anionic phosphate group is responsible for the distortion.

The striking result of the present study is the importance of the polarization of the α-CH bond of a given Schiff base species in determining its reactivity. In species III, the combined polarizing effects of the proton on the phosphate group and the divalent metal ion leads to the high reaction rates. At the other extreme, species V lacks the proton on its phosphate group and, further, the effective charge on Cu(II) is reduced by binding to the hydroxide ion. This leads to a reaction rate which is about 36 times lower than that of III.

Acknowledgment. The authors gratefully acknowledge the support of this research under Grants AM 15707 and AM 21568 from the National Institutes of Health.

Registry No. DL-*O*-phosphoserine, 17885-08-4; glyoxylic acid, 298-12-4; Cu^{2+}, 15158-11-9; D, 16873-17-9; ML_2^{4-}, 67711-55-1; MLA^{2-}, 67711-56-2.

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Mixed-Valence Thiophosphorus Compounds. Fluoro- and (Trifluoromethyl)(thiophosphorylthio)phosphines with Chiral Phosphorus Centers

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Received April 27, 1978

Reactions of the acids $(CF_3)_2PS_2H$ and F_2PS_2H with the fluoro(trifluoromethyl)aminophosphine $CF_3(F)PN(CH_3)_2$ and the reaction of the new acid $F(CF_3)P(S)SH$ with the fluoro- or (trifluoromethyl)aminophosphines $X_2PN(CH_3)_2$ ($X = F$, CF_3) provide new isomeric (thiophosphorylthio)phosphines XYP(S)SPX′Y′ (X, Y, X′, Y′ = F, CF_3) with chiral phosphorus centers. The compounds were characterized chemically and by NMR spectroscopy. Geminal CF_3–CF_3 (9.0 Hz for CF_3 on pentavalent P; 7.2 Hz for CF_3 on trivalent P) and F–F (82.5 Hz for F on pentavalent P; 92.5 Hz for F on trivalent P) coupling constants are revealed in the NMR spectra of the molecules as a result of the presence of the chiral phosphorus centers. Directly bound geminal fluorine atoms on trivalent P show large chemical shift difference between the two fluorine atoms (4.4 ppm) accompanied by substantially different $^1J_{PF}$ coupling constants (1370 and 1291 Hz). Similar but smaller differences prevail between geminal CF_3 substituents. Reaction of the new acid $F(CF_3)P(S)SH$ with $CF_3(F)PN(CH_3)_2$ gave a mixture of (thiophosphorylthio)phosphine isomers each with two chiral phosphorus centers. Only partial assignment of the major features of this spectrum could be made.

Introduction

Studies of the symmetrically substituted mixed-valence (thiophosphorylthio)phosphines $F_2P(S)SPF_2$ (I)[1] and $(CF_3)_2P(S)SP(CF_3)_2$[2] (II) were recently extended[3] to include nonsymmetrically substituted compounds $F_2P(S)SP(CF_3)_2$ (III) and $(CF_3)_2P(S)SPF_2$ (IV). We have now synthesized the new acid $CF_3(F)P(S)SH$ which, when reacted with fluoro(trifluoromethyl)(dimethylamino)phosphine,[4] $F(CF_3)PN(CH_3)_2$, or the related phosphine sulfide[5] $F(CF_3)P(S)N(CH_3)_2$ gave additional mixed-valence compounds with chiral phosphorus centers. The new compounds $F(CF_3)P(S)SP(CF_3)_2$ (V), $F(CF_3)P(S)SPF_2$ (VI), $(CF_3)_2P(S)SP(CF_3)F$ (VII), $F_2P(S)SP(CF_3)F$ (VIII), and $F(CF_3)P(S)SP(CF_3)F$ (IX) described herein allow the determination of geminal F–F and CF_3–CF_3 NMR coupling constants. In addition the existence of two isomers of IX was demonstrated by NMR spectroscopy.

Results and Discussion

A. Synthetic Considerations. The general synthetic route for mixed-valence compounds[1-3] (eq 1) gave good yields of VII and VIII from the appropriate acid and $CF_3(F)PN(CH_3)_2$.

$$2XYP(S)SH + X'Y'PN(CH_3)_2 \rightarrow XYP(S)SPX'Y' + (CH_3)_2NH_2^+XYPS_2^- \quad (1)$$
$$X, Y = F, CF_3$$

The new compounds were characterized by spectroscopy and by alkaline hydrolysis with identification of residual CF_3P ions in the hydrolysate[8] (where possible) and also by means of the reaction of the mixed-valence compound with dimethylamine which gave, without rearrangement of X and Y with X′ and Y′, the aminophosphine and dithiophosphinic acid salt.

$$XYP(S)SPX'Y' + 2(CH_3)_2NH \rightarrow (CH_3)_2NH_2^+XYPS_2^- + X'Y'PN(CH_3)_2 \quad (2)$$
$$X, Y, X', Y' = F, CF_3$$

All syntheses of the acid $CF_3(F)P(S)SH$ yielded a product contaminated with a little $F_2P(S)SH$. Addition of elemental sulfur to $CF_3(F)PN(CH_3)_2$ at elevated temperatures, previously shown to be nonstoichiometric,[5] gave $CF_3(F)P(S)N(CH_3)_2$ and smaller quantities of $CF_3P(S)[N(CH_3)_2]_2$, $CF_3P(S)F_2$, and $F_2P(S)N(CH_3)_2$.[9] These undesirable products may arise from rearrangement reactions of the desired compound at the elevated temperatures required. Separation of $F_2P(S)N(CH_3)_2$[9] from the desired major component $CF_3(F)P(S)N(CH_3)_2$ by conventional vacuum techniques was difficult, and propagation through the synthetic chain (vide infra) to $CF_3(F)PS_2H$ and the mixed-valence compounds gave no improvement in the ease of separation.

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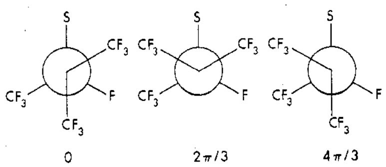


Figure 1. Newman projections of the rotamers of $F(CF_3)P(S)S-P(CF_3)_2$ (V).

Reaction of $CF_3(F)P(S)N(CH_3)_2$ with H_2S produced $(CH_3)_2NH_2{}^+S_2P(CF_3)F^-$, the NMR spectrum of which agreed well with that predicted empirically from the parameters[5,7] of $(CF_3)_2PS_2{}^-$ and $F_2PS_2{}^-$. The solid products contained considerably higher relative amounts of the difluoro acid salt than expected from the initial impurity level of $F_2P(S)-N(CH_3)_2$ suggesting that further disproportionation of $CF_3(F)P(S)N(CH_3)_2$ had occurred during salt formation in contrast to the lack of scrambling in aminolysis reactions. Undoubtedly the higher reaction temperatures involved are responsible. Reaction of these salts with concentrated H_2SO_4 under vacuum easily liberated $F(CF_3)PS_2H$ contaminated with F_2PS_2H. Infrared, mass spectral, and molecular weight analyses, compensating for the F_2PS_2H impurity, were consistent with the formation of the new acid $F(CF_3)PS_2H$, which was readily identified by its NMR spectrum.

