Perfluorovinyl-Substituted Phosphines

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Abstract: The synthesis and some reactions of the compounds $(CF_2=CF)_3P$, $(CF_2=CF)_2PN(CH_3)_2$, $CF_2=CFP[N(CH_3)_2]_2$, $(CF_2=CF)_2PCl$, $CF_2=CFPCl_2$, and $CF_2=CFPF_2$ are described. With the exception of $CF_2=CFPF_2$, the ambient-temperature stability of these perfluorovinylphosphines is not high. Decomposition appears to take place by both disproportionation and fluoride ion migration. The olefinic double bond of perfluorovinylphosphines is fairly reactive with respect to the addition of Cl_2 or HCl, although Cl_2 will also add to the phosphorus atom of, *e.g.*, $CF_2=CFPCl_2$. If the chlorination is allowed to proceed rapidly, it is possible to cleave the P–C bond. The ^{19}F nmr spectra of most of the above compounds have been recorded, and the possibility of a relationship between the geminal F–F coupling, the chemical shift of the *trans*-fluorine atom, and the extent of π bonding in the C-heteroatom linkage of perfluorovinyl compounds is discussed.

The present paper is concerned with some perfluorovinyl derivatives of trivalent phosphorus.[2] The particular interest in employing the perfluorovinyl group as a substituent is based on the consideration that this moiety is both unsaturated and electronegative. The presence of α,β unsaturation offered the promise of an interesting variation on the theme of perfluoroalkylphosphorus chemistry, a field which has provided several unusual structures and reactions. The points of emphasis in the present study are the reactivity of the olefinic double bond, the ^{19}F nmr spectra, and the nature of the bonding between phosphorus and the perfluorovinyl group. Previously reported perfluorovinylphosphorus compounds comprise $(CF_2=CF)_3P$,[3] $(CF_2=CF)_2PN(C_2H_5)_2$,[3] $CF_2=CFP[N(C_2H_5)_2]_2$,[3] $(CF_2=CF)_2PCl_2$,[3] $CF_2=CFPCl_2$,[3] $(CF_2=CF)_2PF$,[3] $CF_2=CFPF_2$,[3] and $CF_2=CFP(O)(OC_2H_5)_2$.[4]

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. Most of the ^{19}F experiments were run with internal lock. However, a few spectra were run in the "HR" mode.

Ir Spectra. Most of the infrared spectra were measured on a Perkin-Elmer Model 337 grating spectrophotometer. Beckman IR-7 and IR-11 instruments were employed when more accurate data were desirable.

Materials. Iodotrifluoroethylene, Mg, $(CH_3)_2SnCl_2$, PCl_3, $(CH_3)_2NH$, HCl, Cl_2, and SbF_3 were procured commercially and were used without subsequent purification. All solvents were dried prior to use. The compounds $(CH_3)_2Sn(CF=CF_2)_2$,[5] B_2H_6,[6] $B(CH_3)_3$,[7] $(CH_3)_2NPCl_2$,[8] and $[(CH_3)_2N]_2PCl$[8] were prepared by literature methods.

The Attempted Reaction of $(CH_3)_2Sn(CF=CF_2)_2$ with PCl_3. A mixture of 1.00 g (3.22 mmoles) of $(CH_3)_2Sn(CF=CF_2)_2$ and 0.87 g (6.33 mmoles) of PCl_3 was sealed in a Pyrex tube and allowed to stand 12 hr at ambient temperature. Infrared spectroscopic examination of the mixture indicated that no reaction had taken place. Heating the reaction mixture at 75° for 24 hr and at 140° for 24 hr produced only traces of decomposition products. The starting materials were recovered in almost quantitative yield.

The Reaction of $CF_2=CFLi$ with PCl_3 and PBr_3.[9] Perfluorovinyllithium was prepared in 0.1-mole quantities by the halogen exchange between n-C_4H_9Li and $CF_2=CFI$.[10] The lithium reagent was treated with 33 mmoles of PCl_3 or PBr_3 in the temperature range −20 to −78°. In each case, work-up of the reaction mixture yielded a white crystalline precipitate and a reddish brown high-boiling liquid, neither of which have been characterized. However, no $(CF_2=CF)_3P$ was isolated.

