The Synthesis and Structures of Some Perfluorovinyl-Substituted Phosphoranes

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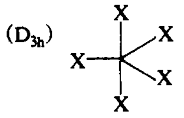
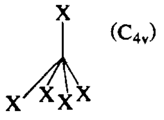
Abstract: The preparation of the new phosphorus(V) halides $CF_2{=}CFPF_4$, $(CF_2{=}CF)_2PF_3$, and $CF_2ClCFHPCl_4$ is described. Since $CF_2ClCFClPCl_2$ is the only nonpolymeric species which can be isolated upon dehydrochlorination of $CF_2ClCFHPCl_4$, it appears that $CF_2{=}CFPCl_4$ is unstable with respect to transfer of Cl_2 from phosphorus to the olefinic double bond. The structures of $CF_2{=}CFPF_4$ and $(CF_2{=}CF)_2PF_3$ are discussed on the basis of ^{19}F nmr and ir spectroscopic data. In both cases a trigonal-bipyramidal structure is favored with equatorial perfluorovinyl group substitution.

One of the more convenient areas of the periodic table to study the pentacoordination problem is group V. Particular emphasis is placed on PF_5 and its derivatives because of their volatility and the availability of ^{31}P and ^{19}F nmr as a structural tool.

The two idealized geometries which are possible for an MX_5 species are the trigonal bipyramid (I) and the square pyramid (II). However, all the pentacoordinate phosphorus compounds investigated thus far[2] possess the trigonal-bipyramidal structure (I). In fact, the only square-pyramidal structure (II) in group Va appears to be pentaphenylantimony.[3]



I



II

The currently available evidence[2] indicates that the most electronegative ligands occupy the axial sites of a trigonal bipyramid. Particular interest focuses on this generalization when the substituent electronegativities are close. Thus in CF_3PCl_4 the CF_3 group adopts an axial position in a trigonal bipyramid[4] as anticipated on the basis of the electronegativity sequence[5] $F > CF_3 > Cl$. Similarly, the observation[6] that the perfluoroalkyl groups adopt equatorial sites in $(CF_3)_3PF_2$ and $(C_2F_5)_3PF_2$ also conforms to expectation. However, the disubstituted phosphoranes $(CF_3)_2PF_3$ and $(C_2F_5)_2PF_3$ showed nmr spectroscopic F(P) equivalence down to −120°, suggesting (but not proving) axial substitution of the perfluoroalkyl groups.[6] Recent microwave[7] and ir[8] studies are not in agreement regarding the structure of CF_3PF_4.

In view of the foregoing it seemed worthwhile to investigate the stereochemistry of other phosphoranes bearing electronegative substituents. The perfluorovinyl group obviously fits into this category and has the added attraction that it introduces α,β unsaturation into the phosphorane. Synthetically it was of interest to see if perfluorovinyl-substituted phosphoranes could, in fact, be isolated in view of the possibility of decomposition *via* halogen transfer from phosphorus to the olefinic double bond[9] and/or fluoride ion migration.

Experimental Section

All volatile materials were handled in high-vacuum manifolds with U traps interconnected by chlorofluorocarbon-greased stopcocks. Molecular weights were determined by vapor density. Materials of low volatility were handled under a dry nitrogen atmosphere or in a helium-filled drybox.

Nmr Spectra. The ^1H and ^{19}F spectra were recorded on Varian A-60 and HA-100 spectrometers, respectively. The ^{19}F experiments were run with internal lock and the chemical shifts are realtive to internal CCl_3F.

Ir Spectra. Most of the infrared spectra were measured on a Perkin-Elmer Model 337 grating spectrophotometer. A Beckman IR-7 instrument was employed when more accurate data were desirable.

Materials. Antimony pentafluoride (Peninsular ChemResearch) and Cl_2 (Matheson) were procured commercially and were used without subsequent purification. Triethylamine and all solvents were dried and distilled prior to use.

Reaction of $CClF_2CHFPCl_2$ with Cl_2. A mixture of $CClF_2CHFPCl_2$[10] and excess Cl_2 in a sealed ampoule produced a colorless involatile liquid upon warming from −78° over an 8-hr period. Removal of the traces of volatiles left the phosphorane $CClF_2CHFPCl_4$. *Anal.* Calcd for $C_2HCl_5F_3P$: C, 8.28; H, 0.35; P, 10.67. Found: C, 8.37; H, 0.73; P, 10.93. Liquid-phase ir spectra displayed the expected features: namely C–Cl stretching at 736 and 785 cm^{-1}, C–F stretching at 981, 1040, 1111, 1140, 1195, 1295, and 1323 cm^{-1}, and C–H stretching at 2940 and 2983 cm^{-1}.