Reaction of $CF_3(F)P(S)SH$ with the aminophosphines $(CF_3)_2PN(CH_3)_2$, $F_2PN(CH_3)_2$, and $(CF_3)FPN(CH_3)_2$ gave V, VI, and IX, respectively, according to eq 1, slightly contaminated with small variable proportions of III, I, and VIII, respectively, due to the presence of $F_2P(S)SH$ impurity in the acid. The NMR parameters of the impurities are generally well separated from those of the new compounds permitting useful analysis of the NMR spectra of V, VI, and IX.

B. NMR Spectroscopic Studies. All of the new compounds synthesized herein contain chiral[10,11] phosphorus centers which confer magnetic nonequivalence in the molecule. In the case of V the four different ligands on the pentavalent phosphorus atom create a chiral phosphorus center which in turn makes the two trifluoromethyl groups on the trivalent phosphorus (as illustrated by Newman projections (Figure 1) of the various rotamers of V) magnetically nonequivalent. While internal rotation of the molecule does not destroy the nonequivalence of the two trifluoromethyl groups, inversion of the trivalent phosphorus atom would exchange these environments. Since we find that two unique CF_3 chemical shifts are preserved in V throughout the temperature range studied (+30 to −80 °C), it appears that phosphorus inversion is slow relative to the time scale of the NMR experiment in agreement with other results.[12]

Spectra were analyzed by visually matching observed spectra with those calculated and plotted from estimated parameters using the program NUMARIT.[13] Most of the spectra contain typical second-order features and can only be satisfactorily analyzed with computer techniques; however, with this approach, all pertinent features have been obtained from the spectra. The labeling scheme and best-fit parameters are given in Table I. Detailed analysis of some of the spectra of the series of compounds V–VIII, shown in part in Figures 2–5, are discussed in the Experimental Section.

The final member of this series of mixed-valence compounds, $CF_3(F)P(S)SP(F)CF_3$ (IX), is a mixture of two racemates with different NMR spectra. Since both starting materials consisted of racemic mixtures of the *d* and *l* optical isomers, four mixed-valence isomers labeled *dd′*, *dl′*, *ld′*, and *ll′*, resulted. Of these *dd′* and *ll′* form one racemate and *dl′* and *ld′* form the other. The two racemic mixtures are distinguishable (illustrated by Newman projections (Figure 6)) from one another in the NMR (Figures 7 and 8) and relative intensities show one configuration to be more prevalent than the other (A (65%), B (35%)) in the mixture.

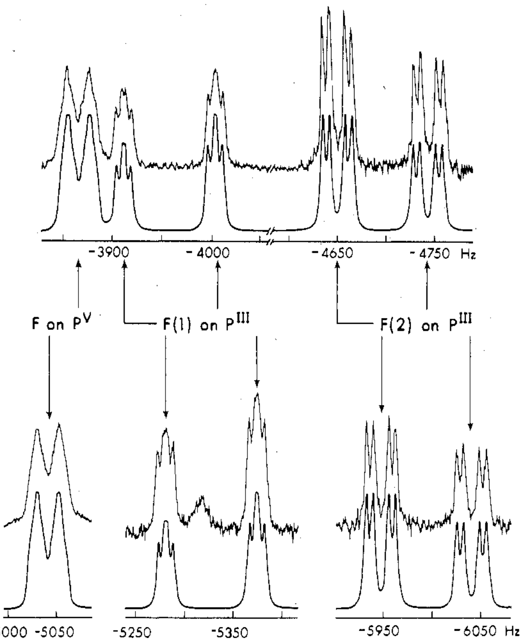


Figure 2. Observed and calculated partial ^{19}F NMR spectrum (94.1 MHz) of $F(CF_3)P(S)SPF_2$ (VI) at −120 °C for a 30% v/v CF_2Cl_2 solution. The frequency scale gives offset frequencies in Hz relative to the CF_2Cl_2 lock, negative values indicating resonance to high field of the standard. The spectrum shows the unique F on P^V and the two (F(1) and F(2)) different fluorine atoms on P^{III}.

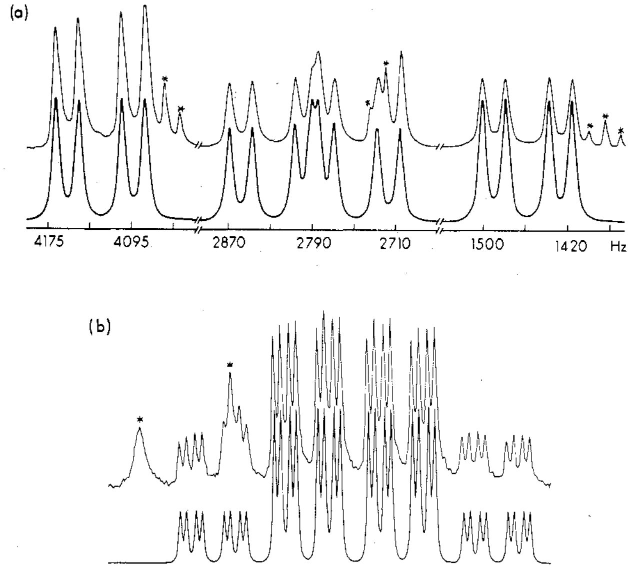


Figure 3. Observed and calculated Fourier transform ^{31}P NMR spectrum (36.4 MHz) of $F(CF_3)P(S)SPF_2$ (VI) measured at −120 °C on a 30% v/v CF_2Cl_2 solution: (a) complete ^{31}P spectrum of P^{III}, impurity lines (*) due to P^{III} of $F_2P(S)SPF_2$ (I); (b) high field of the ^{31}P spectrum due to P^V, impurity lines (*) not identified. The frequency scale actually measured from the heteronuclear CF_2Cl_2 lock has been converted to the P_4O_6 scale by independent measurement. Negative-scale values indicate resonance to high field of the standard.