The Preparation of $(CF_2=CF)_3P$ (I). Perfluorovinylmagnesium iodide was prepared from 2.43 g (100 mmoles) of Mg and 20.8 g (100 mmoles) of $CF_2=CFI$ in 50 ml of ether following the published procedure,[11] except that the flask temperature was maintained at −20° rather than 0°. The Grignard reagent was cooled to −78° and a solution of 8.93 g (33 mmoles) of freshly distilled PBr_3 in 25 ml of ether was added dropwise with stirring. Stirring was continued overnight, during which time the reaction mixture warmed gradually to 0°. The solvent was then stripped off and the volatiles were transferred to a −196° trap by prolonged pumping. After standing for a few days over mercury in a sealed ampoule at ambient temperature (during which time the liquid turned from red to colorless and deposited' a fine yellow-green precipitate), the mixture was fractionated with U traps held at −30, −60, and −196°. A 9.2% yield of I (0.833 g, 3.04 mmoles) condensed in the −30° trap. *Anal.*[12] Calcd for I: C, 26.28; F, 62.41; P, 11.31. Found: C, 26.13; F, 62.26; P, 11.10. Vapor tensions of I in the range −10 to 54° determine the equation $\log P_{mm} = 8.689 − 2184/T$ leading to an extrapolated boiling point of 102.7° which is in reasonable agreement with the literature value[3] of 99–101°. Freshly distilled I is colorless, but turns pink and deposits a yellow precipitate after standing *in vacuo* for ∼1 day at room temperature. Storage of the ampoules below 0° arrests this decomposition.

Strangely, the substitution of PCl_3 for PBr_3 in the above synthesis (*i.e.*, the method of Sterlin, *et al.*[3]) led only to apparently polymeric products.

The Attempted Reaction of $(CF_2=CF)_3P$ with $B(CH_3)_3$. A mixture of 0.39 mmole of $(CF_2=CF)_3P$, 0.50 mmole of $B(CH_3)_3$, and 1.0 ml of CH_2Cl_2 was sealed in an nmr tube. The pmr spectrum

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

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Table I. ^{19}F and ^{1}H Nmr Data of Perfluorovinyl-Substituted Phosphines

Compound	Chemical shifts				
	H^a	$F(1)^{b,c}$	$F(2)^{b,c}$	$F(3)^{b,c}$	$F(4)^{b,c}$
$(CF_2{=}CF)_3P$ (I)^d	...	82.6	106.3	175.9	...
$(CF_2{=}CF)_2PN(CH_3)_2$ (II)	7.22	89.04	110.05	179.28	...
$CF_2{=}CFP[N(CH_3)_2]_2$ (III)^d	7.55	89.4	107.8	181.3	...
$CF_2{=}CFPF[N(CH_3)_2]$ (IV)^d	7.44	90.1	113.0	190.0	126.3
$(CF_2{=}CF)_2PCl$ (VIII)	...	81.87	103.92	180.97	...
$CF_2{=}CFPCl_2$ (IX)	...	82.50	103.59	186.43	...
$CF_2{=}CFPF_2$ (XIII)	...	79.90	112.00	199.14	103.60

Compound	Coupling constants, Hz						
	J_{FCF}	J_{PCF}	$J_{FCCF}(cis)$	$J_{FCCF}(trans)$	$J_{PCCF}(cis)$	$J_{PCCF}(trans)$	Miscellaneous
$(CF_2{=}CF)_2PN(CH_3)_2$ (II)	53	24	32	119	53	8	$J_{PNCH} = 10.3$; $J_{FCPNCH} = 0.6$
$CF_2{=}CFP[N(CH_3)_2]_2$ (III)	...	...	...	...	...	...	$J_{PNCH} = 9.4$; $J_{FCPNCH} = 0.8$
$CF_2{=}CFPF[N(CH_3)_2]_2$ (IV)	...	...	...	...	...	...	$J_{PF} = 995$; $J_{PNCH} = 9.7$; $J_{FPNCH} = 6.2$; $J_{FCPNCH} = 0.9$
$(CF_2{=}CF)_2PCl$ (VIII)	36	e	e	121	70	e	
$CF_2{=}CFPCl_2$ (IX)	39	17	32	123	84	7	
$CF_2{=}CFPF_2$ (XIII)	42.4	20.8	31.0	123.5	69.6	4.8	$J_{PF} = 1202$; $J_{FPCF} = 11.1$; trans $J_{FPCCF} = 13.2$; cis $J_{FPCCF} = 2.8$

^{a} In τ units relative to internal TMS. ^{b} In ppm relative to internal CCl_3F. ^{c} Numbering system is shown below.

$$F_2{\diagdown} \quad {\diagup}PX_2$$
$$C{=}C$$
$$F_1{\diagup} \quad {\diagdown}F_3$$
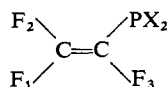
^{d} ^{19}F run in "HR" mode. ^{e} Evaluation of these couplings not possible without detailed analysis.

was identical with that of pure $B(CH_3)_3$ in the same solvent.