A mixture of 1.1395 g (5.19 mmoles) of $CCl_2CHFPCl_2$ and 5.07 mmoles of Cl_2 was allowed to react as above. After removal of the volatiles, 26.0 mmoles of $(C_2H_5)_3N$ and 3.0 ml of benzene were added, and the ampoule was resealed and allowed to warm slowly from −10°. Fractionation of the volatiles with U traps held at −40 and −196° yielded a mixture of C_6H_6 and $(C_2H_5)_3N$ in the

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[1] Abstracted from the Ph.D. Dissertation of M. W. Taylor, The University of Texas at Austin, 1969.

[2] For an excellent review on pentacoordination, see E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), **20**, 245 (1966).

[3] P. J. Wheatley, *J. Chem. Soc.*, 3718 (1964); P. J. Wheatley and G. Wittig, *Proc. Chem. Soc.*, 251 (1962); A. L. Beauchamp, M. J. Bennett, and F. A. Cotton, *J. Am. Chem. Soc.*, **90**, 6675 (1968).

[4] J. E. Griffiths, *J. Chem. Phys.*, **41**, 3510 (1964).

[5] J. J. Lagowski, *Quart. Rev.* (London), **13**, 233 (1959); J. E. Huheey, *J. Phys. Chem.*, **69**, 3284 (1965).

[6] E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963); E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *ibid.*, **3**, 1298 (1964).

[7] E. A. Cohen and C. D. Cornwell, *ibid.*, **7**, 398 (1968).

[8] J. E. Griffiths, *J. Chem. Phys.*, **49**, 1307 (1968).

[9] This does not appear to be a factor with vinyl-substituted phosphoranes such as $CH_2{=}CHPF_4$ and $C_6H_5CHCH{=}PF_4$; see P. M. Treichel and R. A. Goodrich, *Inorg. Chem.*, **4**, 1424 (1965); R. Schmutzler in "Advances in Fluorine Chemistry," Vol. 5, M. Stacey, J. C. Tatlow, and A. G. Sharpe, Ed., Butterworth & Co., Ltd., London, 1965, p 31, and references therein.

[10] The synthesis of perfluorovinylphosphines and related compounds is described in the preceding paper: A. H. Cowley and M. W. Taylor, *J. Am. Chem. Soc.*, **91**, 1929 (1969).

Table I. ^{19}F Nmr Chemical Shift Data for Perfluorovinylphosphorus(V) Fluorides[a]

	$(CF_2{=}CF)_2PF_3$ Ambient	$(CF_2{=}CF)_2PF_3$ −60°	$CF_2{=}CFPF_4$ Ambient
F(1)[b]	69.3	66.8	64.7
F(2)[b]	85.3	83.0	79.4
F(3)[b]	181.3	180.7	177.8
F(P) axial		41.3	54.9 (av)
F(P) equatorial		76.8	

[a] All chemical shifts in ppm relative to internal CCl_3F. [b] Numbering system is given in structure III.

Table II. ^{19}F Nmr Coupling Constant Data for $(CF_2{=}CF)_2PF_3$[a]

Coupling	Ambient	−60°
$P\text{–}F_{eq}$	. . .	975
$P\text{–}F_{ax}$	. . .	641
$F_{eq}\text{–}P\text{–}F_{ax}$	. . .	52
P–C–F	91	91
$F\text{–}C\text{–}P\text{–}F_{eq}$	2.5	0
$F\text{–}C\text{–}P\text{–}F_{ax}$		2.5
cis-P–C–C–F	15	15
trans-P–C–C–F	30	31
cis-$F\text{–}C\text{–}C\text{–}P\text{–}F_{eq}$	37	5
cis-$F\text{–}C\text{–}C\text{–}P\text{–}F_{ax}$		58
trans-$F\text{–}C\text{–}C\text{–}P\text{–}F_{eq}$	8.5	0
trans-$F\text{–}C\text{–}C\text{–}P\text{–}F_{ax}$		12
F–C–F	. . .	5
cis-F–C–C–F	40	39
trans-F–C–C–F	111	111

[a] All coupling constants in hertz.

−196° trap and 7.0 mg (0.026 mmole) of $CF_2ClCFClPCl_2$ (identified by ir and molecular weight[10]) in the −40° trap.