C. Geminal Nonequivalence in Mixed-Valence Compounds with Chiral Phosphorus Centers. NMR spectra of molecules V–VIII yield the magnitude of the normally nonobservable coupling between geminal fluorine or trifluoromethyl ligands on phosphorus. Geminal CF_3–CF_3 coupling constants in V and VII where the CF_3 groups involved are bound to trivalent and pentavalent phosphorus, respectively, are similar (9 and 7 Hz). The chemical shift *differences* in this case are small

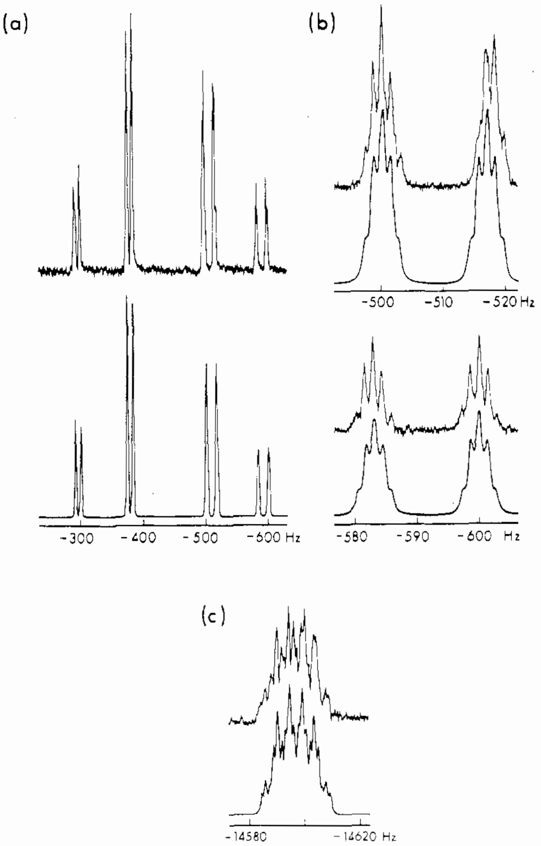


Figure 4. Portions of the observed and calculated ^{19}F (94.1 MHz) spectra of $F_2P(S)SP(CF_3)F$ (VIII) obtained on a 30% v/v CF_2Cl_2 solution at -80 °C: (a) the low-field half of the ^{19}F spectral region arising from F on P^V (observed and calculated), (b) expansion of the two portions of the spectrum due to one of the geminal fluorine atoms on P^V (observed and calculated), (c) the low-field half of ^{19}F spectral region arising from F on P^{III} (observed and calculated). The frequency scale gives offset frequencies with respect to the reference CF_2Cl_2 signal, negative values indicating resonance to high field of the standard.

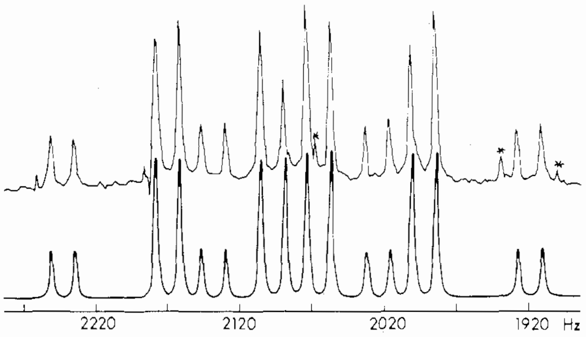


Figure 5. Observed and calculated partial ^{31}P (36.4 MHz) Fourier transform spectrum of $F_2P(S)SP(CF_3)F$ (VIII) obtained on a 30% v/v CF_2Cl_2 solution at -80 °C. The frequency scale, measured with respect to the CF_2Cl_2 heteronuclear lock has been converted to the P_4O_6 scale. Positive offset frequencies indicate resonance to low field of standard. Illustrated is the low-field half of the P^{III} spectrum.

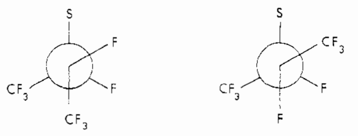


Figure 6. Newman projection of the isomers of IX.

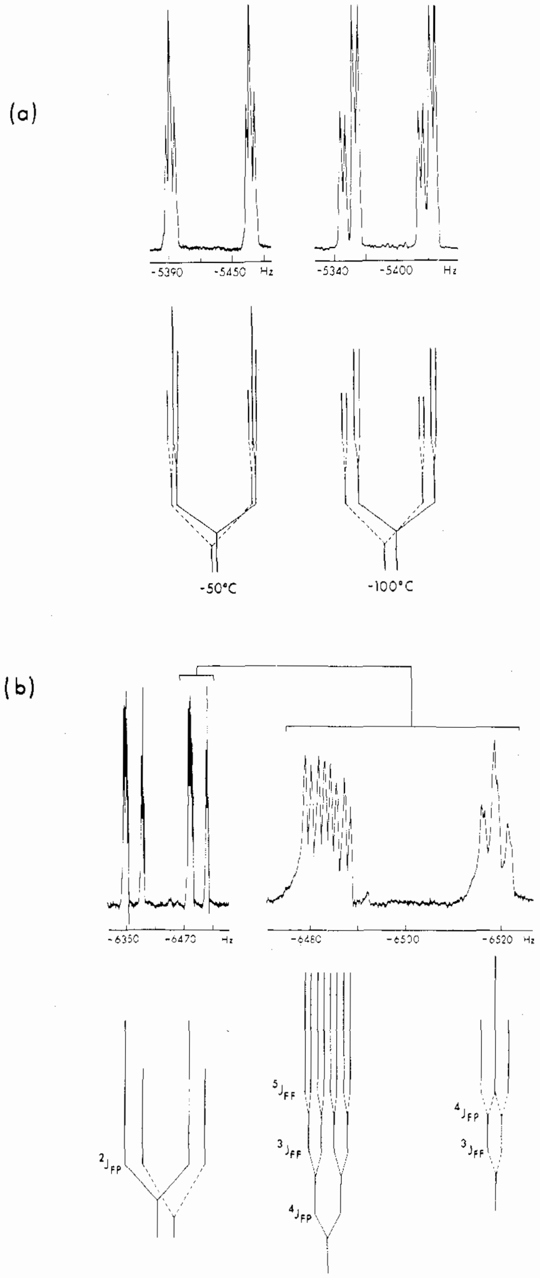
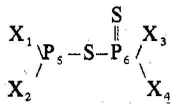


Figure 7. Observed and calculated partial ^{19}F (94.1 MHz) spectra of the isomers of $F(CF_3)P(S)SP(CF_3)F$ (IX) obtained in 20% v/v CF_2Cl_2 solution: (a) -50 and -100 °C ^{19}F spectra of the region assigned CF_3 on P^{III}, (b) the -50 °C ^{19}F spectral region assigned to CF_3 on P^V. Spectra were measured with respect to CF_2Cl_2 at -50 and -100 °C. Negative values of the offset frequency scale indicate resonance to high field of standard.

(0.3 and 0.2 ppm), probably because of the attenuation effect of the intervening carbon atom. These geminal CF_3 coupling constants are similar to analogous parameters reported for $(CF_3)_2NCXYZ$ (J, ~10 Hz) arising from an adjacent chiral alkyl group.[14] The chemical shift differences in that case[14] were larger (~1-7 ppm) than those observed herein.