The Reaction of $(CF_2{=}CF)_3P$ with B_2H_6. A mixture of 0.297 g (1.08 mmoles) of $(CF_2{=}CF)_3P$ and 0.81 mmole of B_2H_6 was allowed to warm from $-78°$ to room temperature over a period of 7 hr. High-vacuum fractionation of the volatiles resulted in the recovery of 0.25 mmole of $(CF_2{=}CF)_3P$ in a $-78°$ trap and 0.67 mmole of B_2H_6 in a $-196°$ trap. A yellowish viscous liquid remained in the reaction bulb. The apparently polymeric residue is insoluble in ether, acetone, and 1,1,1-trichloroethane. On the basis of the recovered starting materials, the combining ratio of $(CF_2{=}CF)_3P$ to BH_3 units is 2.96:1.

The Preparation of $(CF_2{=}CF)_2PN(CH_3)_2$ (II). A solution of 218 mmoles of $CF_2{=}CFMgI$ in 55 ml of ether was prepared as described in the synthesis of I. The Grignard reagent was cooled to $-45°$, and a solution of 13.51 g (92.6 mmoles) of $(CH_3)_2NPCl_2$ in 60 ml of ether was added dropwise while vigorous stirring was maintained. When the addition was complete, the reaction mixture was allowed to assume ambient temperature over a period of $\sim$1 hr. After filtration, the ether was stripped from the filtrate to yield a dark red oil, the volatiles from which were transferred to the vacuum line in the usual manner. Fractionation of the volatiles with U traps held at -78 and $-196°$ resulted in the condensation of 7.33 g (30.9 mmoles) of II in the $-78°$ trap. This represents a 33.3% yield of II based on the consumption of $(CH_3)_2NPCl_2$. Compound II is not stable. Decomposition is evident in a matter of hours at room temperature; hence our identification of this material is based on its nmr spectra (Table I) and the characterization of the products of subsequent reactions.

The Reaction of $CF_2{=}CFMgI$ with $[(CH_3)_2N]_2PCl$. A solution of 150 mmoles of $CF_2{=}CFMgI$ in 60 ml of ether was treated with 23.2 g (150 mmoles) of $[(CH_3)_2N]_2PCl^8$ in 40 ml of ether at $-45°$. The same procedure was employed as that described for the synthesis of II. The volatiles were resolved into two main fractions by distillation with traps at -78 and $-196°$. The $-78°$ trap contained a mixture of $CF_2{=}CFP[N(CH_3)_2]_2$ (III), $CF_2{=}CFPF[N(CH_3)_2]$ (IV), and $[(CH_3)_2N]_2PF$ (V). Traces of $(CH_3)_2NPF_2$ (VI) and $(CH_3)_2NPFCl$ (VII) condensed in the $-196°$ trap. Compounds V and VI have been reported previously,^{13} and our identification of these compounds is based on agreement with the published nmr data. Compounds III and IV are not stable at room temperature; hence our identification is based on the nmr data of freshly prepared samples (Table I) and the characterization

of the products of subsequent reactions of these compounds. The characterization of the mixed halide VII is less certain. The pmr of VII consists of a doublet of doublets centered at τ 7.28, which is in the region where dimethylaminophosphines absorb.^{14} If the larger doublet splitting of 11.3 Hz is assigned to $PNCH$ coupling, then both the τ value and J_{PNCH} are intermediate between those of $(CH_3)_2NPCl_2$ (τ 7.18, 13.03 Hz)^{14} and $(CH_3)_2NPF_2$ (τ 7.36, 9.2 Hz).^{13} The presence of a large splitting (1162 Hz) centered at $+70.1$ ppm in the ^{19}F nmr spectrum is indicative of a fluorine attached to trivalent phosphorus. Since the pmr is a doublet of doublets, there can be only one such fluorine, and therefore the smaller doublet splitting of 3.2 Hz is assigned to $FPNCH$ coupling. In our hands, the relative quantities of the products III–VII varied considerably from run to run. In three typical runs, the contents of the $-78°$ trap were 13% III, 5% IV, and 14% of a mixture of III and IV. (All yields are based on the $[(CH_3)_2N]_2PCl$ consumed.) The only obvious variable seemed to be that a fast work-up of the reaction mixture resulted in larger yields of III and IV. Compounds III, IV, and V are difficult to separate. However, it is possible to obtain pure III by repeated distillation through a $-45°$ trap in which III condenses.

