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THE PREPARATION AND SOME REACTIONS OF F₂PSPF₂ AND F₂PC(CF₃)₂OPF₂,
AND THE SYNTHESIS OF THE BIS-BORANE ADDUCT OF F₂PSSPF₂

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To Professor George H. Cady on his 70th Birthday

SUMMARY

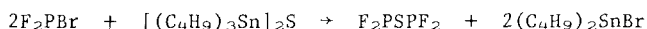
The potentially bidentate fluorophosphine ligand F₂PSPF₂ can be prepared in 75% yield from the reaction of F₂PBr and [(C₄H₉)₃Sn]₂S. On the basis of infrared and Raman spectra, the compound has been assigned a bent conformation of point group C_s or C₂. Nuclear magnetic resonance data confirm the assigned formula; but, as indicated by Rudolph and Newmark, low rigidity in the P-S-P backbone is probable and several rotamers might be expected. The compound is pyrophoric in air, but decomposes slowly at 25° and low pressure in the absence of air and water. It reacts with HCl and H₂O. With an excess of B₂H₆ at room temperature it gives the bis-borane adduct of the formerly elusive disulfide F₂PSSPF₂. The free disulfide has not yet been obtained from the adduct. A related fluorophosphine bidentate ligand, F₂PC(CF₃)₂OPF₂ was prepared in 80% yield from the reaction of P₂F₄ and hexafluoroacetone. The compound can be unequivocally characterized from its ¹⁹F nmr spectrum alone, although other data are given.

Trifluorophosphine has been very extensively studied as a ligand for coordination to metals of low oxidation state. Bidentate ligands containing two or more F₂P groups separated by atoms of different types would give a new dimension to the study of the coordination properties of the fluorophosphine groups. In earlier reports molecules such as F₂PPF₂,¹ F₂POPF₂,¹ and F₂PCH₂PF₂,² have been described. In this paper

we describe the synthesis, characterization, and some of the reactions of F_2PSPF_2 and $F_2PC(CF_3)_2OPF_2$. The systematic variation of the groups separating the F_2P units causes the expected dramatic changes in the chemistry of the systems involved.

THE PREPARATION AND FORMATION OF F_2PSPF_2

Preparation. The oxygen prototype of F_2PSPF_2 (i.e., F_2POPF_2) was first synthesized by the reaction of PF_2I and Cu_2O .¹ The analogous procedure involving PF_2I and Cu_2S did not yield the desired F_2PSPF_2 . On the other hand, it was found that a much superior procedure for the generation of F_2POPF_2 could be adapted to the successful synthesis of F_2PSPF_2 . Centofanti³ found that the reaction of F_2PBr with $[(C_4H_9)_3Sn]_2O$ is the preferred method for the synthesis of F_2POPF_2 . The comparable reaction using $[(C_4H_9)_3Sn]_2S$ gave a 75% yield of F_2PSPF_2 (based on the F_2PBr used). The relevant equation is:



The μ -sulfo-bis(difluorophosphine) is a liquid at 0° with an extrapolated boiling point of 21° . It undergoes slow decomposition upon standing in the gas phase at 25° and low pressure. The identity of the compound was established by a vapor density molecular weight (170 ± 2 at a pressure of 189 mmHg vs. theoretical value of 170), a mass spectrum showing the highest peak at an m/e value of 170, and by vibrational and nuclear magnetic resonance spectroscopy.

The Vibrational Spectra. The Raman and the infrared spectra are shown in Table I along with tentative assignments. Such assignments are based on analogy to related molecules and do not represent the results of isotope substitution studies.

The formula and the method of synthesis of F_4P_2S would be consistent with at least two reasonable structures: $F_2P-S-PF_2$ and $F_2P(S)PF_2$. The former involving a P-S-P bridge arrangement is preferred to that involving a sulfur atom bound to one of the phosphorus atoms of F_2PPF_2 molecule. A related compound showing both these structural features $F_2P(S)SPF_2$ has been reported by Cavell, Charlton, and Pinkerton⁴ as a product of the slow reaction between $F_2P(S)I$ and a stoichiometric quantity of mercury metal. It was also made by the reaction of dithiodifluorophosphoric acid [$HSP(S)F_2$] with dimethylaminodifluorophosphine $[(CH_3)_2NPF_2]$. A comparison

of the infrared data for $F_2P(S)SPF_2$ with the spectrum seen for our compound supports the sulfur bridged model. In the molecule $F_2P(S)SPF_2$ strong P-F stretching vibrations were seen at 925 and 898 cm^{-1} and were attributed to the P-F links to the pentavalent phosphorus. Such absorptions are not present in Table I indicating the absence of fluorine bonds to P(V). On the other hand, strong bands at 850-830 cm^{-1} in Table I are best assigned to P-F bonds in trivalent phosphorus compounds.^{2,3,4,5} Further, compounds containing P=S linkages involving pentavalent phosphorus usually show strong absorptions in the region^{2,4,5} 650 to 750 cm^{-1} yet the spectrum of F_4P_2S shows no peak in this region. On the other hand, the strong peaks at 500 cm^{-1} and/or 449 cm^{-1} indicate a P-S-P linkage if the usual assignments of Cavell and others are accepted.⁴ On the basis of the foregoing arguments, a P-S-P bridge structure is assigned with a high level of confidence.