Geminal F-F couplings for VI and VIII (92 and 82 Hz, respectively) are likewise similar to each other. The chemical shift difference between the geminal fluorine atoms bound to pentavalent P (2 ppm for VIII) contrasts with the greater difference noted for VI (4 ppm) where the nonequivalent geminal groups are bound to trivalent phosphorus. In both of these compounds, the directly bound phosphorus-fluorine coupling constants to each of the nonequivalent fluorine atoms is large and unequal with VI showing a greater difference (~80 Hz) than VIII (about 20 Hz). Short range P-F

Table I. Numbering Scheme and NMR Parameters for the (Thiophosphorylthio)phosphines V–IX



	V	VI	VII	VIII	IX	
					major (A)^d	minor (B)^e
Position No. of Substituent						
CF_3	1, 2, 3	3	1, 3, 4	2	1, 3	2, 3
F	4	1, 2, 4	2	1, 3, 4	2, 4	1, 4
Major Coupling Constants						
1–5	78.5^f	1370.0^g	77.8^f	1154.0^g	74^f	1148^g
2–5	78.5^f	1291.0^g	1161.2^g	72.6^f	1156^g	75^f
3–6	134.5^f	136.0^f	112.5^f	1224.0^g	134^f	134^f
4–6	1173.4^g	1174.0^g	112.5^f	1203.0^g	1165^g	1180^g
5–6	100.0^h	63.0^h	92.4^h	104.7^h	86^h	103^h
Minor Coupling Constants						
1–2	9.0	92.5	3.4	4.2	5.0	4.3
1–3	0.0	0.0	0.0	8.8	0	<0.5
1–4	1.2	6.0	0.0	1.3	0	n.r.^{c}
1–6	0.0	9.0	0.0	1.2	0	4
2–3	0.0	0.0	1.4	0.0	1.2	0
2–4	0.0	7.0	0.0	1.3	n.r.^{c}	0
2–6	0.0	23.0	3.8	0.0	5	0
3–4	0.0	2.6	7.2	82.5	2.8	2.8
3–5	7.0	0.0	6.0	0.5	5.2	2.8
4–5	10.5	22.0	2.5	16.3	n.r.	n.r.
Chemical Shifts^{a,b}						
ϕ_1	54.2	59.3	62.0	167.1	63.6	166.4
ϕ_2	54.5	63.7	164.7	64.1	164.8	63.6
ϕ_3	74.0	80.1	68.5	16.1	74.1	74.5
ϕ_4	59.2	56.3	68.7	18.0	59.1	58.9
ϕ_5	100.5	−76.5	−34.6	−37.2	−38.0	−38
ϕ_6	34.8	39.0	67.3	31.3	28.6	30.6

[a] ^{19}F chemical shifts (ϕ_1–ϕ_4) are given in ppm from $CFCl_3$ at 94.1 MHz. Except for V which was measured directly against $CFCl_3$, all values were measured with respect to CF_2Cl_2 and converted to the $CFCl_3$ scale by the addition of the measured difference between the two scales (5.9 ppm). Positive values indicate resonance to high field of standard. [b] ^{31}P chemical shifts (ϕ_5, ϕ_6) measured in ppm from P_4O_6 at 36.4 MHz. Positive values indicate resonance to high field of standard. The chemical shift of H_3PO_4 is +112 ppm on the P_4O_6 scale.[21] [c] n.r. = not resolved. [d] 65%. [e] 35%. [f] $^2J_{PF}$, Hz. [g] $^1J_{PF}$, Hz. [h] $^2J_{PP}$, Hz.

couplings for the nonequivalent groups (in this case $^2J_{FP}$) were not observed for V and VII, probably because the couplings are much smaller in the first instance as a consequence of the presence of an intervening carbon atom.

Greater geminal nonequivalence effects are consistently associated with the trivalent phosphorus center as opposed to the pentavalent center suggesting that the latter is a more effective chiral center. Since a planar environment about the phosphorus would destroy the chirality, this difference probably reflects a trend toward planarity in the trivalent phosphorus centers compared with the four-coordinate pentavalent phosphorus centers. The large variations in directly bound coupling constants involving trivalent phosphorus probably has a similar origin in that these changes reflect the changes in hybridization at phosphorus with substitution.[15,16] In general the coupling constants and chemical shifts are typical of values expected for trivalent fluoro- and (trifluoromethyl)phosphorus compounds and in all cases the values are consistent with previous assignments.[5,8,17,18]

While the largest values of $^2J_{PP}$ are found with CF_3 substitution on trivalent phosphorus, and it is clear that this parameter is sensitive to CF_3 substitution, the range of values is relatively small (63–104 Hz) and systematic trends cannot be reliably established. It is, however, notable that the value of $^2J_{PP}$ is markedly different (86 and 103 Hz) in the two isomers of IX indicating a conformational dependence of $^2J_{PP}$.

It is also notable that the four-bond CF_3 fluorine coupling to the distant phosphorus has a larger magnitude when CF_3 is bound to pentavalent P than the corresponding coupling when the CF_3 is bound to trivalent P. This follows the same order as $^2J_{FP}$ which is larger for CF_3 bound to pentavalent P than for CF_3 bound to trivalent P. No such behavior is observed for $^3J_{FP}$ as seen in Table II.

The chemical shift of the trifluoromethyl groups in these compounds is relatively insensitive to changes in the degree of CF_3 substitution (Table III), but the chemical shifts of fluorine atoms bound directly to phosphorus change significantly with substitution at both trivalent and pentavalent P. In both cases, the chemical shift of the directly bound fluorine increases when a CF_3 substituent is introduced with the trivalent cases showing the most dramatic increase. This may be due to increased P–F π interactions in $CF_3(F)P$ compounds compared to F_2P (where the two F substituents compete with each other) compounds which result in higher shielding and hence larger chemical shifts in the former case. At the same time, the phosphorus chemical shift increases from a range of −78 to −80 ppm for the compounds containing difluorinated trivalent phosphorus to a range of −35 to −38 ppm for $F(CF_3)P^{III}$ compounds and to a range of +100 to +107 ppm for those $(CF_3)_2P^{III}$ containing compounds. The chemical shift trend for pentavalent compounds is not as prominent and the F_2P^V (31–42 ppm) and $F(CF_3)P^V$ (28–40 ppm) range of shifts overlaps. The $(CF_3)P^V$ compounds with a shift range of 65–80 ppm are well separated. The highest ^{31}P shift for both trivalent and pentavalent phosphorus arises with complete CF_3 substitution.

D. Dynamic NMR Spectral Behavior of the Mixed-Valence Compounds. A remarkable range of temperature dependence

Table II. Collected NMR Coupling Constants for Fluoro- and (Trifluoromethyl)(thiophosphorylthio)phosphines

compd	substituents		$^1J_{FP}$		$^2J_{FP}$		$J_{FF}{}^d$		$^4J_{FP}$		$^3J_{FP}$		$^2J_{PP}$
	on P^{III}	on P^V	P^{III}	P^V	P^{III}	P^V	P^{III}	P^V	CF_3 on P^{III}	CF_3 on P^V	F on P^{III}	F on P^V	
I[a]	F, F	F, F	1323.6	1209.9							22.5	14.3	67.8
II[b]	CF_3, CF_3	CF_3, CF_3			81.3	111.7			0.6	4.9			103.0
III[c]	CF_3, CF_3	F, F		1223	78				n.o.			2	96.5
IV[c]	F, F	CF_3, CF_3	1331			113				1.8	18		73
V	CF_3, CF_3	CF_3, F		1173.4	78.5	134.5	9.0[e]	3.0	0.0	7.0		10.5	100.0
VI	F, F	CF_3, F	1370.0[e] 1291.0[e]	1174.0		136.0	92.5[e]	2.6		0.0	9.0[e] 23.0[e]	22.0	63.0
VII	CF_3, F	CF_3, CF_3	1161.2		77.8	112.5	3.4	7.2[e]	0.0	6.0[e] 2.5[e]	3.8		92.4
VIII	CF_3, F	F, F	1154.0	1124[e] 1203[e]	72.6		4.2	82.5[e]	0.0		1.2	0.5[e] 16.3[e]	104.7
IX A (major)	CF_3, F	CF_3, F	1156	1165	74	134	5.0	2.8	0.0	5.2	5	n.r.	86
B (minor)	CF_3, F	F, CF_3	1148	1180	75	134	4.3	2.8	0.0	2.8	4	n.r.	103

[a] Reference 1. [b] Reference 2. [c] Reference 3. [d] Between groups on the same P atom. Long range F–F couplings across the P–S–P bridge were in general small (see Table I for values of those coupling constants in V–IX which were resolved). [e] Geminal pair couplings.

