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Mixed-Valence Derivatives of Phosphorus Sulfides. Two New Isomeric Thiophosphoryl- μ -thio-phosphines Containing Fluorine and Trifluoromethyl Substituents and a Discussion of Their Exchange Properties

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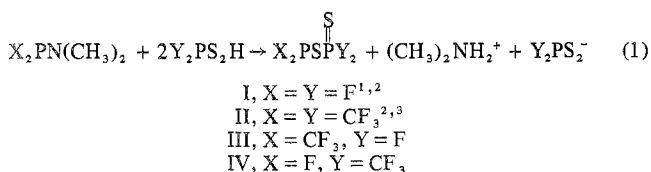
Two new mixed-valence phosphorus compounds $F_2P(S)SP(CF_3)_2$ and $(CF_3)_2P(S)SPF_2$ are formed by the reaction of the acids F_2PS_2H or $(CF_3)_2PS_2H$ with the aminophosphines $(CF_3)_2PN(CH_3)_2$ or $F_2PN(CH_3)_2$, respectively. Temperature-dependent nmr spectroscopy demonstrates the presence of an exchange process which destroys P-P coupling at room temperature in $(CF_3)_2P(S)SPF_2$ but not in $F_2P(S)SP(CF_3)_2$. The directly bound substituents are not interchanged by the exchange process and phosphorus valence is maintained. Concentration-dependent nmr studies indicate an intermolecular process and a plausible bimolecular process is described which accounts for the exchange process in $X_2P(S)SPX_2$ ($X = F, CF_3$) molecules. When combined, the two new mixed-valence compounds equilibrate to form the two known symmetrically substituted isomers $F_2P(S)SPF_2$ and $(CF_3)_2P(S)SP(CF_3)_2$ and the equilibrium mixture can also be approached from these compounds. Thermal stability trends indicate a lower stability for compounds containing the PF_2 moiety. Chemical reaction with protic species occurs with cleavage at the P^{III} -S link to yield phosphines and the parent acid and with halogens to yield halogeno phosphines and thiophosphinates. The reactions with mercury yield dithiophosphinato complexes and diphosphines or their decomposition products. Alkaline hydrolysis of CF_3 species proceeds to yield 2 mol of CF_3H per CF_3 phosphino group and 1 mol per thiophosphinato group.

Introduction

Chemical and spectroscopic studies showed that the compounds $F_2P(S)SPF_2$ (I)^{1,2} and $(CF_3)_2P(S)SP(CF_3)_2$ (II)^{2,3} possess the indicated mixed-valence structure in contrast to the symmetric P(V) structure of $[(CH_3)_2P(S)]_2$.⁴ The trifluoromethyl compound II, however, exhibited all coupling constants at ordinary temperatures³ whereas the fluoro-substituted analog I did not show long-range P-F and P-P coupling constants until cooled to low temperatures¹ suggesting that some environmental exchange process might occur in these molecules. In order to provide further insight into the behavior of these systems we have now synthesized additional analogs with both F and CF_3 substituents in the same molecule and extended the range of chemical and spectroscopic studies of these compounds.

Results and Discussion

A. Synthesis. The compounds were prepared by means of the general reaction¹⁻³



These reactions are nearly quantitative and best yields were obtained when nearly stoichiometric quantities of reactant were used because of the difficulty of separating the product from reactants. The compounds were characterized by nmr spectroscopy, by chemical behavior (*vide infra*), and by alkaline hydrolysis. Compound III yielded 2 molar equiv of CF_3H per mole of III whereas IV yielded only 1 equiv. Species remaining in solution are in agreement with those expected⁵ from the hydrolysis of the indicated trivalent and

pentavalent $(CF_3)_2P$ species obtained by splitting the molecule at the trivalent P-S bond.

B. Nmr Spectra. The principal couplings apparent in the room-temperature ^{19}F nmr spectra are clearly consistent with the indicated mixed-valence structures of III and IV which are analogous to the structures demonstrated for I^{1,2} and II.^{2,3} Particular values of $^1J_{PF}$ and $^2J_{PF}$, given in Table I, are typical of one- and two-bond couplings of fluorine to phosphorus in the penta- and trivalent oxidation states⁶⁻¹⁰ in agreement with the proposed formulation of the compounds.

In addition to the major $^2J_{PF}$ coupling, the trifluoromethyl region of the ^{19}F nmr spectrum of III shows at room temperature what is apparently a five-bond CF_3 -F coupling ($^5J_{FF}$) of about 1 Hz which splits the major lines into asymmetric triplets. This asymmetry was also observed in I¹ and may be due to undetected differences in cis- and trans-coupling constants. It seems odd that there is no observable interaction of the trifluoromethyl groups in III with the pentavalent phosphorus atom ($^4J_{PF}$) in either the ^{19}F or ^{31}P spectra especially in view of the existence of P^{III} - P^V and long-range F-F couplings in this molecule. The ^{19}F spectrum of the fluorine atoms bound to pentavalent P in III consists of the large doublet due to $^1J_{PF}$ and a further poorly resolved splitting of approximately 1 Hz to form apparent septets presumably due to coupling of these F atoms to the equivalent fluorine atoms of the CF_3 groups bound to trivalent phosphorus. The coupling of the fluorine atoms on pentavalent P to trivalent P, $^3J_{PF}$, was not observed at room temperature.

Lowering the temperature resulted in the loss of the fine structure arising from $^5J_{FF}$ in the fluorine spectrum of III and this coupling remained unresolved to the low-temperature limit of the spectrometer. At -120° the CF_3 region of

- (1) T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, **8**, 2436 (1969).
 (2) R. G. Cavell, T. L. Charlton, and A. A. Pinkerton, *J. Chem. Soc. D*, 424 (1969).
 (3) R. G. Cavell and A. A. Pinkerton, *J. Amer. Chem. Soc.*, **93**, 2384 (1971).
 (4) A. H. Cowley and H. Steinfink, *Inorg. Chem.*, **4**, 1827 (1965).
 (5) A. A. Pinkerton and R. G. Cavell, *Inorg. Chem.*, **10**, 2720 (1971).

- (6) (a) T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, **8**, 281 (1969); (b) R. W. Mitchell, M. Lustig, F. A. Hartmann, J. K. Ruff, and J. A. Merritt, *J. Amer. Chem. Soc.*, **90**, 6329 (1968).
 (7) R. C. Dobbie, L. F. Doty, and R. G. Cavell, *J. Amer. Chem. Soc.*, **90**, 2015 (1968).
 (8) R. Schmutzler, *Advan. Fluorine Chem.*, **5**, 31 (1965).
 (9) H. G. Horn and A. Muller, *Z. Anorg. Allg. Chem.*, **346**, 266 (1966); A. Muller, E. Niecke, and O. Glemser, *ibid.*, **350**, 246, 256 (1967).
 (10) K. J. Packer, *J. Chem. Soc.*, 960 (1963).

