for gaseous $F_2PCH_2CH=CH_2$ are presented using the same format as was used for F_2PCH_2I . Tentative assignments are based on analogy to assignments given for allyl chloride and allyl bromide[5]. 3068 (w) ν_{CH} ; 300 (w) ν_{CH} ; 2984

(w) ν_{CH} ; 2900 (w) ν_{CH} ; 1860 (vw)—; 1637 (m) $\nu_{C=C}$; 1422 (w) δ_{CH_2} ; 1390 (w)—; 1222 (w)—; 1192 (mw)—; 1036 (m)—; 996 (m) δ_{HCC} in $CH_2=$; 945 (ms) δ_{HCC} in $=CH-$; 828 (vs) $\nu_{as}PF$; 816 (vs) ν_sPF ; 740 (m) ν_{CP} ; 590 (ms)—; 210 (w)—.

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