Table III. Collected Chemical Shifts for Fluoro- and (Trifluoromethyl)(thiophosphorylthio)phosphines

compd	substituents on		$\phi_F{}^a$ on P^{III}	$\phi_F{}^a$ on P^V	$\phi_{CF_3}{}^a$ on P^{III}	$\phi_{CF_3}{}^a$ on P^V	$\phi_P{}^b$ for P^{III}	$\phi_P{}^b$ for P^V
	P^{III}	P^V						
I[c]	F, F	F, F	60.8	14.4			−78	38.2
II[d]	CF_3, CF_3	CF_3, CF_3			53.8	68.7	106.0	65.2
III[e]	CF_3, CF_3	F, F		17.9	55.0		107.2	42.1
IV[e]	F, F	CF_3, CF_3	61.2			71.2	−81.4	80.5
V	CF_3, CF_3	CF_3, F		59.2	54.2[f] 54.5[f]	74.0	100.5	34.8
VI	F, F	CF_3, F	59.3[f] 63.7[f]	56.3		80.1	−76.5	39.0
VII	CF_3, F	CF_3, CF_3	164.7		62.0	68.5[f] 68.7[f]	−34.6	67.3
VIII	CF_3, F	F, F	167.1	16.1[f] 18.0[f]	64.1		−37.2	31.3
IX A (major)	CF_3, F	CF_3, F	164.8	59.1	63.6	74.1	−38	28.6
B (minor)	CF_3, F	F, CF_3	166.4	58.9	63.6	74.5	−38	30.6

[a] ^{19}F chemical shifts given relative to $CFCl_3$. [b] ^{31}P chemical shifts measured relative to P_4O_6. [c] Reference 1. [d] Reference 2. [e] Reference 3. [f] Geminal pair shifts.

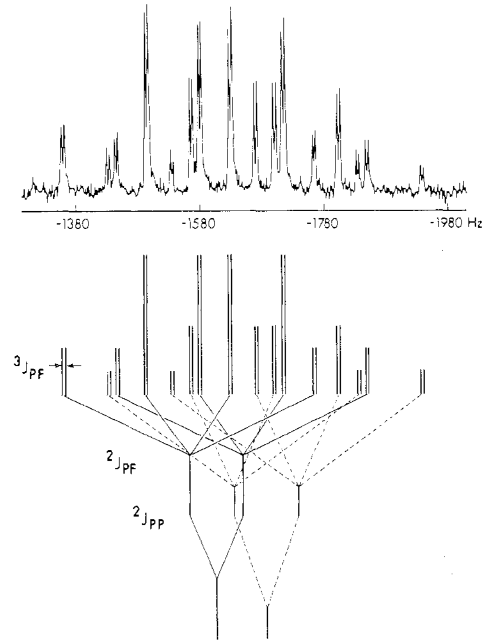
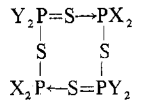


Figure 8. The high-field half of the ^{31}P Fourier transform (36.4 MHz) NMR spectrum of both isomers of the P^V region of $F(CF_3)P(S)SP(CF_3)F$ (IX) at −50 °C in a 30% v/v CF_2Cl_2 solution. The scale quotes offset shifts relative to P_4O_6 converted from values measured with respect to CF_2Cl_2 by means of the heteronuclear lock system. Negative values indicate resonance to high field of standard.

is demonstrated by this closely related series of compounds. The diagnostic parameter for exchange is the $^2J_{PP}$ coupling constant, which in the case of II, V, and VII is observable at normal temperatures. In contrast, temperatures of the order of −40 to −80 °C are required to observe the $^2J_{PP}$ coupling constant in IV, IX, and VIII. The most mobile, VI, requires cooling to −120 °C to reveal the $^2J_{PP}$ coupling constant. Once resolved, however, this coupling constant, typically 60–105 Hz, does not change significantly with temperature. This behavior is readily explained in terms of an exchange process which preserves the identity of the phosphorus valence in each compound.[3] The behavior of the present compounds is compatible with an exchange involving the bimolecular (or equivalent polymeric) intermediate.



$$\begin{array}{c} Y_2P{=}S{\rightarrow}PX_2 \\ \;|\qquad\quad | \\ S\qquad\; S \\ \;|\qquad\quad | \\ X_2P{\leftarrow}S{=}PY_2 \end{array}$$

The least mobile compound is that in which all substituents are CF_3 (II)[2] or where both trivalent phosphorus substituents are CF_3 groups (III,[3] V). In these cases $^2J_{PP}$ is observed at normal probe temperatures. High mobility is demonstrated by I[1] and VI wherein two F atoms are bound to trivalent P. Intermediate behavior is shown by the remaining compounds. For a given set of P^{III} substituents, replacing F on pentavalent phosphorus with CF_3 also reduces the apparent rate of exchange but the effect is not as pronounced as replacement of F on trivalent phosphorus by CF_3. Detailed study of the systems is plagued by the difficulty of obtaining absolutely pure samples, by the complexity of the spectra, and by some nonreproducibility of the dynamic behavior which suggests possible catalysis of the process. In no case was the lack of reproducibility pronounced (i.e., resolution temperatures differed by no more than 20 °C in the worst case) so we do not think that catalysis is a severe problem. We have also not been able to establish a reliable concentration dependence (or lack thereof) in any of these systems although the suggested exchange mechanism implies a concentration dependence. An alternative process traversing the acid intermediate formed by proton-containing species HQ (e.g., H_2O)

$$X_2P(S)SPY_2 + HQ \rightleftharpoons X_2P(S)SH + QPY_2 \qquad (4)$$

would also account for the NMR behavior and possibly also for the apparent concentration independence and poor reproducibility. These difficulties precluded detailed barrier studies. Whatever the mechanism, it is notable that there appears to be no interchange of CF_3 or F between trivalent and pentavalent phosphorus centers.