Table I. Coupling and Chemical Shift Parameters of Mixed-Valence Compounds

	$F_2P(S)SP(CF_3)_2$	$(CF_3)_2P(S)SPF_2$	$F_2P(S)SPF_2^1$ (I)		$(CF_3)_2P(S)SP(CF_3)_2^3$ (II)	
	(III)	(IV)	Penta	Tri	Penta	Tri
$^1J_{FP}^a$	1223	1331	1209.9	1323.6		
$^2J_{FP}$	78	113			111.7	81.3
$^3J_{FP}$	$>2^d$	18^d	14.3	22.5		
$^4J_{FP}$	n.o. ^e	1.8			4.9	0.6
$^4J_{FF}$			5.9, 0	5.9, 0		
$^5J_{FF}$	0.7	n.o. ^e				
$^6J_{FF}$					1.5	0.5
$^2J_{PP}$	96.5	73	67.8	67.8	103.0	103.0
$\phi_F(III)^b$	+55.0	+61.2		+60.8		+53.8
$\phi_F(V)^b$	+17.9	+71.2	+14.4		+68.7	
$\delta_P(III)^c$	+107.2	-81.4		-78 ^f		+106.0
$\delta_P(V)^c$	+42.1	+80.5	+38.2 ^f		+65.2	

^a Coupling constants are given in hertz. ^b ¹⁹F shift from CFC1₃; positive values indicate resonance to high field of internal (solvent) reference. ^c ³¹P shift from P₄O₆; positive values indicate resonance to high field of external capillary reference. The shift of P₄O₆ is -112 ppm relative to H₃PO₄ (85%): A. C. Chapman, J. Homer, D. J. Mowthorpe, and R. T. Jones, *Chem. Commun.*, 121 (1965). ^d Coupling not completely resolved. ^e Not observed. ^f Values given for the ³¹P chemical shifts in ref 1 are incorrect due to an error in relating measured values to P₄O₆ reference. The corrected values given herein are those given by T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, 11, 1583 (1972).

the spectrum consisted of only a doublet due to $^2J_{FP}$. In some samples the spectrum arising from F on pentavalent P was just beginning to show visible doublet structure due to coupling with trivalent P at -120° but this coupling was never completely resolved and its magnitude (although greater than 2 Hz) is uncertain.

The ³¹P spectrum of III at room temperature consists of an overlapping doublet of septets for the trivalent P atom arising from spin coupling with the two CF₃ groups and with the pentavalent P. At the same temperature the spectrum of the pentavalent P atom consists of a triplet of doublets arising from $^1J_{PF}$ and $^2J_{PP}$ coupling. The spectra of some samples at room temperatures showed additional fine structure in the trivalent P region which may be due to a small coupling with F on pentavalent P but the observation was not reproducible.

The ³¹P spectrum of the pentavalent phosphorus atom of III did not show any coupling to CF₃ on trivalent P and, further, remained unchanged as the temperature was lowered. Thus it must be small and unresolvable rather than obliterated by exchange processes. The fine structure which was observed occasionally in the trivalent P spectrum at room temperatures was always observed at low temperatures as asymmetric "triplets" and is presumably due to the long-range $^3J_{PF}$ coupling to F atoms which are in general not equivalent to each other. It is not clear why this coupling was not observed in the ¹⁹F spectrum of F on pentavalent P but it may have been obscured as a result of overlap of lines arising from $^3J_{PF}$ and $^5J_{FF}$ with loss of the outermost weak lines of the multiplet in the background noise. Except for the differences in temperature required for the resolution of $^3J_{PF}$ in the ³¹P spectra obtained on different samples, the spectra of III were fairly reproducible and did not show excessively marked dependence on temperature. The phosphorus-phosphorus coupling constant $^2J_{PP}$ was observed at all temperatures and the observed magnitude of this coupling was unaffected by temperature.

The ¹⁹F nmr spectra of IV at room temperature showed no couplings other than $^1J_{FP}$ and $^2J_{FP}$ in most samples although occasionally some samples also showed a splitting which could be assigned to $^3J_{FP}$. Cooling all samples gave rise to the expected $^3J_{FP}$ coupling pattern with a separation of about 18 Hz but the temperature at which this coupling was resolved varied markedly from one sample to another. In no case was $^4J_{FP}$, the coupling of the CF₃ groups on pentavalent P with the distant trivalent P atom, nor the long-

range $^5J_{FF}$ coupling observed in the ¹⁹F spectra of IV. All ¹⁹F spectral regions were however rather broad at low temperatures and the couplings may not have been resolved.

Most samples of IV did not show the $^2J_{PP}$ couplings in the ³¹P spectra until the temperature was lowered although in one sample (Figure 1) this interaction was observed at room temperature and in this case the temperature was only slightly below that required for coalescence. The ³¹P spectra at -40° in this case consist of a doublet of septets of triplets for pentavalent P due to $^2J_{PF}$, $^2J_{PP}$, and $^3J_{PF}$. The spectral region assigned to trivalent P shows a triplet of doublets of septets due to $^1J_{PF}$, $^2J_{PP}$, and $^4J_{PF}$. Samples of different concentrations showed different coalescence temperatures suggesting an intermolecular exchange process. The ³¹P spectrum of a 29 mol % solution of IV in CF₂Cl₂ did not show $^2J_{PP}$ or $^3J_{PF}$ at +40° in the pentavalent P region although the trivalent region is just below the coalescence temperature for $^2J_{PP}$ at this temperature. (The origin of the different coalescence temperatures is discussed in greater detail below.) Cooling this sample to 20° caused $^3J_{FP}$ and $^2J_{PP}$ to appear in the pentavalent P region but the trivalent region did not show $^4J_{FP}$. All couplings including $^4J_{FP}$ were well resolved on this sample at -40°. A 1 mol % sample in CF₂Cl₂ from the same preparation of IV displayed all of these couplings at +40° although they were not particularly well resolved at this temperature. Good resolution of all couplings was obtained, however, at 20° for this sample. This behavior supports the postulate of an intermolecular mechanism since a higher concentration is expected to yield a higher exchange rate and hence a more poorly resolved spectrum. A similar study on III did not show pronounced concentration dependence but, as noted previously, the ³¹P spectra of this compound are not markedly influenced by the temperature.