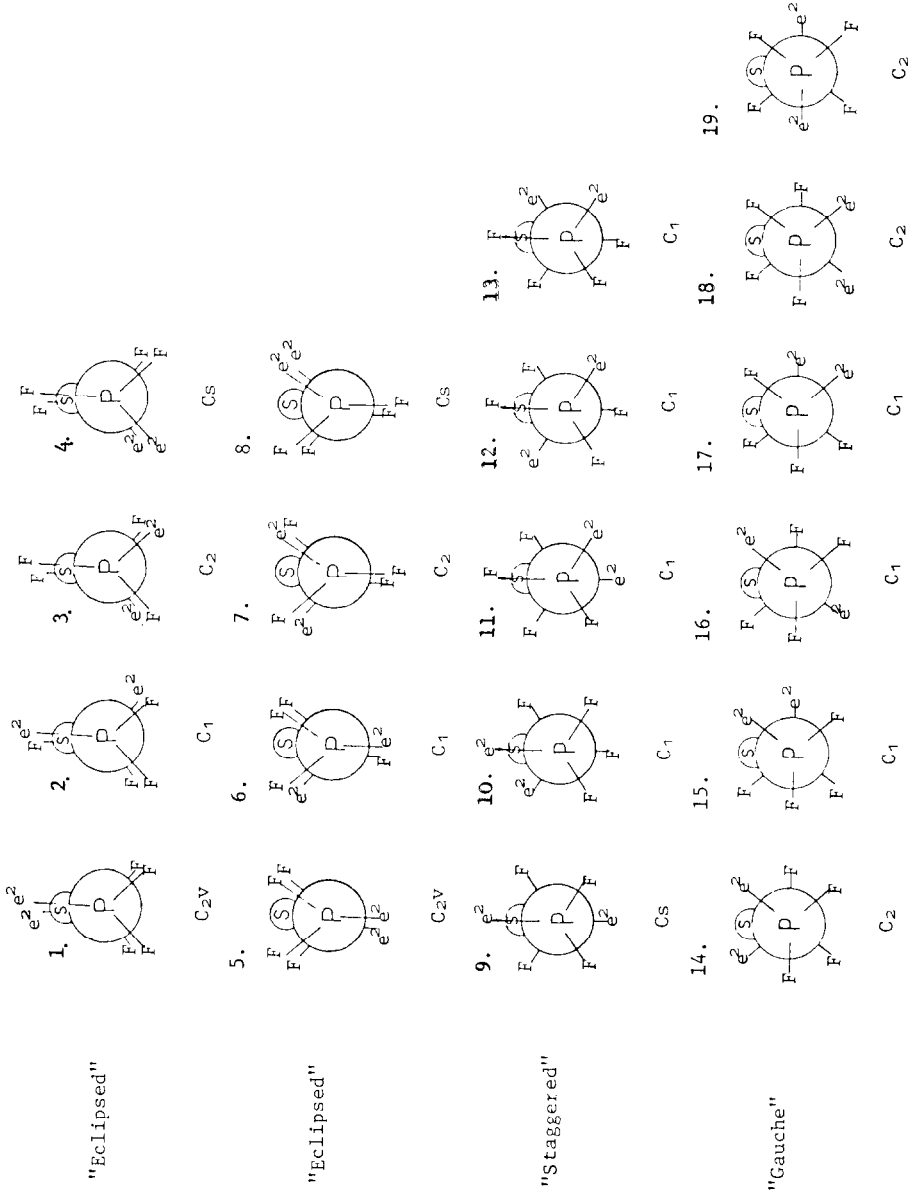
The infrared and Raman data can also help establish the favored conformation of the molecule. The vibrational spectra of a compound of formula F_4P_2S should show a maximum of 15 vibrations in both the infrared and Raman if the numbers were not reduced by symmetry. On the basis of the electron pair repulsion model the P-S-P linkage should be bent. For the molecule under study here, symmetry arguments will be invoked to show that all linear

TABLE I
THE VIBRATIONAL SPECTRA OF F_2PSPF_2

Infrared - (gas)			Raman - (liquid, -60°C)		
Frequency cm^{-1}	Intensity	Tentative Assignment	Frequency cm^{-1}	Intensity	Polariz.
850-830	vvs	$\nu_S PF$	862	m	p
		$\nu_{as} PF$	824	m	dp
		$\nu_S PF$	795	m	p
580	m	$\nu_S PS, \nu_{as} PS$	579	s	p
516	w, sh	$\delta_S FPF$	511	m	p
500	s	$\nu_S PSP$	484	w	p?
449	vs	$\delta_{as} FPF$	440	s	dp
407	w	$\delta_S FPS$	405	s	p
302	m	$\delta_{as} FPS$	313	w	dp
		δPSP	234	s	p
		τPF_2	173	w	p
		τPF_2	121	m	dp

FIGURE 1

Point Groups for Conformers of F₂PSPF₂



models but one rather improbable one can be eliminated by the spectral data^{*}

Three possible point groups for the different configurations of a bent form of $F_2P-S-PF_2$ can be assigned. Possible forms and their point groups are shown in Fig. 1 using a modified Newman projection. The point groups to be considered are: C_{2v} , C_2 , C_s , C_1 . The number of infrared and Raman lines expected by symmetry arguments for each is shown in Table II.