Conclusions

Mixed-valence diphosphorus compounds are readily prepared by metathetical reactions of dithiophosphinic acids and aminophosphines. Chiral centers create observable magnetic nonequivalence revealing geminal coupling constants. Chirality in the molecule has a more dramatic effect on equivalent groups bound to trivalent as compared to pentavalent phosphorus. Two-bond $^2J_{PP}$ coupling constants are destroyed in some cases (especially with fluorine substituents on trivalent phosphorus) by an exchange mechanism which preserves the valence of and the substituents on a particular phosphorus atom.

Experimental Section

General Considerations. Manipulations of air-sensitive compounds were carried out in a standard Pyrex vacuum system with stopcocks lubricated with Apiezon N grease. Separation of volatile compounds was effected by passage through a series of U-traps cooled by slush baths at various temperatures or, in difficult cases, by means of a micro reflux column which has been described previously.[19]

Reactions were carried out in sealed Pyrex tubes of 10, 25, or 75 mL volume. Reactions of amines with fluorides were generally performed in 1-L vessels similar to those described elsewhere[9] in which all components could be maintained in the gas phase.

Materials. Reagent grade commercially available materials were used where possible and were fractionated before use to remove gross impurities. Other compounds required were prepared by indicated literature methods. The (trifluoromethyl)phosphines were prepared by heating CF_3I, phosphorus, and iodine at 220 °C.[20]

Instrumental Techniques

Infrared spectra were obtained with Perkin-Elmer 337, 457, and 421 spectrometers. Routine purity checks by NMR were obtained on Varian A60 or A56/60A instruments operating at 60 MHz for ^1H and at 56.4 MHz for ^{19}F. Preliminary temperature-dependent spectra were obtained with these instruments utilizing the Varian V6040 temperature controller. High-resolution spectra and lower temperature spectra were obtained on a Varian HA 100 instrument, equipped with a V6040 temperature controller capable of attaining temperatures as low as about −120 °C. Fluorine (94.1 MHz) and room-temperature ^{31}P (40.5 MHz) spectra were obtained with the Varian system, but since the Varian system was unsatisfactory for recording ^{31}P spectra at low temperatures due to the difficulty in finding a suitable low-temperature lock signal, the Bruker HFX90 system with Fourier transform capability and heteronuclear lock was used for low-temperature ^{31}P studies at 36.4 MHz. The low-temperature phosphorus spectra were obtained on samples dissolved in fluorinated solvents such as $CFCl_3$ or CF_2Cl_2 which also doubled as the lock compound. All these phosphorus spectra were run in Fourier transform mode on the Bruker spectrometer and either 5000 or 10 000 Hz sweep widths were collected in either 8K or 16K data points on a Nicolet 1085 computer associated with the system. Good quality spectra were generally obtainable after 250 to 1000 pulses depending on the concentration of the sample and the number of lines in the pattern. Some low-temperature ^{19}F spectra were obtained with the Bruker HFX 90 operating at 84.6 MHz in the CW (frequency sweep) mode. Since the Varian and Bruker spectrometers used a different CW offset procedure, the spectral scales appear to be opposite. We have consistently used throughout the paper negative offset frequencies to mean high-field shifts and vice versa but have not reversed the Bruker CW spectra. The Bruker FT spectra have the same sense as the Varian CW spectra.

Volatile samples for NMR were prepared under vacuum in 5-mm diameter tubes and were generally about 25% by volume in $CFCl_3$ or CF_2Cl_2. Fluorine chemical shifts are measured relative to $CFCl_3$ unless otherwise specified while phosphorus chemical shifts are given relative to neat P_4O_6.[21] These latter values are not very accurate, especially at low temperatures, because the position of the P_4O_6 resonance can be measured only above +23 °C, the freezing point of the compound, and because the resonance frequency of the lock compound (CF_2Cl_2) was markedly temperature dependent. NMR spectra of solid compounds were obtained in either water or CD_3CN solutions and samples were prepared in the atmosphere.

Mass spectra were obtained on the AEI MS9 mass spectrometer, operating at an ionizing voltage of 70 eV; the compounds were introduced as gases using the heated inlet system.

1. Preparation of $F(CF_3)P(S)SH$. (a) Reaction of $(CF_3)FPN(CH_3)_2$ with Sulfur. $CF_3(F)PN(CH_3)_2$[4] (0.664 g; 4.07 mmol) was heated at 150 °C for 3 days with an excess of sulfur. Fractionation of the volatile products through −45 °C yielded a mixture (0.310 g) of $F(CF_3)P(S)N(CH_3)_2$,[5] $CF_3P(S)N(CH_3)_2$,[6] and two other unidentified products in much smaller amounts. The −96 °C trap contained $F(CF_3)P(S)N(CH_3)_2$ (0.241 g) contaminated with about 5% of $F_2P(S)N(CH_3)_2$[9] while the −196 °C fraction was pure $CF_3P(S)F_2$ (0.163 g) identified by comparison of its properties with a sample prepared by a different method.[22]

(b) Reaction of $F(CF_3)P(S)N(CH_3)_2$ with H_2S. $F(CF_3)P(S)N(CH_3)_2$ (0.166 g) contaminated with about 5% $F_2P(S)N(CH_3)_2$ and H_2S (0.030 g; 0.9 mmol) was combined in a sealed tube and placed in an oven at 170 °C for 4 days. The volatile products were unreacted H_2S (0.017 g; 0.50 mmol) and unreacted $F(CF_3)P(S)N(CH_3)_2$ (0.081 g; 0.41 mmol). An oily liquid which remained in the tube was dissolved under a nitrogen atmosphere in dry CD_3CN. The NMR spectrum of the sample showed the presence of $(CH_3)_2NH_2^+F_2PS_2^-$[7] and $(CH_3)_2NH_2^+F(CF_3)PS_2^-$ ($^1J_{FP}$ = 1071 Hz, $^2J_{FP}$ = 103 Hz, $^3J_{FF}$ = 1 Hz; ϕ_F = 37.4; ϕ_{CF_3} = 77.8) in the approximate molar ratio 1:2.

(c) Reaction of $F(CF_3)PS_2^-$ with H_2SO_4. To approximately 2.14 mmol of the dimethylammonium salt of $F(CF_3)PS_2^-$ (contaminated with the $F_2PS_2^-$ salt) was added a large excess of concentrated H_2SO_4 under vacuum. An immediate reaction ensued with liberation of volatile products (0.334 g). The ^{19}F NMR spectrum indicated the presence of a mixture of F_2PS_2H[7] (27.5%) and $F(CF_3)PS_2H$ (72.5%) which was found to be inseparable by fractionation. The vapor-phase molecular weight of the mixture was 171.4. By the assumption of equal volatility of the two compounds and ideal gas behavior a molecular weight of 185.5 (calcd 184) for $F(CF_3)PS_2H$ was found. The parent ion of $F(CF_3)PS_2H$ was measured in the mass spectrometer (*m/e* found 183.9194, calcd for CF_4PS_2H 183.9194). The NMR spectrum was consistent with that which was expected for the new compound. The ^{19}F spectrum showed a doublet of doublets ($^2J_{FP}$ = 132 Hz; $^3J_{FF}$ = 3.1 Hz; ϕ_{CF_3} = 75.0) corresponding to a CF_3 group coupling to phosphorus and to a single fluorine atom and a doublet of quartets ($^1J_{FP}$ = 1169 Hz; $^3J_{FF}$ = 3.1 Hz; ϕ_F = 54.1) due to coupling of a fluorine nucleus to phosphorus and to a CF_3 group. The proton gave rise to a singlet centered at τ = 6.67 in the ^1H NMR spectrum. The IR spectrum recorded using a reference cell containing F_2PS_2H[7] was consistent with that expected for $F(CF_3)P_2SH$ (2600 (w), 2580 (vw), ν_{SH}; 1190 (vs, br), ν_{CF}; 910 (s), 830 (m, br), ν_{PF}, δ_{SH}; 765 (m), 725 (s), δ_{sym,CF_3}, $\nu_{P=S}$; 570 (s), 535 (m), 415 (m) cm^{-1}, δ_{as,CF_3}, ν_{PS}, ν_{PC}). The amount of F_2PS_2H present as impurity varied from one preparation to another.