Some difficulty with the interpretation arises as a result of some nonreproducible spectral behavior. In one instance, for example, a sample of intermediate composition to those mentioned above which showed all couplings ($^1J_{PF}$, $^2J_{PP}$, and $^4J_{PF}$) in the trivalent region of the spectrum at room temperature did not show $^4J_{PF}$ when reinvestigated 24 hr later although the sample had been kept at liquid nitrogen temperatures between measurements. Since IV is the least stable of the two new compounds (*vide infra*), it is possible that the apparent exchange is catalyzed by impurities arising from decomposition of the compound and is not directly dependent on the concentration of the compound.

tion of the CF_3 fluorines and the phosphorus can be ignored and the trivalent P spectrum viewed approximately as arising from the two possible spin states of the pentavalent P nucleus. Table IIb shows the spin states and the fraction of exchanges leading to them. Thus in a series of exchanges a pentavalent phosphorus atom is coupled to a new $-\text{PF}_2$ group in a different spin state (and hence gives rise to a different spectral line) in seven of eight exchanges. In contrast a trivalent phosphorus atom is coupled to a group of distinguishable pentavalent $(\text{CF}_3)_2\text{P}$ spin states in four out of eight exchanges. The pentavalent phosphorus atom therefore appears to have a faster chemical exchange rate than the trivalent one and therefore a greater apparent reduction in rate is necessary to achieve the same spectral resolution of the P-P coupling.

To demonstrate the feasibility of the above postulate, eq 3, derived from the modified Bloch equations,¹² was used to calculate the theoretical line shapes for the two phosphorus nuclei at various exchange rates. The spectral intensity $I(\omega)$ at frequency ω is given by

$$I(\omega) = \text{Im} - i\vec{f}(\mathbf{D} - i\Delta\omega)^{-1} \cdot \vec{1} \quad (3)$$

where

$$D_{ij} = \begin{cases} \frac{1}{\tau_i} - \frac{1}{T_{2i}} & \text{if } i = j \\ P_{ij}/\tau_i & \text{if } i \neq j \end{cases}$$

$$\Delta\omega_{ij} = \begin{cases} \omega_{0i} - \omega & \text{if } i = j \\ 0 & \text{if } i \neq j \end{cases}$$

and

$$1/\tau_i = (1 - f_i)k$$

where ω_{0i} is the frequency of the i th line in the absence of exchange, T_{2i} is the transverse relaxation time, P_{ij} is the probability of exchange from state i to state j , and k is the rate constant for exchange in sec^{-1} .

Figure 2 shows the results of these calculations at various rates of exchange k . It can be seen that at a rate of 250 sec^{-1} the trivalent P shows more resolution than pentavalent P although the difference is not quite as great as was observed (see Figure 1). Clearly the pentavalent and trivalent regions of the spectra show different resolutions at the same exchange rate thus accounting for the difference in observed coalescence temperatures. Further detailed analysis was not pursued because the actual spectra, containing additional small coupling constants, are much more complex than the computational model employed. Inclusion of these coupling constants increases the complexity of the line shapes making them more difficult to compare with the experimental spectra. Furthermore, however, the value of such extensive and detailed quantitative analysis of the exchange process is dubious in view of the lack of completely reproducible spectral behavior which suggested that the process may well be catalyzed by impurities. The model proposed does however clarify the origin of apparent rate differences observed in the temperature-dependent spectra of these mixed-valent species.

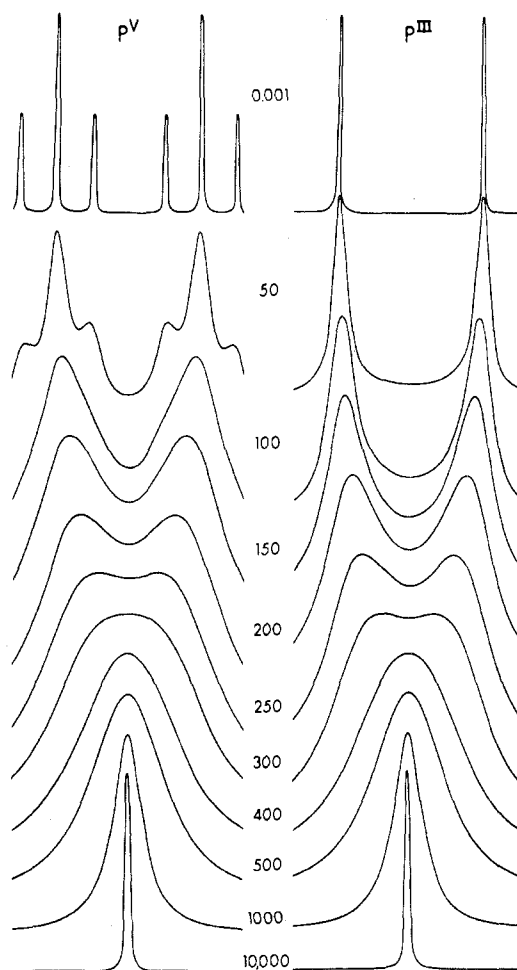
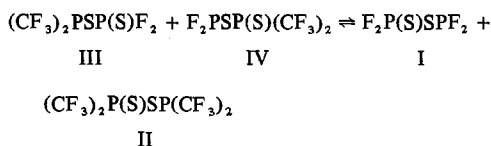


Figure 2. Theoretical line shapes of the ^{31}P nmr spectra of $(\text{CF}_3)_2\text{-P(S)SPF}_2$ at exchange rates varying from 0.001 to $10,000 \text{ sec}^{-1}$. The trivalent phosphorus spectrum on the right represents the central portion of the triplet and shows only the coupling to the pentavalent phosphorus. The pentavalent phosphorus spectrum on the left illustrates the central line of the septet structure split by coupling to the pentavalent phosphorus and the two remote fluorine atoms.

D. Intermolecular Exchange Phenomena and Thermal Stability. Since the concentration-dependent nmr studies suggested that intermolecular processes were important, we investigated the possibility of exchange of trivalent P and pentavalent P fragments with unique substituents.

Mixing III and IV in CFCl_3 solution resulted in a visible reaction with initial formation of a white solid which quickly dissolved on shaking. Immediate analysis of the mixture by ^{19}F nmr spectroscopy showed the presence of all four mixed-valence compounds I-IV. Assignments and normalized integrated proportions are given in Table III. Low-temperature spectra of the mixture resulted in resolution of long-range coupling not observed at room temperature which served to confirm the assignments. A small change in relative proportions of the species was also observed.