TABLE II

Point Group	Special Form	Expected IR Lines	Raman Lines	
			Polarized	Depolarized
C_{2v}	--	12	5	10
C_2	--	15	8	7
C_s	σ thru S	15	8	7
C_s	σ thru PSP	15	9	6
C_1	--	15	15	0

The observed spectrum shows 7 infrared and 12 Raman lines with 7 Raman lines definitely polarized and one probably polarized. On the basis of the polarization data alone one can exclude C_{2v} and C_1 point groups, but C_2 , and C_s remain possible providing that one assumes that missing bands in ir and Raman can be attributed to a lack of resolution, very weak bands, or accidental degeneracies. One must further assume for C_s that one of the unseem Raman lines is polarized. The exact conformer can not be identified from vibrational spectra but one can eliminate by symmetry arguments all forms of figure 1 but 3, 4, 7, 8, 9, 14, 18 and 19. If one supplements the symmetry arguments by electron pair repulsion arguments in which the 2 electron pairs on sulfur play a role, the conformer giving minimum electron repulsion would probably be number 3 (Fig. 1) although the data are thoroughly consistent with a molecule having a flexible PSP backbone as suggested by Rudolph and Newmark⁷ to explain their nmr data, (i.e., other rotational conformers populated).

^{*}Footnote: All linear PSP models but one can be eliminated by the data. Possible point groups for linear PSP structures are C_{2h} , D_{2d} , C_2 , C_{2v} , and C_{2h} . The spectra expected for each are summarized as D_{2h} (R: 3p and 3dp; IR: 8), D_{2d} (R: 3p and 8dp; IR: 7), C_2 (R: 8p and 7dp; IR: 15), C_{2v} (R: 5p, 10dp; IR: 12), and C_{2h} (R: 4p and 2dp; IR: 9). All but the C_2 point group can be eliminated by the data. C_2 is judged to be quite improbable based on known sulfur structures. D_{2h} and C_{2h} which have an inversion center can be eliminated unequivocally by the exclusion rule.

Nuclear Magnetic Resonance Spectra. The ^{19}F and ^{31}P nmr spectra show patterns expected for the sulfur bridged rather than the phosphorus-phosphorus bond model. Each spectrum exhibits a complex group of peaks symmetrically centered about one point. The patterns are clearly those expected for the second order spectra which would be characteristic of the sulfur-bridged structure. A phosphorus-phosphorus bonded model would be expected to show two phosphorus triplets such as are described later for $\text{F}_2\text{PC}(\text{CF}_3)_2\text{OPF}_2$ and two groups of fluorine peaks. The compound $\text{F}_2\text{PC}(\text{CF}_3)_2\text{OPF}_2$ is described later using first order rules; hence, first order rules might well be expected for the P-P bonded model.

A careful study of the signs and the temperature dependence of the F-F, P-F, and P-P coupling constants of $\text{F}_2\text{PSPF}_2^\dagger$ was published by Rudolph and Newmark⁷ and by Newmark, Norman and Rudolph.⁸ A sulfur bridge model, as demanded by the spectra, was used. An anomalously large change in the $p^{\text{S}}\text{S}_p$ coupling constant with temperature was tentatively attributed to a relatively non rigid PSP backbone with a concomitant change in the populations of the various rotameric forms of the molecule as viewed by nmr. The vibrational spectra are consistent with such a postulate.

THE REACTIONS OF F_2PSPF_2 AND THE SYNTHESIS OF A
BIS-BORANE ADDUCT OF $\text{F}_2\text{P}(\text{S})\text{SPF}_2$

The Decomposition of F_2PSPF_2 . The parent F_2PSPF_2 like $\text{F}_2\text{PCH}_2\text{PF}_2$, is pyrophoric in air, but is fairly stable in the absence of oxygen or water. A sample allowed to stand one day at 25°C ., and under a pressure of 26 mmHg showed 2% decomposition. The compound is somewhat less stable than F_2POPF_2 ,¹ but the decomposition products, PF_3 and a solid, appeared similar.

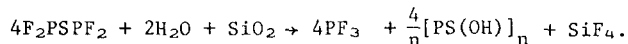
The Reactions of F_2PSPF_2 with Brønsted Acids. By analogy to known chemistry of F_2POPF_2 ,⁹ a Brønsted acid should cleave the PSP bond of F_2PSPF_2 to give F_2PSH and F_2PX . In the oxygen case F_2POH rearranged rapidly to give $\text{F}_2\text{P}(\text{O})\text{H}$.⁹ The same type of rearrangement was found with F_2PSH . Only $\text{F}_2\text{P}(\text{S})\text{H}$ was found in the system. These observations contrast quite sharply with observations of Griffiths and Burg¹⁰ on the somewhat related compound,

[†]Samples of F_2PSPF_2 used in their study were prepared by the procedures described in the dissertation of G.N.B.¹³

(CF₃)₂POP(CF₃)₂ and of Cavell and Emeleus¹¹ on the more closely related compound (CF₃)₂PSP(CF₃)₂. Observations on the CF₃ compounds establish quite clearly that rearrangement does not take place and the products of the reaction with HX are (CF₃)₂PSH and (CF₃)₂PX. The reasons for this difference remain controversial and unclear. It has been suggested⁹ that steric effects might be important and that the larger size of the CF₃ groups as compared to fluorine would be effective in stabilizing phosphorus with a coordination number of 3 rather than 4 for the larger group. Another suggestion⁹ involved the π-bonding capability of F as opposed to CF₃. In terms of this argument back-donation of electrons from F to P in pπ - dπ bonding would render the lone pair of electrons more available for the bonding of the H⁺ unit, thus F₂P(S)H would be more easily formed and would be more stable than (CF₃)₂P(O)H. If indeed these π-bonding arguments were valid one would expect extensive back donation and π-bonding in F₃P=O and relatively little in (CF₃)₃P=O. The π-bonding in F₃PO might well be expected to reduce the double bond character of the P=O bond in F₃PO. In the absence of back donation the P=O bond of (CF₃)₃P=O should retain its original double bond character. Under these arguments the P=O stretching frequency of (CF₃)₃P=O should be higher than that of F₃P=O. The frequencies are just the opposite; the P=O band in F₃P=O is higher than is the comparable band in (CF₃)₃P=O, and follow the electronegativity pattern as indicated for >S=O by Sauer and Shreeve.¹⁹