2. Preparation of $F(CF_3)P(S)SP(CF_3)_2$ (V). A sample of $F(CF_3)PS_2H$ contaminated with F_2PS_2H (0.185 g; 1.00 mmol based on $F(CF_3)PS_2H$) was combined with $(CF_3)_2PN(CH_3)_2$[4,23] (0.118 g; 0.56 mmol). Fractionation of the products yielded $F(CF_3)P(S)SP(CF_3)_2$[3] (III) and $F(CF_3)PS_2H$. An oily involatile liquid formed in the reaction was identified by NMR spectroscopy as $(CH_3)_2NH_2^+F(CF_3)PS_2^-$ contaminated with $(CH_3)_2NH_2^+F_2PS_2^-$.

3. Reactions of $F(CF_3)P(S)SP(CF_3)_2$ (V). (a) Reaction with $(CH_3)_2NH$. A sample of $F(CF_3)P(S)SP(CF_3)_2$ from the previous preparation (0.085 g; 0.24 mmol) reacted immediately at room temperature with $(CH_3)_2NH$ (0.024 g; 0.54 mmol) to yield $(CF_3)_2PN(CH_3)_2$ (0.050 g; 0.24 mmol) as the only volatile product.

(b) Alkaline Hydrolysis. Reaction of V (0.069 g; 0.196 mmol) with a 20% aqueous solution of NaOH yielded fluoroform (0.0232 g; 0.332 mmol) as the only volatile product.

4. Preparation of $F(CF_3)P(S)SPF_2$ (VI). A sample of $F(CF_3)PS_2H$ (0.293 g; 1.59 mmol) contaminated by a small amount of F_2PS_2H and a trace of SiF_4 reacted immediately on warming to room temperature with $F_2PN(CH_3)_2$[17,24] (0.091 g; 0.80 mmol) with formation of a clear viscous liquid. The only volatile product was $F(CH_3)P(S)SPF_2$ (0.176 g; 0.70 mmol) contaminated with $F_2P(S)SPF_2$[1] (I) which could not be removed. The viscous liquid reacted with concentrated H_2SO_4 to yield $F(CF_3)PS_2H$ (0.128 g; 0.70 mmol).

5. Reactions of $F(CF_3)P(S)SPF_2$ (VI). (a) Reaction with $(CH_3)_2NH$. A mixture of $F(CF_3)P(S)SPF_2$ (0.113 g; 0.45 mmol) and $(CH_3)_2NH$ (0.041 g; 0.82 mmol) reacted on warming to give $PF_2N(CH_3)_2$ (0.036 g; 0.314 mmol) and PF_3 (0.0109 g; 0.124 mmol) and a yellowish solid (0.101 g) which reacted with concentrated H_2SO_4 to give $F(CF_3)PS_2H$ (0.054 g; 0.29 mmol) containing a small amount of F_2PS_2H.

(b) Alkaline Hydrolysis. A sample of $F(CF_3)P(S)SPF_2$ (0.060 g; 0.24 mmol) reacted vigorously with a large excess of a 20% aqueous NaOH solution. No volatile products were detected.

6. Preparation of $(CF_3)_2P(S)SP(CF_3)F$ (VII). A mixture of $(CF_3)_2PS_2H$[5,6] (0.490 g; 2.10 mmol) and $F(CF_3)PN(CH_3)_2$[4] (0.178 g; 1.10 mmol) reacted immediately on warming to room temperature with formation of a white solid identified by NMR spectroscopy[8] as $(CF_3)_2PS_2^-(CH_3)_2NH_2^+$. A volatile liquid which decomposed slowly during room-temperature transfers in the vacuum system was identified as $(CF_3)_2P(S)SP(CF_3)F$. The yield of product purified by fractionation and refluxing from a micro reflux column[19] was 42% (0.156 g; 0.44 mmol).

7. Reactions of $(CF_3)_2P(S)SP(CF_3)F$ (VII). (a) Reaction with $(CH_3)_2NH$. A mixture of $(CF_3)_2P(S)SP(CF_3)F$ (0.078 g; 0.22 mmol) and $(CH_3)_2NH$ (0.022 g; 0.48 mmol) formed a white solid when warmed to 25 °C. This was identified by NMR spectroscopy[8] as $(CF_3)_2PS_2^-(CH_3)_2NH_2^+$. The only volatile product was $F(CF_3)PN(CH_3)_2$ (0.031 g; 0.19 mmol) contaminated with a small amount of $(CH_3)_2NH$.

(b) Alkaline Hydrolysis. A sample of $(CF_3)_2P(S)SP(CF_3)F$ (0.078 g; 0.22 mmol) which slowly decomposed on transferring to the reaction vessel was combined with a 20% aqueous solution of NaOH. The only volatile product isolated was CF_3H (0.027 g; 0.39 mmol).

8. Preparation of $F_2P(S)SP(CF_3)F$ (VIII). Warming a mixture of F_2PS_2H (0.734 g; 5.47 mmol) and $F(CF_3)PN(CH_3)_2$ (0.446 g; 2.73 mmol) to 25 °C resulted in immediate formation of $F_2PS_2^-(CH_3)_2NH_2^+$ (0.450 g; 2.52 mmol) which was identified by NMR spectroscopy.[7] The only volatile product was identified as $F_2P(S)SP(CF_3)F$ (0.534 g; 2.12 mmol).

9. Reactions of $F_2P(S)SP(CF_3)F$ (VIII). (a) Reaction with $(CH_3)_2NH$. A pure sample of $F_2P(S)SP(F)CF_3$ (0.171 g; 0.68 mmol) reacted immediately at 25 °C with $(CH_3)_2NH$ (0.060 g; 1.33 mmol) to form a white solid (0.120 g; 0.67 mmol) identified from its NMR spectrum as $F_2PS_2^-(CH_3)_2NH_2^+$. The only volatile product was $F(CF_3)PN(CH_3)_2$ (0.108 g; 0.67 mmol).