The Preparation of $(CF_2{=}CF)_2PCl$ (VIII). A yellowish solid was formed when 7.33 g (30.9 mmoles) of II and 65.0 mmoles of HCl were warmed together in an evacuated bulb from $-78°$ to room temperature during 3 hr. High-vacuum fractionation with traps at -60, -78, -100, and $-196°$ resulted in the condensation of a 77.0% yield of VIII (5.43 g, 23.8 mmoles) in the $-60°$ trap. A trace of $CF_2{=}CFPF_2$ (vide infra) was found in the $-100°$ trap. Anal. Calcd for VIII: C, 21.03; P, 13.56; mol wt, 228. Found: C, 20.89; P, 13.48; mol wt, 236. The ^{19}F nmr data for VIII are presented in Table I.

The Preparation of $CF_2{=}CFPCl_2$ (IX). A mixture of 4.70 g (23.5 mmoles) of III and 93.2 mmoles of HCl produced a yellowish solid on warming from $-78°$ to ambient temperature over a 3-hr period. Fractionation of the volatiles with U traps held at -45, -85, and $-196°$ resulted in the condensation of 3.59 g (19.6 mmoles) of IX in the $-85°$ trap. This represents an 83.4% yield of IX based on the consumption of III. Purification of IX may be effected by redistillation with traps at -45, -65, and $-196°$. Pure IX condenses in the $-65°$ trap (molecular weight, calcd for IX, 183; found, 185). Vapor tensions of IX conformed to the

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equation $\log P_{mm} = 7.9236 - 1810.4/T$ from which a normal boiling point of 85.8° may be estimated. Vapor-phase ir spectra of IX exhibited the expected features, namely, P-Cl stretching at 509 cm^{-1}, C-F stretching at 1051, 1211, and 1328 cm^{-1}, and C=C stretching at 1731 cm^{-1}. The ^{19}F nmr data for IX are shown in Table I. The thermal stability of IX is not high. After ~12 hr at 25° a white involatile solid is formed. Infrared spectroscopic examination of the volatiles indicated the presence of a new band at 850 cm^{-1}, which is in the P-F stretching region. Presumably, the decomposition is responsible for our disappointing analytical data. *Anal.* Calcd for IX: C, 13.13; P, 16.93. Found: C, 14.82; P, 19.07. However, all the other data leave little doubt as to the correct identity of the compound.

The Reaction of CF₂=CFPCl₂ with Cl₂. (a) **Slow Reaction.** Equimolar quantities of IX (0.108 g, 0.59 mmole) and Cl₂ (0.59 mmole) were sealed in an ampoule at −196°. The ampoule was allowed to attain ambient temperature over a 12-hr period. Removal of the volatiles left a light yellow solid, CClF₂CClFPCl₄ (X), in the reaction tube. *Anal.* Calcd for X: C, 7.40; P, 9.54. Found: C, 7.46; P, 9.41. Fractionation of the volatiles with U traps at −60 and −196° resulted in the condensation of 0.21 mmole (35.6% yield) of CClF₂CClFPCl₂ (XI) in the −60° trap. *Anal.* Calcd for XI: C, 9.46. Found: C, 9.58. The ^{19}F nmr spectrum of XI was of the ABMX type. The AB portion of the spectrum was centered at +60.3 ppm relative to internal CCl₃F. The M portion consisted of a pair of "triplets" centered at +130.8 ppm. The vapor-phase ir spectrum of XI consisted of strong peaks at 525 cm^{-1} in the P-Cl stretching region, 777 and 812 cm^{-1} in the C-Cl stretching region, and 1015, 1057, 1078, 1117, 1171, and 1206 cm^{-1} in the C-F stretching region.

(b) **Fast Reaction.** A fairly vigorous exothermic reaction ensued when a mixture of IX (0.24 g, 1.33 mmoles) and Cl₂ (1.30 mmoles) was allowed to warm rapidly from −196°. After standing 1 hr at room temperature, the reaction mixture was subjected to several high-vacuum fractionations. The following compounds were identified on the basis of their vapor-phase ir spectra: XI, PF₂Cl,[15] PFCl₂,[16] PCl₃,[17] CCl₂F₂,[18] and CClF₂CCl₂F.[18]