Arguments based on the high electronegativity of the CF₃ group¹⁰ and its ability to render the free pair incapable of holding a proton are rendered dubious by the fact that the electronegativity of the CF₃ is usually placed below that of F.¹²

The reaction of F₂PSPF₂ with water in a glass tube produced a set of products different than the expected F₂P(S)H and F₂P(O)H. The data are roughly consistent with the equation:



At relatively early times in the reaction process, infrared data identified small amounts of F₂P(O)H and F₂P(S)H in the reaction mixture, but neither of the materials was detected in the final system. These facts suggest that F₂P(O)H and F₂P(S)H may indeed be produced initially, but that they react rapidly with additional water and SiO₂ in the system. One set of equations which is reasonable and consistent with the foregoing postulate is:

Detailed ^{19}F , ^{31}P , ^{11}B , and ^1H nmr spectra are displayed elsewhere.^{13b} The data indicate a structure involving an F_2PSSPF_2 with a BH_3 group bound to each sulfur atom. The ^{19}F spectrum consists of one doublet located 69.9 ppm upfield from CFCl_3 which indicates one kind of fluorine bound directly to a phosphorus atom ($J_{\text{PF}} = 1252\text{Hz}$). The spectrum showed no fine structure under high resolution—a fact which argues against a direct P-B bond.

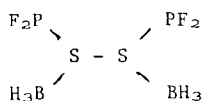
The ^{31}P spectrum showed a 1:2:1 triplet centered -187 ppm from H_3PO_4 . The value of J_{PF} estimated from this spectrum of relatively low quality was $1240 \pm 15\text{Hz}$. The chemical shift value of the phosphorus atom is consistent with, but does not prove the existence of a phosphorus atom of coordination number 3. The phosphorus spectrum showed no evidence of direct P-B coupling—a fact which also argues against a direct P-B linkage.

The ^{11}B nmr showed a 1:3:3:1 quartet, attributable to boron—hydrogen coupling ($J_{\text{BH}} = 120\text{Hz}$, $\delta = +122$ pp from trimethylborane). The integrity of the coordinated BH_3 group is established by this pattern and the lack of further splitting again argues against a direct B-P bond.

The ^1H spectrum showed a very weak broad signal which could best be interpreted as a 1:1:1:1 quartet at -2.0 ppm from TMS with $J_{\text{BH}} = 120 \pm 15$.

The infrared spectrum of $\text{F}_2\text{PS}(\text{BH}_3)\text{S}(\text{BH}_3)\text{PF}_2$ shows the expected absorptions for the BH_3 groups at 2500 cm^{-1} and 2445 cm^{-1} ($\nu_{\text{as}}\text{B-H}$ and $\nu_{\text{s}}\text{B-H}$),¹⁴ and at 1110 and 1000 cm^{-1} ($\delta_{\text{as}}\text{BH}_3$, $\delta_{\text{s}}\text{BH}_3$). The foregoing peaks further confirm the integrity of the BH_3 unit. Two bands at 910 and 890 cm^{-1} are assigned to the B-S stretching motion by comparison to a literature¹⁵ B-S mode assignment at 914 cm^{-1} . The P-F stretching motions are assigned at 885 and 865 cm^{-1} . (These values are between those of PF in F_3PBH_3 and in F_2PSPF_2 .) No band was found in the $600\text{--}650\text{ cm}^{-1}$ region which would be characteristic of a P-B stretching motion.^{13b,14,16} A detailed listing of the frequencies of this compound appears in the experimental section.

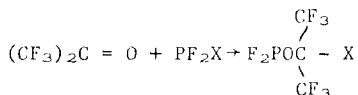
As in the case of other compounds containing F, P, and B, conventional analytical procedures did not give good results, but the sum total of the instrumental information provides very strong evidence for a compound of formula:



THE PREPARATION AND CHARACTERIZATION OF $F_2PC(CF_3)_2OPF_2$.

In an earlier report² a molecule containing two PF_2 groups separated by a CH_2 group was described. While the CH_2 group effectively blocked any π interaction between phosphorus atoms, it placed an electron donating group between PF_2 units and thus altered significantly the analogy to PF_3 as a π ligand. In order to minimize this electron donating contribution a molecule containing two PF_2 units separated by a CF_2 unit was desired. All of our efforts to synthesize this molecule were unsuccessful. It was possible, however, to prepare a somewhat related molecule $F_2PC(CF_3)_2OPF_2$ by the reaction of F_2PPF_2 with hexafluoroacetone.