From normalized integrated intensities the equilibrium constant for the reaction



(12) C. S. Johnson Jr., *Advan. Magn. Resonance*, 1, 33 (1965). We are indebted to Dr. R. E. D. McClung of this department for assistance with the calculations and helpful discussion.

Table III. Chemical Exchange of Mixed-Valence Compounds

	ϕ , ^a ppm	J_{FP} , ^a Hz	III + IV at room temp		III + IV at -80°		I + II at room temp	
			Integral	Normalized integral ^b	Integral	Normalized integral ^b	Integral	Normalized integral ^b
I(tri)	60.8	1324	40 ^c	23	144	144	40 ^c	25
I(penta)	14.4	1210	27	27	123	123	19	19
II(tri)	53.8	81.3	75	25	480	160	28	9
II(penta)	68.7	111.7	80	27	440	147	27	9
III(tri)	55.0	79	75	25	350	117	39	13
III(penta)	17.9	1225	27	27	115	115	16	16
IV(tri)	61.2	1331	40 ^c	17	78	78	40 ^c	15
IV(penta)	71.2	113	60	20	250	83	32	11
<i>K</i>			1.6 ± 0.7		2.1 ± 0.7		1.1 ± 0.7	

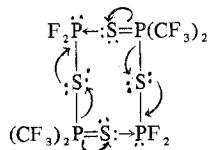
^a ϕ and J from pure room-temperature samples; ¹ J_{FP} for directly bound fluorine and ² J_{FP} for trifluoromethyl groups bound to phosphorus. ^b Integrals normalized to two fluorines per phosphorus. ^c Peaks overlap. Intensities were obtained from ratios of other end of the molecule.

was obtained, *i.e.*

$$K = \frac{[\text{I}][\text{II}]}{[\text{III}][\text{IV}]} = 1.6 \pm 0.7 (40^\circ), 2.1 \pm 0.7 (-80^\circ)$$

The reaction (as written) is exothermic by no more than 500 cal but, considering the accuracy of K , is probably more nearly thermoneutral. The reverse reaction was demonstrated by mixing equal proportions of I and II which equilibrated at room temperature to give a K (as defined above) of 1.1 at 40°. The data are included in Table III. This labile equilibration is notable in that it does not involve a change in the valence state of the phosphorus atom associated with a particular substituent. Since the nmr spectra indicate a similar preservation of the identity of the substituents on and the valence of a particular phosphorus atom, we suggest that the same exchange mechanism proposed above for the nmr behavior will account for this chemical exchange.

The compounds have different thermal stability with those containing trifluoromethylphosphino groups being the most stable. Thus II is thermally stable³ and III suffered negligible decomposition upon heating to 200° for prolonged periods. In contrast IV deposited a white solid even at room temperature. Nmr analysis of the products of decomposition of IV at 70° showed a mixture of II, III, IV, and PF₃. Compound I may also have been present and escaped detection because of its low concentration and small fluorine content, but it is more likely that it decomposes to PF₃¹ under the conditions employed. Since the substituents are interchanged in this "redox" rearrangement, the process involved cannot be the same as that proposed for the nmr exchange (*vide supra*). Starting from the same bimolecular intermediate as proposed above, however, an alternate rearrangement can be proposed which results in apparent interchange of substituents on phosphorus

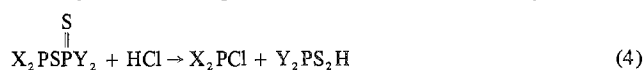


This process appears to be a much slower one than the nmr exchange process and it only appears to be important in compounds containing difluorophosphino groups which are apparently more easily oxidized than trifluoromethylphosphino groups.

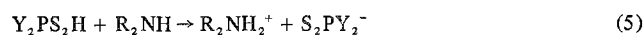
E. Chemical Reactions. Reaction of these mixed-valence compounds with protic species, HZ,^{1,2,4} appears to proceed generally with cleavage of the trivalent P-S bond to form trivalent phosphines, R₂PZ, and dithiophosphinic acids or

their salts (eq 2). The products, particularly in the case of the difluorophosphino compounds, are however greatly influenced by the stability of the phosphines.

Anhydrous hydrogen chloride reacted according to

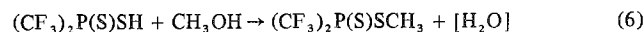


with either (CF₃)₂PCl or F₂PCl being recovered in expected amounts. Dimethylamine behaves similarly yielding stable aminophosphines (CH₃)₂NPF₂ or (CH₃)₂NP(CF₃)₂ (eq 2) plus the dimethylammonium salt of the appropriate acid expected from



Methyl mercaptan appears to react in a similar fashion since III gave (CF₃)₂PSCH₃¹³ and F₂P(S)SH⁶ and IV gave (CF₃)₂-PS₂H^{7,14}, PF₃, and a bright yellow solid. The mercaptophosphine, F₂PSCH₃,¹⁵ expected from the reaction of IV and methyl mercaptan was not observed, since it is not very stable¹⁵ and probably decomposes under the present reaction conditions. Similar behavior was observed with I.¹

Methanol reacts with III forming a very complex mixture of products, the main constituents of which were (CF₃)₂-PSH¹³ and (CF₃)₂POCH₃¹⁶ in the ratio 4:3 plus a mixture of eight of ten products in which only F₂PS₂H could be identified with certainty. The isomer IV reacted with methanol to form only (CF₃)₂P(S)SCH₃,¹⁴ PF₃, and a small amount of unidentified involatile material. We can reasonably suggest that the initial step is a trivalent P-S cleavage by methanol according to eq 4 to give (CF₃)₂P(S)SH and F₂POCH₃¹⁷ followed by reaction of the acid with methanol to give (CF₃)₂P(S)SCH₃, also demonstrated by a separate experiment



Since F₂POCH₃ is known and relatively stable¹⁷ and since H₂O was not observed in the reaction products, we may speculate that limited hydrolysis of F₂POCH₃, perhaps through such intermediates as OPF₂H,^{18,19} leads eventually to PF₃.

(13) (a) A. B. Burg and K. Gosling, *J. Amer. Chem. Soc.*, **87**, 2113 (1965); (b) R. G. Cavell and H. J. Emeleus, *J. Chem. Soc.*, 5825 (1964).

(14) K. Gosling and A. B. Burg, *J. Amer. Chem. Soc.*, **90**, 2011 (1968).

(15) R. Foester and K. Cohn, *Inorg. Chem.*, **11**, 2590 (1972).