Extraction of the yellow residue with ether produced a red nonvolatile liquid, the ^{19}F nmr spectrum of which consisted of a complex multiplet at +60.8 ppm. The ether-insoluble portion of the residue was shown to be $(C_2H_5)_3NHCl$.

Preparation of $CF_2{=}CFPF_4$. A white solid was formed when a mixture of 0.7497 g (4.1 mmoles) of $CF_2{=}CFPCl_2$[10] and excess SbF_5 (3.0 g, 13.8 mmoles) warmed slowly from −196° to room temperature. After standing 3.5 hr at room temperature, the ampoule was opened and the volatiles were fractionated with U traps held at −95, −130, and −196°, resulting in the condensation of $CF_2{=}CFPF_4$ in the −130° trap. *Anal.* Calcd for C_2F_7P: C, 12.68; mol wt, 188. Found: C, 12.77; mol wt, 190. The ^{19}F nmr and ir spectra of this compound will be presented later in the paper.

Preparation of $(CF_2{=}CF)_2PF_3$. Antimony pentafluoride (3.0 g, 13.8 mmoles) was transferred in the drybox into a 25-ml bulb equipped with a magnetic stirring bar, side arm, and 7/25 standard taper joint. The reaction vessel was then evacuated and 1.21 g (5.30 mmoles) of $(CF_2{=}CF)_2PCl$[10] condensed into the side arm. A smooth reaction ensued upon warming as evidenced by the formation of a white solid on the vessel walls. After ~1 hr the reaction was completed by condensing the remaining $(CF_2{=}CF)_2PCl$ onto the SbF_5 and allowing the reaction mixture to stand a further hour at ambient temperature. Fractionation of the volatiles with U traps held at −50, −78, and −196° resulted in the condensation of $(CF_2{=}CF)_2PF_3$ in the −78° trap. *Anal.* Calcd for C_4F_9P: C, 19.22; P, 12.39; mol wt, 250.0 Found: C, 19.42; P, 12.31; mol wt, 245. The ^{19}F nmr and ir spectroscopic data for this compound are presented in the next section.

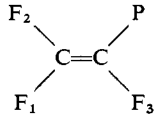
Initial direct mixing of the reagents or allowing the reaction to proceed for more than ~2 hr leads to the formation of a difficultly separable material of higher molecular weight which appears to be $CF_2{=}CF(C_2F_5)PF_3$ on the basis of its ^{19}F nmr spectrum.

The fluorophosphoranes $CF_2{=}CFPF_4$ and $(CF_2{=}CF)_2PF_3$ are both colorless liquids which are reactive toward air and water.

Results and Discussion

We have shown earlier[10] that the usual approach to the synthesis of chlorophosphoranes, *viz.*, the chlorination of a tertiary phosphine or a chlorophosphine, is inappropriate for perfluorovinylphosphorus compounds because of concomitant chlorination of the olefinic double bond. The dehydrochlorination of, *e.g.*, $CF_2ClCFHPCl_4$ did not meet with success either since $CF_2ClCFClPCl_2$ was the only nonpolymeric phosphorus compound which could be isolated from this reaction. Inferentially $CF_2{=}CFPCl_4$ is unstable with respect to transfer of Cl_2 from phosphorus to the C=C bond, thus dissuading us from further attempts to synthesize this type of compound. The new fluorophosphoranes $CF_2{=}CFPF_4$ and $(CF_2{=}CF)_2PF_3$ can be conveniently prepared by the action of SbF_5 on the corresponding phosphinous chlorides.

It was not possible to detect the phosphorane fluorine resonance in the ^{19}F nmr spectrum of $(CF_2{=}CF)_2PF_3$ at ambient temperature, presumably because of exchange broadening. The spectrum was not improved by allowing the $(CF_2{=}CF)_2PF_3$ to stand over NaF. However, the presence of the PF_3 moiety was evident in the $CF_2{=}CF$ portion of the spectrum since the F(1), F(2), and F(3) resonances each consisted of eight equally intense quartets. The chemical shifts and coupling constants derived therefrom are presented in Tables I and II. Cooling to −20° resulted in the appearance of peaks which are attributable to two F(P) environments in 2:1 abundance. Further improvements became apparent in the spectrum upon cooling the sample to −60°. The basis of the assignments set forth in Tables I and II are the chemical shift and coupling constant orders $\delta(F_3) > \delta(F_2) > \delta(F_1)$; $\delta(F_{eq}) > \delta(F_{ax})$; $J_{F_2F_3} > J_{F_1F_3}$ or $J_{F_1F_2}$, and $J_{PF_{eq}} > J_{PF_{ax}}$, which have been established from previous work on other phosphorus(V) fluorides[6] and perfluorovinylphosphines.[10] The infrared data for $(CF_2{=}CF)_2PF_3$ also indicate two F(P) environments since two absorptions are present in the P–F stretching region (Table III). *Per se* the nmr and ir data cannot distinguish between an equatorially substituted trigonal-bipyramidal structure and a basally substituted square-pyramidal structure. However, the former is favored because the nmr data for $(CF_2{=}CF)_2PF_3$ are consistent with those of Muetterties, *et al.*,[6] on a large number of fluorophosphoranes, which, in turn, show self-consistency only for trigonal-bipyramidal geometry.