The Preparation of $F_2PC(CF_3)_2OPF_2$. Hexafluoroacetone adds tetrafluoro-diphosphine across the carbonyl double bond to give $F_2PC(CF_3)_2OPF_2$ in 80% yield. The reaction is very similar to the addition reaction between hexafluoroacetone and F_2PBr or F_2PI , reported some time ago by Lustig and Hill.¹⁷



Lustig and Hill further reported that the addition process really represents an equilibrium system in which starting materials are also present. This same observation is appropriate for P_2F_4 , but the P_2F_4 decomposed irreversibly in the mixture to give PF_3 and $(PF)_n$. Such behavior prevented evaluation of an equilibrium constant by a separation procedure. It was clear, however, that the position of the equilibrium strongly favored $F_2PC(CF_3)_2OPF_2$.

The mass spectrum fragmentation pattern compares appropriately with the pattern observed by Lustig and Hill for the PF_2Br adduct of hexafluoroacetone. The expected parent peak at 304 is very weak (only .06% of PF_2 peak), but it is still the highest value of m/e for any visible peak and confirms the vapor density molecular weight of 310 ± 6 . A mass peak at m/e of 138 is identified as $P_2F_4^+$ and indicates the probable existence of P_2F_4 in the original reaction system as postulated in the equilibrium hypothesis.

The NMR Spectra of $F_2PC(CF_3)_2OPF_2$. The basic ^{19}F spectrum of the neat liquid at 0° consists of 1) a low field doublet, 2) an intermediate field singlet, and 3) a high field doublet; the relative areas are 1:3:1. The low field doublet at $\delta = +40.9$ ppm from $CFCl_3$ corresponds to fluorine atoms of the PF_2 bound to oxygen ($J_{PF} = 1381\text{Hz}$), by analogy to the spectrum of $BrC(CF_3)_2OPF_2$.¹⁷ The high field doublet at $\delta = +97.3$ ($J_{PF} = 1275$) corresponds to fluorine atoms of the PF_2 group bound to carbon. The high intensity singlet at 69.8 ppm clearly corresponds to the two CF_3 units.

First order rules also provide a reasonable basis for the interpretation of the high resolution ^{19}F spectrum. Each member of the OPF_2 doublet consists of two overlapping septets. The spectrum is shown in Fig. 2a. As shown by the fork diagram in the figure, the original doublet results from PCOPF coupling with a J_{PCOPF} of 9.0 Hz. The septet into which each member of this doublet is split results from coupling with the six equivalent fluorine atoms of the hexafluoroacetone. The value of J_{FCCOPF} is 3.1 Hz. Finally each of the septet lines is split into a 1:2:1 triplet by the other PF_2 group. The J_{FPOCPF} value is also 3.1 Hz.

For the complex C- PF_2 multiplet (Fig. 2b) one can recognize a doublet assignable to POCPF coupling with a J_{POCPF} value of 24.3 Hz. Each member of this doublet is split into a septet by the two CF_3 groups. The value of J_{FCCPF} is 8.9 Hz. Finally each member of the set of overlapping septets is clearly split into a triplet through coupling with the two fluorine atoms of the other PF_2 group. The value of J_{FPOCPF} is 3.1 Hz.

Finally the singlet attributable to the CF_3 fluorines can be resolved into the complex multiplet shown in Fig. 2c. One can recognize an initial doublet due to POCFF coupling with a J_{POCFF} value of 26.0 Hz (compare with the value of 24.3 Hz for J_{POCPF} as given above; each member of this doublet is split again into a doublet through coupling with the other phosphorus atom where J_{PCCF} is 16.7 Hz. Each member of the doublet is split into a 1:3:1 triplet by coupling to the fluorine atoms of the CPF_2 unit. Finally each member of the above triplet is split into a 1:2:1 triplet by FPOCFF coupling with a J_{FPOCFF} value of 3.1 Hz.

It is significant that this one nmr spectrum establishes with a very high level of certainty the formula and the gross structural features of this molecule. The details of ^{19}F fine structure leave little real room for question.

The ^{31}P nmr spectrum of the neat liquid at -20° confirms the structural conclusions of the ^{19}F spectrum. The ^{31}P spectrum consists of two 1:2:1 triplets resulting from two F_2P groups existing in two different chemical environments. The triplet at -175 ppm from H_3PO_4 and $J_{\text{P-F}} = 1275$ Hz, (note: $J_{\text{PF}} = 1275$ Hz from ^{19}F spectrum) is assigned to the phosphorus of the PF_2 group bound to carbon. The triplet assignable to the phosphorus of the PF_2 group bound to oxygen appears at $\delta = -122$ ppm from H_3PO_4 with a J_{PF} of 1368. (The value of J_{PF} from ^{19}F spectrum was 1381 Hz; the fluorine spectrum gives the better value because of a better quality spectrum.) Each of the peaks in the ^{31}P spectrum has fine structure under high resolution, but because