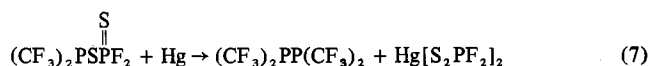
(16) A. B. Burg and I. B. Mishra, *Inorg. Chem.*, **8**, 1199 (1969).

(17) E. L. Lines and R. L. Centofanti, *Inorg. Chem.*, **12**, 2111 (1973).

(18) T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, **6**, 2204 (1967).

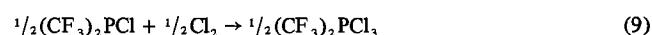
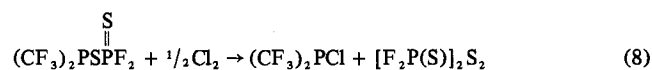
(19) L. F. Centofanti and R. W. Parry, *Inorg. Chem.*, **9**, 744 (1970).

Both compounds react with metallic mercury to yield dithiophosphinates.²⁰ The reaction of III is straightforward proceeding nonquantitatively but according to



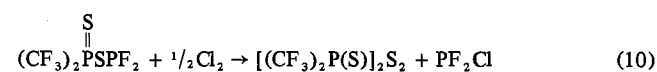
The reaction of IV is more complex; the solid products contained both $\text{Hg}[\text{S}_2\text{P}(\text{CF}_3)_2]_2$ and $\text{Hg}[\text{S}_2\text{PF}_2]_2$ and the latter occurs in a substantial majority. Also found was a relatively large amount of $[(\text{CF}_3)_2\text{P}]_2\text{S}$ and an approximate 3% yield of the diphosphine, $(\text{CF}_3)_4\text{P}_2$. The diphosphine F_2PPF_2 was not found, probably on account of its instability,²¹ but only a small fraction of PF_2 product appeared as PF_3 (the volatile decomposition product of F_2PPF_2 ²¹).

Chlorine reacts vigorously with III and IV with cleavage of the trivalent P-S bond followed in some cases by oxidation of the resultant trivalent phosphorus compounds to pentavalent phosphorus species. Compound III yields $(\text{CF}_3)_2\text{PCl}$, $(\text{CF}_3)_2\text{PCl}_3$, and a species which is probably $(\text{SPF}_2)_2\text{S}_2$.²² The stoichiometry agrees with the sum of eq 8 and 9. Small amounts of SPF_2Cl were also found and



are probably due to reaction of Cl_2 (or Cl radicals) with the $[\text{F}_2\text{P}(\text{S})]_2\text{S}_2$ product although other sources cannot be entirely excluded.

The isomer IV reacts with Cl_2 to give $[(\text{CF}_3)_2\text{P}(\text{S})]_2\text{S}_2$ ³ and F_2PCl as major products indicating a similar cleavage of trivalent P-S to form F_2PCl and $(\text{CF}_3)_2\text{PS}_2$ radicals (or perhaps $(\text{CF}_3)_2\text{P}(\text{S})\text{Cl}$) which couple to form the tetrasulfide



Most of the $(\text{CF}_3)_2\text{P}(\text{S})\text{Cl}$ probably arises from subsequent reaction of the tetrasulfide with excess Cl_2 and these three products account for the major proportion of the volatile products. In addition, SPF_2Cl (4 mol %) was also found along with trace amounts of $(\text{CF}_3)_2\text{PCl}_3$, $(\text{CF}_3)_2\text{PCl}$, and PF_3Cl_2 .

Experimental Section

Materials, Apparatus, and Techniques. All manipulations were carried out using standard vacuum techniques in a system constructed with Pyrex glass with stopcocks lubricated with Apiezon N grease. Involatile materials which remained in the reaction vessels were handled in a nitrogen atmosphere while aqueous solutions were handled in the air since it had been found by experience that such products were invariably air stable.

Instrumental Techniques. Infrared spectra of gases were obtained using a 9-cm gas cell with potassium bromide windows. All spectra were recorded with a Perkin-Elmer 457 spectrophotometer. Mass spectra were recorded with an AEI MS-9 spectrometer operating at an ionizing voltage of 70 eV. Samples were introduced as gases using a heated inlet, as low volatile liquids in a heated capillary, or as solids using a direct probe. All nmr spectra were recorded with either a Varian A56/60, a Varian HA 100, or a Bruker HFX-90 spectrometer. Proton spectra were recorded at 60.0 MHz and fluorine spectra at 56.4 MHz using the A56/60 instrument. In the case of the HA 100 instrument, proton spectra were recorded at 100 MHz and fluorine spectra at 94.1 MHz while for the Bruker instrument

the proton spectra were recorded at 90 MHz and the fluorine spectra at 84.67 MHz. Phosphorus spectra were obtained with the Bruker instrument operating at 36.4 MHz utilizing a heteronuclear fluorine lock. Proton, fluorine, and phosphorus spectra were routinely recorded on samples containing an approximate 10% solution of the compound in CFCl_3 or CF_2Cl_2 . Samples were prepared under vacuum by distilling the compound and the solvent into a glass tube of appropriate dimensions and sealing the tube under vacuum. Nmr spectra of involatile materials were obtained on solutions in CD_3CN or H_2O . Fluorine chemical shifts were measured relative to internal CFCl_3 solvent. In cases where other solvents were employed an external CCl_3F (capillary) reference was used. Proton chemical shifts were measured relative to external tetramethylsilane (TMS) as a 5% solution in CCl_3F in all cases. Phosphorus chemical shifts were measured relative to an external capillary of P_4O_6 ²³ in all cases. Each instrument was equipped with a variable-temperature controller which was established as accurate to within $\pm 5^\circ$ of the temperature indicated on the controller by calibration.

Materials. Commercially available chemicals of "reagent" grade were used without further purification. Gaseous reagents were usually fractionated before use to remove any moisture or gross impurities.