Reaction of CF₂=CFPCl₂ with HCl. In a typical experiment, a mixture of 1.84 g (9.2 mmoles) of III and 46.1 mmoles of HCl was allowed to stand for 1 week at ambient temperature in a 1-l. bulb. The volatiles were then fractionated with U traps held at −78 and −196°. A 56.5% yield of the adduct CF₂ClCFHPCl₂ (XII) (1.14 g, 5.2 mmoles) was isolated in the −78° trap. *Anal.* Calcd for XII: C, 10.95; H, 0.46; mol wt, 219. Found: C, 11.47; H, 0.90; mol wt, 220. The pmr spectrum of XII consisted of four triplets centered at τ 4.88 (internal TMS) with J_{FCH} = 46 Hz, J_{PCH} = 9.6 Hz, and J_{FCCH} = 8.7 Hz. The ^{19}F nmr spectrum of the α-fluorine consisted of four triplets centered at 196.2 ppm (internal CCl₃F), and the β-fluorine resonance involved eight equally intense lines centered at +59.2 ppm. The ^{19}F nmr spectrum yielded the following coupling constants: J_{PCF} = 59.8 Hz, J_{HCF} = 45.6 Hz, J_{FCCF} = 20.8 Hz, J_{PCCF} = 12.6 Hz, and J_{HCCF} = 8.4 Hz. The basis of the nmr assignments is considered in the Results and Discussion. A weak C-H stretching mode at 2940 cm^{-1} was detectable in the vapor-phase ir of XII. The other anticipated spectral features were also evident, namely P-Cl stretching at 518 cm^{-1}, C-Cl stretching at 750, 781, 814, and 834 cm^{-1}, and C-F stretching at 995, 1032, 1077, 1114, 1152, 1170, 1222, and 1325 cm^{-1}.

The Preparation of CF₂=CFPF₂ (XIII). Compound IX (1.68 g, 9.2 mmoles) was exposed to excess SbF₃ in a sealed tube. After standing overnight at ambient temperature, the tube was opened and the volatiles fractionated with traps at −100, −130, and −196°. A 65.2% yield of XIII (0.90 g, 6.0 mmoles) condensed in the −130° trap. *Anal.* Calcd for XIII: C, 16.01; P, 20.65; mol wt, 150. Found: C, 16.24; P, 20.40; mol wt, 149. The ^{19}F nmr data for XIII are presented in Table I. Vapor-phase ir spectra of XIII also displayed the expected features, namely P-F stretching at 848 cm^{-1}, C-F stretching at 1059, 1209, and 1330 cm^{-1}, and C=C stretching at 1733 cm^{-1}.

The Preparation of CClF₂CHFPF₂ (XIV). Similarly, XI was heated with excess SbF₃ for 1 hr at 55°. Separation of the volatiles

with −78, −90, −110, and −196° traps resulted in the condensation of XIV in the −90 and −110° traps. *Anal.* Calcd for XIV: C, 12.88; mol wt, 186. Found: C, 12.77; mol wt, 185. The vapor-phase ir spectra of XIV exhibited P-F stretching at 850 cm^{-1}, C-Cl stretching at 786 and 813 cm^{-1}, and C-F stretching at 980, 999, 1037, 1084, 1115, 1181, 1223, and 1320 cm^{-1}.

Results and Discussion

Our attempts to reproduce the previously reported syntheses[3] of (CF₂=CF)₃P, (CF₂=CF)₂PN(C₂H₅)₂, and CF₂=CFPN[N(C₂H₅)₂]₂ led to apparently polymeric products. A successful synthesis of (CF₂=CF)₃P was effected by substitution of PBr₃ for PCl₃ in the synthetic procedure of Sterlin, *et al.*[3] Efforts to develop alternative approaches to the synthesis of (CF₂=CF)₃P using (CH₃)₂Sn(CF=CF₂)₂[5] and CF₂=CFLi[10] were unsuccessful. The former does not react appreciably with PCl₃ up to 140°; the latter reacts with PCl₃ and PBr₃ but only unidentified products of low volatility could be isolated. The synthesis of the new dimethylamino-phosphines (CF₂=CF)₂PN(CH₃)₂ and CF₂=CFP-[N(CH₃)₂]₂ was undertaken because these compounds are sufficiently volatile for vacuum-line handling.

Most of the perfluorovinyl phosphorus compounds examined in the present work are unstable. The only compound which appears to be stable in sealed Pyrex ampoules for long periods of time at room temperature is CF₂=CFPF₂. The least stable compound is CF₂=CFP[N(CH₃)₂]₂. Although we have not examined the decomposition mechanisms in details, the nature of the decomposition products suggests that both disproportionation and fluoride ion migration processes are operative. The latter type of decomposition is a notable feature of perfluorovinyl-substituted boranes.[19] Presumably, the mechanism involves nucleophilic attack of the phosphorus atom by the fluorine atoms of the CF₂=CF− group.