FIGURE 2

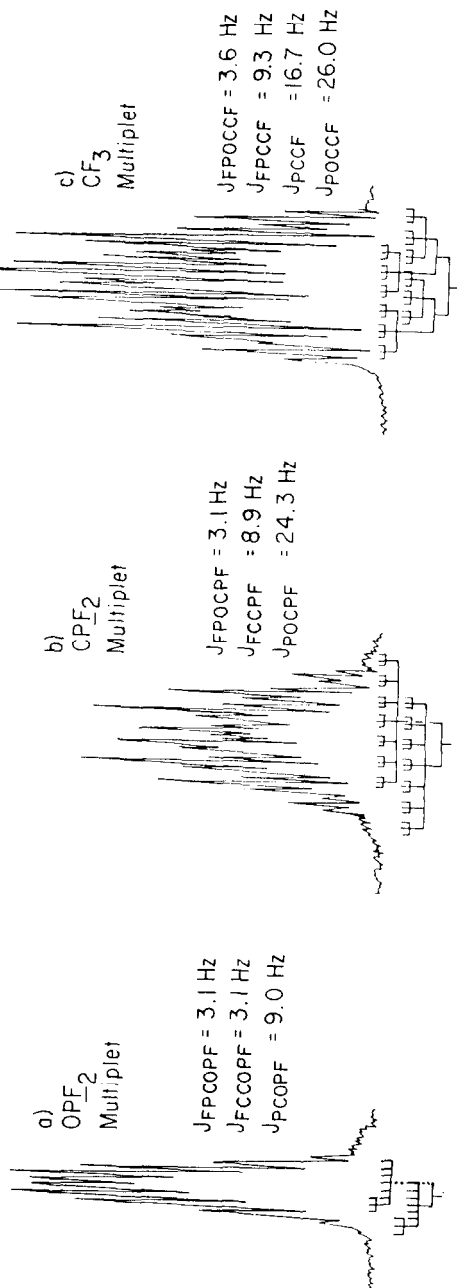
High Resolution Fluorine NMR Spectra of $\text{F}_2\text{PC}(\text{CF}_3)_2\text{OPF}_2$

TABLE III

NMR Values of $F_2PC(CF_3)_2OPF_2$

		Chemical Shift				
		$\frac{PF_2C(CF_3)_2OPF_2}{OPF_2}$	$\frac{CF_3}{CF_3}$	$\frac{CPF_2}{OPF_2}$	$\frac{IC(CF_3)_2OPF_2}{OPF_2}$	$\frac{BrC(CF_3)_2OPF_2}{OPF_2}$
^{19}F nmr(CFCl ₃)		+40.9	+69.8	+97.3	+46.9	+45.9
^{31}P nmr(OPA)		-122		-175	+74.5	+77.8
Coupling Constants (cps)						
$\frac{PF_2C(CF_3)_2OPF_2}{OPF_2}$	$\frac{CF_3}{CF_3}$	$\frac{CPF_2}{OPF_2}$	$\frac{19F}{19F}$	$\frac{31P}{31P}$	$\frac{IC(CF_3)_2OPF_2}{OPF_2}$	$\frac{BrC(CF_3)_2OPF_2}{OPF_2}$
^{19}F	^{19}F	^{19}F	^{19}F	^{31}P	^{19}F	^{19}F
J _{FP}	1381	1368	--	1275	1384	1384
J _{FPOCP}	9.0	--	--	8	--	--
J _{FPOCCF}	3.1	--	3.6	--	0.9	1.6
J _{FPOCPP}	3.1	--	--	2.9	--	--
J _{FPCOP}	--	22	--	24.3	--	--
J _{FPCCF}	--	--	9.3	8.9	--	--
J _{FCCP}	--	--	16.7	--	16	--
J _{FCCOP}	--	25	26.0	--	8	12

of the reduced quality of the phosphorus spectrum, the interpretations can not be claimed as unequivocal. One can, however, identify reasonable line patterns using coupling constants taken from the fluorine spectrum (See Table 3).

The Infrared Spectrum of $F_2PC(CF_3)_2OPF_2$. The rather complex spectrum is presented in the experimental section as a characterization aid. The infrared data support the structure assigned.

DISCUSSION

In this and the preceding paper the synthesis and characterization of three bidentate ligands carrying two F_2P groups separated by different types and/or numbers of atoms have been described. The use of such ligands in organometallic synthesis is in progress.

EXPERIMENTAL

General Techniques. Standard vacuum line procedures were used throughout. Most of the infrared spectra were obtained with a Beckman IR-12 using a gas cell with a 75 mm path length and CsI windows. Raman spectra were obtained with a Gaertner two prism spectrograph with a dispersion of approximately 180 cm^{-1} per mm in the blue region and a resolution of about 10 cm^{-1} as used here. The nmr spectra were obtained with a Varian HR-100 spectrometer. Chemical shifts were obtained by tube interchange. Equipment was designed such that all products could be condensed into nmr tubes on the vacuum system without any contact with the air. A consolidated Electro Dynamics Model 21-103B mass spectrometer operating at 70 eV was used for all mass spectra.

Reagents. Tributyltin sulfide was obtained from Alpha Inorganic, Inc., and was distilled before use (175°C . and 10^{-2} mmHg); bromodifluorophosphine was prepared by the reaction of HBr with $F_2PN(CH_3)_2$.¹⁸ The P_2F_4 was prepared by the reaction of PF_2I and Hg as described in Ref. 1. Hexafluoroacetone was obtained from Matheson Gas Products. Diborane was obtained from Callery Chemical Co. All other reagents were "Chemically Pure" grade reagents.

The Preparation of F_2PSPF_2 . A 10.24 mmole quantity (6.27g) of dried distilled $[(C_4H_9)_3Sn]_2S$ was measured under a dry nitrogen atmosphere into a thoroughly dry 500 ml reaction flask on the vacuum line. The flask was evacuated and 20.4 mmoles of PF_2Br were frozen in at -196° . After slowly

warming to 25^o, the system was again frozen. The cycle was repeated several times over a 25 minute reaction period; then the volatile products were distilled through traps held at -98^o, -160^o, and -196^o. The -98^o trap contained 7.72 mmoles of F₂PSPF₂. The -160^o trap held 1.96 mmoles of unreacted PF₂Br plus a little PF₂(S)H, while 0.78 mmole of PF₃ was retained at -196^o.