Trifluoromethylidodiphosphines were prepared from the reaction of CF_3I (Columbia Organic Chemical Co.) with red phosphorus at 220° for 48 hr.²⁴ $(\text{CF}_3)_2\text{PCl}$ ²⁴ was obtained from $(\text{CF}_3)_2\text{PI}$ and mercuric chloride,²⁵ and $(\text{CF}_3)_2\text{PN}(\text{CH}_3)_2$ from $(\text{CF}_3)_2\text{PCl}$ and dimethylamine.²⁶ The acid $(\text{CF}_3)_2\text{PS}_2\text{H}$ ⁷ was prepared as described elsewhere.³ $\text{F}_2\text{PN}(\text{CH}_3)_2$ was obtained from either PF_3 and dimethylamine²⁷ or the method described by Schmutzler.²⁸

Preparation of Difluorodithiophosphinic Acid. A convenient alternate method of preparing $\text{F}_2\text{P}(\text{S})\text{SH}$ ⁶ was employed. SPF_2Cl (0.423 g, 3.10 mmol),⁸ H_2S (0.014 g, 3.12 mmol), and $(\text{CH}_3)_3\text{N}$ (0.368 g, 6.24 mmol) were combined in a sealed tube. Immediate reaction ensued on warming to room temperature. After 12 hr the solid product was transferred to a round-bottom flask. Addition of concentrated H_2SO_4 under vacuum liberated SPF_2SH (0.322 g, 2.40 mmol) contaminated with a trace of SiF_4 and HCl (0.115 g, 3.15 mmol) containing a small amount of SPF_2SH .

Preparation of $(\text{CF}_3)_2\text{PSP}(\text{S})\text{F}_2$ (III). Difluorothiophosphoryl- μ -thio-bis(trifluoromethyl)phosphine was prepared in almost quantitative yield from the reaction of stoichiometric amounts of SPF_2SH ⁶ and $(\text{CF}_3)_2\text{PN}(\text{CH}_3)_2$.^{10,26} In a typical reaction 3.429 g (25.6 mmol) of SPF_2SH and 2.630 g (12.35 mmol) of $(\text{CF}_3)_2\text{PN}(\text{CH}_3)_2$ reacted instantaneously at room temperature in a sealed tube to produce 3.677 g (12.2 mmol; 98.7% yield) of pure $(\text{CF}_3)_2\text{PSP}(\text{S})\text{F}_2$, which was trapped at -63° . A mixture of III and SPF_2SH (0.160 g) passed through this trap and an undetermined amount of solid identified as $\text{F}_2\text{PS}_2^-(\text{CH}_3)_2\text{NH}_2^+$ by nmr spectroscopy²⁹ remained in the reaction tube.

Reactions of III. (1) Alkaline Hydrolysis. Compound III (0.1562 g; 0.518 mmol) was shaken with a large excess of 10% aqueous NaOH for 3 hr at room temperature. The only volatile product was fluoroform (0.0751 g; 1.073 mmol) identified by infrared spectroscopy.

(2) Reaction with Anhydrous Hydrogen Chloride. Compound III (0.472 g, 1.56 mmol) was treated in a sealed tube for 10 days at room temperature with 0.105 g (2.88 mmol) of anhydrous HCl . Separation of the volatile products gave a mixture of SPF_2SH ⁶ (0.268 g) and III (trapped at -96°). The fraction collected at -130° contained 0.248 g (1.21 mmol) of $(\text{CF}_3)_2\text{PCl}$ ^{10,24} contaminated with a trace of III, and at -196° 0.0602 g (1.65 mmol) of HCl containing a trace of SiF_4 and $(\text{CF}_3)_2\text{PCl}$ was found.

(3) Reaction with Dimethylamine. To 0.1602 g (0.53 mmol) of III was added 0.0548 g (1.22 mmol) of anhydrous dimethylamine. An immediate reaction ensued with formation of a white solid material. After 2 days at room temperature the only volatile product obtained was $(\text{CF}_3)_2\text{PN}(\text{CH}_3)_2$ ^{10,26} (0.100 g, 0.47 mmol). The white solid residue was found by nmr spectroscopy²⁹ to be $(\text{CH}_3)_2\text{NH}_2^+\text{S}_2\text{PF}_2^-$.

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(4) **Thermal Behavior.** Compound III (0.1608 g, 0.532 mmol) was heated at 200° for 3 days in a sealed tube. The volatile material (0.1594 g, 0.528 mmol based on III) was found to be almost pure III contaminated with less than 1% of an unidentified contaminant (by nmr). A small amount of an unidentified crystalline solid (1.4 mg) remained in the reaction tube.

(5) **Reaction with Methyl Mercaptan.** Compound III (0.282 g, 0.93 mmol) was sealed in a glass tube with CH₃SH (0.0504 g, 1.05 mmol) and allowed to react overnight at room temperature. The volatile products were separated and identified as CH₃SH (0.0034 g, 0.07 mmol) plus an unseparated mixture of SPF₂SH⁶ and (CF₃)₂-PSCCH₃^{13b} (0.3266 g). The nmr spectrum indicated that the latter two products were present in the approximate molar ratio 1:1.

(6) **Reaction with Mercury.** The reaction of III (0.211 g, 0.70 mmol) with excess mercury (0.0620 g; 0.31 mmol) for 7 days at room temperature with shaking resulted in the formation of an approximate 10% yield of (CF₃)₂PP(CF₃)₂ which was identified in the volatile fraction by nmr spectroscopy^{30,31} and Hg(S₂PF₂)₂³² which was identified by its mass spectrum and mass measurement of the molecular ion (*m/e*: found, 467.8002; calcd for F₄P₂³²S₄²⁰²Hg, 467.8002).

(7) **Reaction with Anhydrous Methanol.** Methanol, dried over sodium methoxide (0.0254 g, 0.794 mmol), was allowed to react with III. A complex mixture of products resulted. The major trifluoromethyl-containing components were (CF₃)₂PSH^{13b} and (CF₃)₂-POCH₃¹⁶ in the approximate molar ratio 4:3 by nmr spectroscopy. A small amount of SPF₂SH was also observed along with eight or ten other compounds (by nmr) in smaller amounts which could not be identified. No further studies were undertaken.

(8) **Reaction with Chlorine.** Chlorine gas (0.0466 g, 0.657 mmol) was allowed to react with III (0.1970 g, 0.653 mmol) in a sealed tube at room temperature. A complex mixture of products was obtained which was not separated since all species but one could be readily identified by nmr spectroscopy. The volatile products were found to be unreacted III (1%), (CF₃)₂PCl^{10,24} (25%), (CF₃)₂-PCl₃³³ (27.5%), SPF₂Cl⁹ (1.5%), and a species which is best formulated as (SPF₂)₂S₂ (45%). This latter species may be one of the related polysulfides (SPF₂)₂S_x (*x* > 2) since nmr parameters are very similar for the *x* > 2 series;²² however it is clear that *x* ≠ 1.