III

It is of interest to compare the structural data for $(CF_2{=}CF)_2PF_3$ with those of the saturated analogs $(C_2F_5)_2PF_3$ and $(CF_3)_2PF_3$. These compounds showed spectroscopic equivalence of the P–F fluorines down to −120°, which means either that the perfluoroalkyl groups are axially disposed, or that the activation energy for intramolecular exchange is somewhat small. If the latter is in fact the reason for spectroscopic F(P) fluorine equivalence in the perfluoroalkyl compounds, it is possible that the barrier for positional exchange in $(CF_2{=}CF)_2PF_3$ is augmented by the presence of $p_\pi\text{–}d_\pi$

Table III. Infrared Data for Perfluorovinylphosphorus(V) Fluorides

$(CF_2{=}CF)_2PF_3$[a] Frequency, cm^{-1}	$(CF_2{=}CF)_2PF_3$[a] Assignment	$CF_2{=}CFPF_4$[a] Frequency, cm^{-1}	$CF_2{=}CFPF_4$[a] Assignment
626 w[b]		631 w	
715 m	P–C stretch (?)	704 m	P–C stretch (?)
813 w		797 vw	
884 s	Ax P–F stretch	811 vw	
915 s	Eq P–F Stretch	888 vs	Ax P–F stretch
1050 s	C–F stretch	912 vs	Eq P–F stretch
1102 s		988 vs	C–F stretch
1222 vs		1102 m	
1279 w		1147 w	
1353 vs	C–F stretch	1224 vs	C–F stretch
1371 sh		1358 vs	
1709 vs	C=C stretch	1393 m	
1728 vs		1713 vs	C=C stretch
		1748 w	

[a] Spectra run in the vapor phase in 100-mm path length KBr cell. [b] s, strong; m, medium; w, weak; sh, shoulder. All intensities are relative.

bonding between the α carbon and a vacant P(3d) orbital.

The ^{19}F nmr spectrum of $CF_2{=}CFPF_4$ showed spectroscopic equivalence of the phosphorane fluorines at ambient temperature with $J_{PF} = 927$ Hz. On cooling the sample the P–F doublet broadened, but no additional splittings were observed down to $-100°$. However, it is possible to make a tenuous argument for the structure of $CF_2{=}CFPF_4$ using the ^{19}F chemical shift data for the axial and equatorial fluorines of $(CF_2{=}CF)_2PF_3$. If the $CF_2{=}CF$ group is in an axial position in $CF_2{=}CFPF_4$, the calculated F(P) chemical shift is 67.9 ppm $[{}^3/_4(76.8) + {}^1/_4(41.3)]$. Similarly for the equatorially substituted model the average F(P) chemical shift is calculated to be 59.1 ppm. Since the observed chemical shift is 54.9 ppm, equatorial $CF_2{=}CF$ substitution is favored.

The ir data for the fluorophosphoranes are presented in Table III. A complete vibrational analysis has not been attempted. However, identification of several of the bands may be made by comparison with the vibrational spectra of other perfluorovinyl compounds.[11] Thus, the C=C stretching frequency occurs in the range 1707–1792 cm^{-1} and the intense bands in the 1000–1350-cm^{-1} range are due to C–F stretching. The P–F stretching frequencies vary widely with the particular phosphorane,[6] but the axial P–F stretching frequencies are lower than the equatorial frequencies. Since the As–C and Si–C stretches have been assigned at 653 and 686 cm^{-1}, respectively,[11a] we tentatively assign P–C stretching in the range 700–720 cm^{-1}.

Acknowledgment. The authors are very grateful to the Robert A. Welch Foundation for financial support.

(11) (a) S. L. Stafford and F. G. A. Stone, *Spectrochim. Acta*, **17**, 412 (1961), and references therein; (b) D. Seyferth, K. Brandel, and G. Raab, *J. Org. Chem.*, **26**, 2934 (1961).