Tris(perfluorovinyl)phosphine resembles (CF₃)₃P[20] in the sense that it appears to be devoid of the Lewis basicity usually associated with a tertiary phosphine. Thus no evidence was found for an interaction between (CF₂=CF)₃P and B(CH₃)₃.[21] A reaction did take place between (CF₂=CF)₃P and B₂H₆ to yield an apparently polymeric oil which was not well characterized. The most likely reaction is the addition of B-H bonds across the olefinic double bond. Polymer formation has been noted previously[22] as one of the reactions which takes place when tetrafluoroethylene is treated with B₂H₆.

The three reactions that might be anticipated upon chlorination of a perfluorovinylphosphine are (a) oxidation to a phosphorane, (b) cleavage of the P-C bond, and (c) addition of Cl₂ across the olefinic double bond. Reaction a is in fact the most common and has been

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(21) B(CH₃)₃ was selected as the reference Lewis acid in this case because this molecule rarely undergoes decomposition reactions with Lewis bases. Although the steric requirements are appreciable with respect to some bases, this consideration is not of great importance for second-row donors. Furthermore, vinyl-substituted phosphines form adducts with B(CH₃)₃; see H. D. Kaesz and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 6213 (1960).

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Table II. ^{19}F Chemical Shift and Coupling Constant Data for Perfluorovinyl Compounds

Compound	$\delta(F_1)^{a,b}$	$\delta(F_2)^{a,b}$	$\delta(F_3)^{a,b}$	$J_{F_1F_2}^{b,c}$	$J_{F_1F_3}^{b,c}$	$J_{F_2F_3}^{b,c}$	Ref
$CF_2{=}CFBF_2$	72.8	99.8	206.6	18	...	117	d
$CF_2{=}CFBCl_2$	71.6	87.9	184.5	7	19	114	d
$(CF_2{=}CF)_3B$	72.7	91.1	185.9	< 5	24	110	d
$CF_2{=}CFCF_3$	93	107	192	57	40	120	e
$CF_2{=}CFCF_2Cl$	95	106	185	56	39	118	e
$(CF_2{=}CF)_2Si(C_2H_5)_2$	83.5	114.3	199.7	62	26	117	d
$CF_2{=}CFPF_2$	79.9	112.0	199.1	42.4	31.0	123.5	f
$CF_2{=}CFPCl_2$	82.5	103.6	186.4	39	32	123	f
$(CF_2{=}CF)_2PCl$	81.9	103.9	181.0	~36	...	121	f
$(CF_2{=}CF)_2PN(CH_3)_2$	89.0	110.1	179.3	~53	32	119	f
$(CF_2{=}CF)_2PF_3$	66.8	83.0	180.7	4.5	39	111	f
$(CF_2{=}CF)_2Ge(CH_3)_2$	86.6	118.6	195.5	72	32	118	d
$(CF_2{=}CF)_4Ge$	80.1	112.7	196.5	71	32	118	d
$CF_2{=}CFSn(C_4H_9)_3$	88.1	123.3	192.7	79	34	115	d
$(CF_2{=}CF)_2Sn(CH_3)_2$	85.9	121.2	194.6	75	34	116	d
$(CF_2{=}CF)_2Sn(C_6H_5)_2$	84.3	118.6	193.2	68	34	118	d
$CF_2{=}CFI$	89.11	113.93	150.15	66.3	52.6	128.8	f
$(CF_2{=}CF)_2Hg$	89.9	124.5	185.0	75	37	109	d

^{a} In ppm relative to internal CCl_3F. ^{b} Numbering system is shown in footnote c of Table I. ^{c} In Hz. ^{d} Reference 30. ^{e} E. Pitcher and F. G. A. Stone, *Spectrochim. Acta*, **17**, 1244 (1961). ^{f} This work.
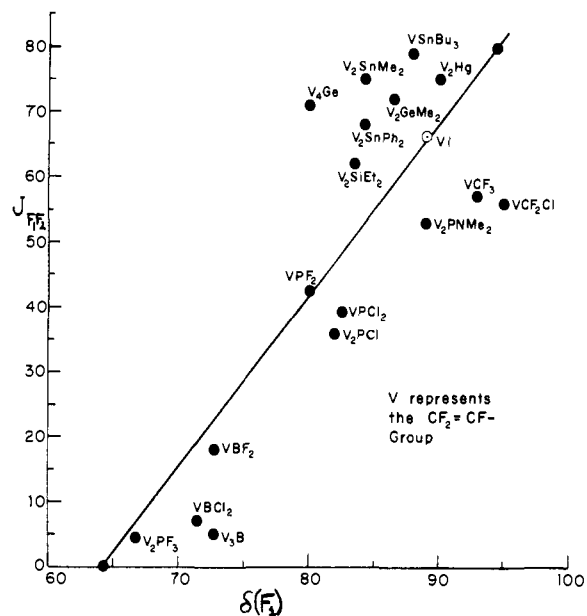