The vapor pressure of the material is given by the equation:

$$\log P_{\text{mmHg}} = \frac{-1623}{T} + 8.086$$

Values are listed here as [Temp., obs.V.P.(calcd.V.P.)]: -45.7^oC., 8.8(8.9); -24,8^o, 35.8(35.5); -15.6^o, 61.6(60.8); + 0.2^o, 140.4(140.5); + 6.3^o, 187.3(189.4). The extrapolated boiling point is 21^o.

The mass spectrum is given as [m/e ratio, relative peak height, (assignment)]; 170, 21.0 (F₂PSPF₂⁺); 101, 11.2, (F₂PS⁺); 84, 3.7 (F³⁺PS⁺); 82, 82.8, (FPS⁺); 69, 100, (F₂P⁺); 63, 26.9, (PS⁺); 50, 18.4, (FP⁺); 32, 8.8, (S⁺); 31, 7.1, (P⁺).

Reactions of F₂PSPF₂ with Brønsted Acids. A 1.58 mmole quantity of HCl and an equimolar quantity of F₂PSPF₂ were condensed into the dried 500 ml reaction system which had been used for the synthesis of F₂PSPF₂. After the system had warmed and stood one hour at 25^o, the volatile materials were fractionated. The -126^o trap contained 1.50 mmoles F₂P(S)H; the 160^o trap held 1.55 mmoles of F₂PCl; and the -196^o trap held .05 mmole of PF₃ (all identified by ir). Reactions with water were done in a similar fashion.

Decomposition of F₂PSPF₂. A 0.75 mmole sample was condensed into the reaction system described above, warmed to 25^o, held 24 hours, and fractionated. A 0.02 mmole sample of PF₃ and a 0.03 mmole sample of F₂P(S)H and F₂POPF₂ were separated. A 0.71 mmole sample of unchanged F₂PSPF₂ was recovered. The percent decomposition was based on the PF₃ formed. Some slight hydrolysis is assumed to be responsible for the F₂P(S)H and F₂POPF₂.

The Synthesis of F₂PS(BH₃)S(BH₃)PF₂. A 2.04 mmole sample of F₂PSPF₂ and a 4.08 mmole quantity of B₂H₆ were condensed into the 500 ml reaction bulb which was open to a manometer. When the system warmed to 25^oC., the initial B₂H₆ pressure was 150 mmHg. Yellow solids began to appear after 0.5 hours and the pressure fell over a 6 hour period. A sample of the 0.11 mmole noncondensable gas was removed and the volatile products were fractionated. The -78^o trap contained 0.726 mmoles of F₂PSSPF₂·2BH₃; the -160^o trap held

1.41 mmole of F_2PHBH_3 and a small amount of $F_2P(S)H$; the -196° trap held a 3.0 mmole mixture of unchanged B_2H_6 and PF_3 . The $F_2PS(BH_3)S(BH_3)PF_2$ was sufficiently stable that it could be handled in vacuum to make vapor density measurements at 25° and 18 mmHg pressure without apparent decomposition.

The mass spectrum is summarized as was done for F_2PSPF_2 , (i.e. [m/e ratio, intensity, (assignment)]: 225, 4.8 ($F_4P_2S_2B_2H^+$); 184, 1.6, ($F_4P_2SBH_3^+$); 159, 35.0, ($F_2PS_2B_2H_4^+$); 158, 43.3, ($F_2PS_2B_2H_3^+$); 157, 62.0, ($F_2PS_2B_2H_2^+$); 156, 25.0, ($F_2PS_2B_2H^+$); 127, 4.3, ($F_2PSPB_2H_4^+$); 125, 8.5 ($F_2PSB_2H_2^+$); 124, 7.9, (F_2PSB_2H); 114, 4.7, ($F_2PSBH_2^+$); 113, 7.3, (F_2PSBH^+); 101, 4.5, (F_2PSH^+); 95, 8.3, ($FPSBH_2^+$); 83, 6.1, ($FPSH^+$); 82, 24.7, (FPS^+); 75, 5.3, ($PSBH^+$); 69, 96.6, (F_2P^+); 65, 7.9, ($P^{34}S^+$); 64, 9.5, (PSH^+ , S_2^+); 63, 100.0, (PS^+); 62, 4.61, (?); 57, 6.2, ($SB_2H_3^+$); 56, 5.5, ($SB_2H_2^+$); 51, 7.5, (FPH^+); 50, 25.1 (FP^+); 49, 8.2, (BF_2^+); 45, 32.8, (SBH_2^+); 44, 19.9 (SBH^+); 43, 7.5, (SB^+); 32, 13.0, (S^+); 31, 27.6, (P^+).

The infrared spectrum of $F_2PS(BH_3)S(BH_3)PF_2$ is summarized as frequency, intensity, (assignment). Intensity is indicated as: s = strong, m = medium, w = weak, v = very, sh = shoulder, b = broad. Assignment is indicated as ν = stretch, ρ = rocking, δ = deformation, and ω = wagging motions.^{††} The values are: 2500, s, ($\nu_{as}BH$); 2445, s, (ν_sBH); 2320, w, (2×1154); 1110, ms, (δBH_3); 1000, ms, (δBH_3); 910, s, (νBS); 890, s, (sh), (νBS); 885, s, (νPF); 865, s, (νPF); 710, s, ($\nu PS?$); 575, w, (δPPF); 510, m (δPPF); 415, ms, (δFPS); 320, m, (δFPS).