Preparation of F₂PSP(S)(CF₃)₂ (IV). The compound was prepared from the reaction of stoichiometric amounts of (CF₃)₂PS₂H⁷ and PF₂N(CH₃)₂^{27,28}. In a typical reaction 2.63 g (11.24 mmol) of (CF₃)₂PS₂H was combined with 0.64 g (5.63 mmol) of PF₂N(CH₃)₂ to yield 0.681 g (2.26 mmol) of pure IV and an undetermined amount of solid (CF₃)₂PS₂(CH₃)₂NH₃⁺ which was identified by nmr spectroscopy.⁵ The product was best purified by passage through a series of traps held at -45, -84, and -196° followed by vacuum distillation of the -84° fraction in a low-temperature micro reflux still³⁴ maintained at -63°. The separation process is rather inefficient and yield of pure material is low.

Reactions of IV. (1) Alkaline Hydrolysis. To an excess of 10% NaOH was added 0.352 g (1.16 mmol) of IV. After overnight reaction at room temperature the only volatile product was fluoroform (0.0846 g, 1.21 mmol).

(2) **Reaction with Anhydrous Hydrogen Chloride.** Compound IV (0.241 g, 0.80 mmol) was combined in a sealed tube with HCl (0.0305 g, 0.84 mmol) and allowed to react for 6 days at room temperature. Separation of the volatile products gave (CF₃)₂PS₂H (0.176 g, 0.76 mmol) and PF₂Cl⁸ contaminated with a trace of PF₃ (0.0781 g, 0.75 mmol). A small amount of unidentified product (15 mg) was also obtained.

(3) **Reaction with Anhydrous Dimethylamine.** To IV (0.232 g, 0.77 mmol) was added (CH₃)₂NH (0.071 g, 1.57 mmol). There was an immediate reaction on warming the tube to room temperature with formation of a white solid. The volatile products were identified as PF₂N(CH₃)₂^{27,28} (0.068 g, 0.603 mmol) and PF₃ (0.008 g, 0.096 mmol). The residual white solid was identified by nmr spectroscopy⁵ as (CF₃)₂PS₂(CH₃)₂⁺ (0.211 g, 0.76 mmol).

(4) **Thermal Behavior.** Compound IV (0.204 g, 0.68 mmol) was heated in a sealed tube for 24 hr at 70° and then for 2 hr at

100°. Fractional distillation of the volatile products yielded PF₃ (0.014 g, 0.16 mmol) and a mixture (0.169 g) analyzed by ¹⁹F nmr as II (38%), III (51%), and IV (11%). Compound I was not observed in the nmr spectrum perhaps as a result of low intensity due to low concentration plus its small F content, however it is also likely to be unstable under the above conditions.¹ An unidentified intractable white solid residue (0.021 g by difference) remained in the reaction tube.

(5) **Reaction with Methyl Mercaptan.** Methyl mercaptan (0.0342 g, 0.713 mmol) was combined with IV (0.202 g, 0.67 mmol) in a sealed tube and allowed to react at room temperature. After 30 min an unidentified bright yellow solid was formed. Separation of the volatile products after 1 day of reaction gave (CF₃)₂PS₂H (0.144 g, 0.614 mmol), (CF₃)₂PSH^{13b} (0.006 g, 0.03 mmol), and PF₃ (0.0426 g, 0.483 mmol).

(6) **Reaction with Mercury.** Triple-distilled mercury (0.107 g, 0.535 mmol) was combined with IV (0.365 g, 1.21 mmol) and shaken at room temperature for several days. The volatile products were (CF₃)₄P₂S^{13b} containing about 3 mol % (CF₃)₄P₂^{30,31} impurity according to the nmr spectrum (0.213 g, ~0.6 mmol) and PF₃ (0.0253 g, 0.288 mmol). A yellow solid residue in the reaction tube was found to contain some Hg[S₂P(CF₃)₂]₂²⁰ (*m/e*: found, 667.7861; calcd for C₄F₁₂P₂³²S₄²⁰²Hg, 667.7877) contaminant in Hg[S₂PF₂]₂³² (*m/e*: found, 467.7989; calcd for F₄P₂³²S₄²⁰²Hg, 467.8002) by mass spectroscopy.

(7) **Reaction with Anhydrous Methanol.** Compound IV (0.225 g, 0.745 mmol) and CH₃OH (0.0245 g, 0.765 mmol) were combined in a sealed tube. After 6 days of reaction at room temperature, the volatile products were identified as (CF₃)₂PS₂CH₃³⁰ (0.156 g, 0.63 mmol), a 6:1 mixture of (CF₃)₂PS₂CH₃ and (CF₃)₂PS₂H (0.045 g) (determined by nmr spectroscopy), and PF₃ (0.032 g, 0.366 mmol). An unidentified solid residue remained in the reaction tube.

(8) **Reaction with Chlorine.** To 0.253 g (0.87 mmol) of IV was added 0.0516 g (0.73 mmol) of Cl₂. This was allowed to react 24 hr at room temperature. No attempt was made to separate the product mixture but the entire volatile fraction was shown by ¹⁹F nmr spectroscopy (mol % given in parentheses) to contain (CF₃)₂P(S)SSP(S)(CF₃)₂³ (28%), (CF₃)₂P(S)Cl⁷ (15%), (CF₃)₂PCl¹⁰ (trace), (CF₃)₂PCl₃¹⁰ (trace), PF₂Cl⁸ (52%), SPF₂Cl⁹ (4%), and PF₃Cl₂⁸ (trace). No solid residues remained in the reaction vessel.

Reaction of (CF₃)₂P(S)SP(CF₃)₂ (II) with Dimethylamine. Anhydrous dimethylamine (0.0573 g, 1.273 mmol) was combined with II (0.2558 g, 0.636 mmol) in a sealed tube and allowed to warm to room temperature. Immediate reaction ensued with formation of a white solid identified by nmr spectroscopy as (CH₃)₂NH₂⁺(CF₃)₂-PS₂⁻ (0.1687 g, 0.605 mmol).⁵ The only volatile product was (CF₃)₂-PN(CH₃)₂¹⁰ (0.134 g, 0.629 mmol).

Reactions of F₂P(S)SPF₂¹ (I). (1) **Reaction with Anhydrous Dimethylamine.** Compound I (0.206 g, 1.02 mmol) and dimethylamine (0.092 g, 2.04 mmol) were combined and allowed to warm to room temperature. A white solid identified as (CH₃)₂NH₂⁺F₂PS₂⁻ (0.1825 g, 1.02 mmol)²⁹ was formed immediately. The volatile products were F₂P(S)N(CH₃)₂³⁵ (0.002 g, 0.01 mmol), PF₃ (0.003 g, 0.04 mmol), and F₂PN(CH₃)₂²⁷ (0.103 g, 0.91 mmol).