Figure 1. A plot of $\delta(F_1)$ vs. $J_{F_1F_2}$ for perfluorovinyl-substituted compounds.

used extensively for the preparation of phosphoranes with a wide variety of substituents. Cleavage of the P–C bonds is facilitated when the substituents are electronegative. An example of the latter is the cleavage of the P–C bond of trifluoromethylphosphines by Br_2 and I_2.[20a,23] At first sight, the addition of halogen across the double bond of a fluoroolefin would seem to be the least likely possibility. However, it was demonstrated several years ago that iodine will add quantitatively to tetrafluoroethylene.[24] Furthermore, Seyferth and coworkers[25] have shown that the double bond of $(C_2H_5)_3SiCF{=}CF_2$ is sufficiently reactive to add Br_2

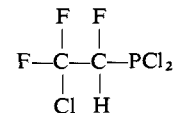(23) A. B. Burg and J. E. Griffiths, *J. Am. Chem. Soc.*, **82**, 3514 (1960).
(24) H. J. Eméleus and R. N. Haszeldine, *J. Chem. Soc.*, 2948 (1949).
(25) D. Seyferth, T. Wada, and G. E. Maciel, *Inorg. Chem.*, **1**, 232 (1962).

and HBr. (However, Cl_2 attacked the alkyl groups.)

In view of the foregoing, it was therefore of interest to examine the chlorination of $CF_2{=}CFPCl_2$. It was found that the course that the reaction took was dependent upon the rate at which the reaction mixture was allowed to warm. With a slow rate of warming, reactions a and c both take place resulting in a mixture of $CF_2ClCFClPCl_2$ and $CF_2ClCFClPCl_4$. Evidently, the olefinic double bond is more reactive than the phosphorus atom since no $CF_2{=}CFPCl_4$ could be isolated. If this phosphorane is formed, it probably reorganizes to $CF_2ClCFClPCl_2$. If the reaction is conducted in a less controlled manner (*i.e.*, a fast rate of warming), reaction b, P–C bond cleavage, also takes place to yield $CClF_2CCl_2F$ and PCl_3. Apparently this is not the only reaction, since PCl_2F and $PClF_2$ were detected spectroscopically. Presumably these chlorofluorides arose from fluoride shift reactions involving the $CF_2{=}CF-$ group prior to P–C bond cleavage.

The reactivity of the double bond toward what are classed "electrophilic" reagents in hydrocarbon chemistry was demonstrated also by the reaction of HCl with $CF_2{=}CFPCl_2$ which gave rise to $CClF_2CHFPCl_2$.

$$
\begin{array}{c}
\quad\quad F \quad\, F \\
\quad\quad | \quad\,\, | \\
F{-}C{-}C{-}PCl_2 \\
\quad\quad | \quad\,\, | \\
\quad\quad Cl \quad H
\end{array}
$$

Our preference for the above structure is based upon the conformity of the assigned coupling constants and chemical shifts (Experimental Section) with previous experimental values.[26] The assignment of the 8.7-Hz spacing of the pmr triplet to $FCCH$ coupling and the assignment of the low-field ^{19}F chemical shift ($+59.2$ ppm) to the β-fluorines are the principal factors which determine the structure. If the adduct involved a β-hydrogen, the 8.7-Hz spacing would have to be assigned to FCH coupling. However, all such couplings are approximately 48 Hz.[26] A similar conclusion was

(26) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance," Vol. 2, Pergamon Press Ltd., 1966, Chapter 11.

reached regarding the structure of the HBr adduct of $(C_2H_5)_3SiCF=CF_2$.[25] However, recent work by Akhtar and Clark[27] indicates that both addition products can be isolated by uv irradiation of mixtures of e.g., $(CH_3)_3$-$SiCF=CF_2$ and $(CH_3)_3SnH$.