The Synthesis of $F_2PC(CF_3)_2OPF_2$. A 1.14 mmole sample of P_2F_4 and a 1.12 mmole quantity of $(CF_3)_2C=O$ were condensed into a 500 ml reactor connected to a manometer. The system was warmed to 25° and held 9 hours, then fractionated. The trap at -95° held 0.90 mmole of $F_2PC(CF_3)_2OPF_2$; the trap at -160° held 0.25 mmole of unchanged hexafluoroacetone while the trap at -196° held 0.12 mmole of PF_3 .

The vapor pressure of the material is given by the equation:

$$\log P_{\text{mmHg}} = \frac{-1808}{T} + 8.397$$

Representative values are given as [temp. obs. v.p.(mmHg)(calcd.v.p.)]: $-45.5^\circ C.$, 2.7, (2.9); -24.1° , 14.0, (13.8); -16.7° , 22.7, (22.3); $+0.2^\circ$, 59.9, (59.7); $+24.5^\circ$, 201.4, (210.8). The extrapolated boiling point is 27° and the melting point is $-121.0^\circ \pm 0.4$. The mass spectrum of $F_2PC(CF_3)_2OPF_2$

^{††} These terms have the usual significance as indicated in Herzberg, "Infrared and Raman Spectra", p331 and 332, Van Nostrand, N.Y. (1945).

is given as [m/e ratio, intensity, (assignment)]: 235, 2.2 ($C_3F_6OP^+$); 216, 6.7, ($C_3F_7OP^+$); 197, 20.7, ($C_2F_5OP_2^+$); 147, 7.2, ($C_3F_5O^+$, $C_2F_4OP^+$); 138, 1.9, ($P_2F_4^+$); 128, 107, ($C_3F_4O^+$, $C_2F_3OP^+$); 119, 1.5, ($C_2F_5^+$, CF_4P^+); 112, 2.4, ($C_3F_4^+$, $C_2F_3P^+$); 100, 2.2, (C_2F_4 , CF_3P^+); 97, 4.4, ($C_2F_3O^+$, CF_2OP^+); 93, 2.1, ($C_3F_3^+$, $C_2F_2P^+$); 81, 1.4, ($C_2F_3^+$); 78, 3.9, ($C_2F_2O^+$, $CFOP^+$); 69, 100, (CF_3^+ , PF_2^+); 50, 10.6 (CF_2^+ , PF^+); 47, 1.7, (CFO^+ , PO^+); 31, 5.3, (CF^+ , P^+).

A summary of nmr data and the corresponding data for $F_2POC(CF_3)_2X$ of Lustig and Hill are shown in Table III.

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BIBLIOGRAPHY

- 1 R.W.Rudolph, R.C.Taylor, and R.W.Parry, J.Am.Chem.Soc., 88, 3729(1966).
- 2 G.N.Bockerman and R.W.Parry, J.Inorg. and Nucl.Chem. In press. H.Hyman Memorial Issue.
- 3a J.F.Centofanti, Ph.D.Dissertation, Univ.of Mich. Ann Arbor, Mich.(1968) p23.;
b L.F.Centofanti and R.W.Parry, Inorg. Syn. 12, 281(1970).
- 4 R.G.Cavell, T.L.Charlton, and A.A.Pinkerton, J.Chem.Soc. D(1969)424;
Inorg.Chem. 8, 2436-40(1969).
- 5 L.J.Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., London(1958),p321.
- 6 R.L.Kuczkowski, H.W.Schiller, and R.W.Rudolph, Inorg.Chem. 10, 2505(1971) and references therein.
- 7 R.W.Rudolph and R.A.Newmark, J.Am.Chem.Soc., 92, 1195(1970).
- 8 R.A.Newmark, A.D.Norman, and R.W.Rudolph, Chem.Comms. (1969)893.
- 9 L.F.Centofanti and R.W.Parry, Inorg.Chem.,7, 1005(1968).
- 10 L.E.Griffiths and A.B.Burg, J.Am.Chem.Soc., 82, 1507(1960).
- 11 R.G.Cavell and H.Emel us, J.Chem.Soc.,(1964)5825.
- 12 J.J.Lagowski, Quart. Rev.,13, 173(1959).
- 13a G.N.Bockerman and R.W.Parry, to be published;
b G.N.Bockerman, Ph.D.Dissertation, Univ. of Mich., Ann Arbor, Mich.(1968).
- 14 R.C.Taylor, R.W.Rudolph, R.J.Wyma, and V.D Dunning, J.Raman Spectroscopy, 2, 175-192(1974).

- 15 A.Cabana, J.Brault, and J.M.Lalancette, *Spectro.Chim. Acta.*, 22, 377(196
- 16 H.W.Schiller and R.W.Rudolph, *Inorg.Chem.* 10, 2500(1971).
- 17 M.LUstig and W.E.Hill, *Inorg.Chem.* 6, 1448(1967).
- 18 J.G.Morse, K.Cohn, R.W.Rudolph, and R.W.Parry, *Inorg.Syn.* 10, 147(1967).
- 19 D.T.Sauer and J.M.Shreeve, *Anales De La Asociacion Quimica Argentina* 59, 157(1971).