(2) **Reaction with Anhydrous Methanol.** Compound I (0.163 g, 0.81 mmol) and methanol (0.0256 g, 0.80 mmol) dried over sodium methoxide were allowed to react at room temperature for 4 hr. The volatile products (0.170 g) were determined by ¹⁹F nmr spectroscopy to be SPF₂SCH₃³⁶ (73%), PF₃ (20%), and SPF₂SH (6%). A small amount of an involatile clear liquid (0.0186 g by difference) which changed to a light yellow solid remained in the reaction tube and was not identified.

(3) **Reaction with Chlorine.** Chlorine (0.0482 g, 0.68 mmol) and I (0.1353 g, 0.67 mmol) were allowed to react 15 hr at room temperature. The volatile products were found by ¹⁹F nmr spectroscopy to be F₂P(S)SSP(S)F₂²² (37%) and F₂PCl⁸ (63%). A small amount of involatile liquid which remained in the reaction tube was not identified.

(4) **Reaction with Methyl Mercaptan.** Methyl mercaptan (0.0266 g, 0.55 mmol) and I (0.1143 g, 0.57 mmol) reacted over 2 hr at room temperature to form an unidentified yellow solid, SPF₂-SH (0.0428 g, 0.32 mmol), and PF₃ (0.0434 g, 0.49 mmol).

Reaction of (CF₃)₂PS₂H with CH₃OH. Sodium-dried methanol (0.085 g, 2.65 mmol) and (CF₃)₂PS₂H¹³ (0.574 g, 2.45 mmol) were combined in a sealed tube and allowed to react overnight. Separation of the volatile products gave pure (CF₃)₂P(S)SCH₃^{13b,30} (0.538

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g, 2.16 mmol) plus a mixture (0.090 g) of $(CF_3)_2P(S)SCH_3$ contaminated with unreacted $(CF_3)_2PS_2H$.

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Registry No. H_2S , 7783-06-4; SPF_2Cl , 2524-02-9; SPF_2SH , 20773-09-5; $(CF_3)_2PN(CH_3)_2$, 432-01-9; $(CF_3)_2PSP(S)F_2$, 52226-01-4; $(CF_3)_2PS_2H$, 18799-75-2; $PF_2N(CH_3)_2$, 814-97-1; $F_2PSP(S)(CF_3)_2$, 52226-02-5; $(CF_3)_2P(S)SP(CF_3)_2$, 23526-69-4; $F_2P(S)SPF_2$, 23526-68-3; HCl , 7647-01-0; $(CH_3)_2NH$, 124-40-3; CH_3SH , 74-93-1; Hg , 7439-97-6; CH_3OH , 67-56-1; Cl_2 , 7782-50-5.

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Spectra and Structure of Phosphorus-Boron Compounds. VI.¹ Vibrational Spectra and Structure of Some Phosphine-Trihaloboranes

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The infrared (33–3000 cm^{-1}) and Raman (20–2700 cm^{-1}) spectra of $H_3P\cdot BX_3$ and $D_3P\cdot BX_3$ ($X = F, Br, I$) in the solid state at -196° have been recorded. The spectra have been interpreted on the basis of C_{3v} symmetry and 11 of the 12 fundamental vibrations have been assigned. A shift to higher frequency of the P–H stretching mode as compared to the corresponding mode in PH_3 is consistent with a shortening of this bond with coordination. A normal-coordinate calculation was carried out and the values obtained for the P–B force constants for this series of molecules are compared to the similar quantities of several other phosphorus-boron molecules. The observation of four lattice modes in solid $H_3P\cdot BF_3$ and $D_3P\cdot BF_3$ indicates that there are at least two molecules per primitive cell which give rise to in-phase and out-of-phase components of the P–B stretch.

Introduction

Investigations of phosphine-borane molecular adducts have demonstrated that the commonly accepted correlation between bond length and dissociative stability does not seem to hold for this class of compounds. For example, in trifluorophosphine-borane,³ the P–B bond distance was found to be 1.836 ± 0.012 Å, whereas the distance for the same bond in trimethyl- and methylphosphine-borane⁴ was found to be 1.901 ± 0.007 and 1.906 ± 0.006 Å, respectively. Therefore, one would expect in terms of bond length that the fluorophosphine-boranes would be more stable whereas, in fact, just the opposite has been observed; the $F_3P\cdot BH_3$ molecule is completely dissociated at 0° , while the methylphosphine-boranes are stable to much higher temperatures.

In order to provide additional information on the P–B bonding, the microwave spectrum of phosphine-borane⁵ has been successfully studied, and a corresponding study of phosphine-trichloroborane was attempted but was unsuccessful because the compound was found to be completely dissociated in the gas phase.⁶ However, phosphine-trichloroborane was studied by vibrational and nuclear magnetic resonance spectroscopy⁶ and a normal-coordinate analysis has also been carried out. In order to complete our studies of the series of phosphine-trichloroboranes and to provide more

data on P–B bonds, the infrared and Raman spectra of phosphine-trifluoro-, -tribromo-, and -triiodoborane and the corresponding deuterated species were recorded. In addition, the 1H and ^{11}B nmr spectra of phosphine-tribromoborane were obtained. The results of this investigation and a normal-coordinate analysis for these molecules are reported herein.

Experimental Section

With the exception of phosphine and phosphine-triiodoborane, all preparations and purifications were carried out in a standard high-vacuum system employing greaseless stopcocks.⁷ Boron trifluoride was obtained commercially (Matheson) and purified by vacuum fractionation until it exhibited a vapor pressure of 301 mm⁷ at -112° (carbon disulfide-liquid nitrogen slush). Boron tribromide was obtained commercially (Columbia Organic Chemicals) and purified by vacuum fractionation until it exhibited a vapor pressure of 19 mm⁷ in a 0° bath. Boron triiodide was obtained commercially (Alfa Inorganics) and purified by vacuum sublimation until all traces of pink color (iodine) had been removed. Phosphine was prepared under a stream of gaseous nitrogen in a fume hood as described in the literature.⁸ Phosphine- d_3 was prepared in a similar manner using D_2O and D_2SO_4 . All phosphine species were purified by passing them through a -131° bath ($n-C_4H_{10}$ slush) into a -196° bath. Purity was monitored by vapor pressure measurements⁷ and infrared spectra.⁹ Phosphine-trifluoroborane^{10,11} and phosphine-tribromoborane^{9,12} were prepared by condensing equimolar amounts of phosphine and the appropriate boron trihalide into an evacuated tube at liquid nitrogen temperatures. The tube was isolated from the vacuum system

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