Inevitably the question of phosphorus–carbon π bonding arises when an unsaturated moiety such as a phenyl group is attached to a trivalent phosphorus atom. From the localized bonding standpoint, the π-bonding effect is considered to be a balance between phosphorus lone pair → ring (p_π-p_π) donation and ring → vacant phosphorus 3d orbital (p_π-d_π) acceptance. On electronic spectral evidence, Jaffé concluded[28] that there is extensive conjugation between the phosphorus lone pair and a phenyl group, while in mixed phenylperfluorophenyl-phosphines ^{19}F nmr evidence[29] suggests that the back-donation effect predominates with the C_6F_5 substituent. Since the latter approach was a correlative one based on ^{19}F chemical shifts and coupling constants, we were encouraged to see if a comparable pattern was evident among the perfluorovinyl compounds. The available data are presented in Table II. As noted by Coyle, Stafford, and Stone,[30] the most significant changes in these nmr data occur with the geminal coupling, $J_{F_1F_2}$. A plot of $\delta(F_1)$ vs. $J_{F_1F_2}$ (Figure 1) reveals a scattering of points about a straight line but permits the recognition of three categories of compounds: (a) the boranes and $(CF_2=CF)_2PF_3$,[31] (b) the tricoordinate phosphines, and (c) the organometallics and $CF_2=CFI$. These categories may have relevance to the nature of the bonding between the heteroatom and the perfluorovinyl group in the following way. The boranes can behave only as π acceptors and the drift of π electrons from the perfluoro-vinyl moiety to the vacant B(2p) orbital results in a diminution of $J_{F_1F_2}$ and $\delta(F_1)$. As explained above, tricoordinate phosphines can exhibit both π-electron donation from the phosphorus lone pair into the per-

fluorovinyl group and π acceptance from the perfluoro-vinyl group into the vacant P(3d) orbitals. Evidently the π acceptance effect predominates in the phosphines since both $J_{F_1F_2}$ and $\delta(F_1)$ are smaller than in $CF_2=CFI$ and $(CF_2=CF)_2Hg$ where π-bonding effects are not anticipated. In previous studies[32] it had been suggested that there is N(2p) → P(3d) dative π bonding in amino-phosphines. Thus, in $(CF_2=CF)_2PN(CH_3)_2$ the α-carbon atom has to compete with nitrogen for π donation into the P(3d) orbital. This results in less back-donation from the perfluorovinyl group; hence the $J_{F_1F_2}$ and $\delta(F_1)$ values are the highest of the phosphines considered. When the phosphorus lone-pair electrons are not available as in the phosphorane $(CF_2=CF)_2PF_3$, only π-electron acceptance is possible; hence both $\delta(F_1)$ and $J_{F_1F_2}$ diminish such that this compound falls in the same category as the perfluorovinylboranes.

If the above hypothesis is accepted, then it is possible to conclude that there is little evidence for π bonding in the perfluorovinyl compounds of Si, Ge, Sn, and Hg. A similar conclusion may be drawn from the ^{19}F nmr data of the C_6F_5 compounds of Sn and Hg.[29] Clearly, more data will be required to explore the utility of the above idea even though the initial results are promising. One obvious omission is the effect of pure π donation into the perfluorovinyl group as in, for instance, a perfluoro-vinylamine.

It will be noted (Table I) that the J_{PCF} values for the perfluorovinyl compounds are smaller than those of the corresponding CF_3[33] and C_3F_7[34] compounds. Presumably this is due to the hybridization change at the α-carbon atom. Two of the five trends noted by Nixon[34] in his study of perfluoropropylphosphines appear to be applicable here, namely (i) the relationship between the chemical shift of the α-fluorine [$\phi(F_3)$] and the halogen on phosphorus, and (ii) $\phi(F_3)$ being larger for RPX$_2$ than for R$_2$PX compounds.

(27) M. Akhtar and H. C. Clark, Can. J. Chem., **46**, 633 (1968).

(28) H. H. Jaffe, J. Chem. Phys., **22**, 1430 (1954).

(29) M. G. Hogben, R. S. Gay, and W. A. G. Graham, J. Am. Chem. Soc., **88**, 3457 (1966).

(30) T. D. Coyle, S. L. Stafford, and F. G. A. Stone, Spectrochim. Acta, **17**, 968 (1961).

(31) The synthesis and stereochemistry of perfluorovinylphosphor-anes is the subject of the following paper: A. H. Cowley and M. W. Taylor, J. Am. Chem. Soc., **91**, 1934 (1969).

(32) Reference 14 and references therein; K. Cohn and R. W. Parry, Inorg. Chem., **7**, 46 (1968).

(33) K. J. Packer, J. Chem. Soc., 960 (1963).

(34) J. F. Nixon, ibid., 777 (1965).