(b) Alkaline Hydrolysis. A sample of $F_2P(S)SP(CF_3)F$ (0.148 g; 0.59 mmol) was combined with an excess of a 20% aqueous solution of NaOH. The only volatile product was CF_3H (0.039 g; 0.56 mmol). The residual alkaline solution contained, according to ^{19}F NMR, F^- or bifluoride (singlet, $\phi = 121$).

10. Preparation of $F(CF_3)P(S)SP(CF_3)F$ (IX). A sample of $F(CF_3)PS_2H$ (0.157 g; 0.85 mmol) reacted immediately with $F(CF_3)PN(CH_3)_2$ (0.076 g; 0.47 mmol) with formation of a viscous oil which was identified as $F(CF_3)PS_2^-(CH_3)_2NH_2^+$ contaminated with a small amount of $F_2PS_2^-(CH_3)_2NH_2^+$ from its NMR spectrum. An undetermined amount of $F(CF_3)P(S)SP(CF_3)F$, identified by means of its NMR spectrum, was obtained as the major volatile product. It was contaminated with a trace of VIII.

Analysis of Certain NMR Spectra. 1. [(Fluoro(trifluoromethyl)thiophosphoryl)thio]bis(trifluoromethyl)phosphine (V) and [(Bis(trifluoromethyl)thiophosphoryl)thio]fluoro(trifluoromethyl)phosphine (VII). The nonequivalent CF_3 groups in V were analyzed as an A_3B_3X second-order system with first-order couplings to the remainder of the molecule. The remaining part of the spectrum could be assigned on a first-order basis.

Similarly the nonequivalent CF_3 groups in VII were analyzed as an A_3B_3X system with $\Delta\nu/J = 2.5$.

In both cases the second-order region is sensitive to small changes in coupling constant.

2. [(Fluoro(trifluoromethyl)thiophosphoryl)thio]difluorophosphine (VI). The NMR spectra of $F(CF_3)P(S)SPF_2$ exemplify the nonequivalence of the two fluorine atoms on trivalent P due to chirality of pentavalent P (Figures 2 and 3). Parameters are listed in Table I.

The CF_3 groups spectral lines are easily recognized in the ^{19}F spectra (Figure 2) and form a doublet of doublets due to coupling to pentavalent P and to the fluorine atom on pentavalent P. The three fluorine atoms bound directly to phosphorus are not easily assigned because all three fluorine atoms have similar chemical shifts and the lines arising from F on pentavalent P are not well separated from those due to F on trivalent P. The interpretation was aided by the presence of two unique ${}^{1}J_{\mathrm{P^{III}}}$ coupling constants in the ^{31}P spectra of P(III). The spectra of the two fluorine atoms on trivalent P were simulated as an ABX system with first-order couplings of different magnitudes for the two fluorine atoms to pentavalent P and to the fluorine atom on pentavalent P. The large chemical shift difference between the nonequivalent fluorine atoms as compared to the coupling between them ($\Delta\nu/J = 7.6$) allows an almost first-order interpretation of the ABX system for this compound. The fluorine atom on pentavalent P yields only a broad doublet, presumably due to the presence of a large number of overlapping lines.

The two unique ${}^{1}J_{\mathrm{FP^{III}}}$ coupling constants in the ^{31}P spectrum give rise to a doublet of doublets for the trivalent phosphorus nucleus (Figure 3a). Further splitting due to ${}^{2}J_{\mathrm{PP}}$ and long range ${}^{3}J_{\mathrm{PF}}$ coupling produces the 16-line spectrum observed. The major features of the spectrum of pentavalent P (Figure 3b) are a large doublet due to ${}^{1}J_{\mathrm{FP}}$ which is further split into quartets of doublets by ${}^{2}J_{\mathrm{FP}}$ and ${}^{2}J_{\mathrm{PP}}$. Additional first-order couplings of unequal magnitudes to the nonequivalent fluorine atoms on trivalent P give rise to the further doublet of doublets structure.

3. [(Difluorothiophosphoryl)thio]fluoro(trifluoromethyl)phosphine (VIII). The fluorine atoms on pentavalent P form the AB part of an ABX spin system with $\Delta\nu/J = 2.2$ (Figure 4a). Unique ${}^{1}J_{\mathrm{PF}}$ values are associated with the nonequivalent fluorine nuclei. The major features of the region of the spectrum due to F on pentavalent P consist of two pseudoquartets due to the AB spin system where two lines may be assigned to nucleus A and two lines to nucleus B. The large interactions of the A and B nuclei (the two nonequivalent fluorine atoms) with the X nucleus (pentavalent P) then splits each pair of two lines by the appropriate value of ${}^{1}J_{\mathrm{FP}}$ and yields the two quartets of unequal spacings. Further first-order couplings are then superimposed on these lines. It is seen in Figure 4a that each of the lines in both quartets is further split into a doublet due in the case of the pair of B lines in the quartet from interaction with trivalent P (16.3 Hz) and in the case of the pair of A lines in the quartet to coupling to F on trivalent P (8.8 Hz). The spectrum of the CF_3 group appears as a doublet of doublets due to interaction with trivalent P and with F on trivalent P. The spectrum of the fluorine atom on trivalent P (Figure 4c) is fairly well resolved and shows the expected couplings.

The ^{31}P spectrum of the pentavalent phosphorus atom shows a different coupling to each of the fluorine atoms bound to it resulting in a doublet of doublets. Further coupling to trivalent P splits each of these lines into doublets. Smaller couplings to the CF_3 groups were not resolved.

The ^{31}P spectrum of the trivalent P (Figure 5) consists of a large doublet from coupling to the directly bound fluorine atom. Further first-order couplings to CF_3 and pentavalent P yield a doublet of quartets and interaction with one of the fluorine atoms on the pentavalent phosphorus splits each of these lines into a doublet.

4. The Racemic Mixtures of [(Fluoro(trifluoromethyl)thiophosphoryl)thio]fluoro(trifluoromethyl)phosphine (IX). Complete assignment of the spectra of the two racemates could not be achieved because of the poor resolution observed in the spectra of the single fluorine atoms bound to both trivalent and pentavalent phosphorus and only chemical shift information was obtained for these nuclei. The extremely complicated ^{31}P spectra of the trivalent phosphorus nuclei could not be analyzed even though they appear to be first order. The similarity of the two racemates and the numerous transitions arising from extensive spin–spin coupling provides spectra containing a large number of overlapping lines. Accidental overlap is seen in the spectra of the CF_3 groups bound to trivalent P (Figure 7a) which appears as a doublet of triplets at −50 °C. However, cooling the sample to −100 °C results in the observation of two sets of doublets of doublets, one of which arises from each of the racemates. These couplings are assigned to the coupling of the CF_3 group with trivalent P and with the unique F on trivalent P, respectively. In this region of the spectrum it is seen that one of the two racemic mixtures is present in higher concentration (A, 65%) than the other (B, 35%) and it is this feature alone which allows assignment of the transitions in the various regions of the spectrum to one particular racemate.

At −50 °C, the spectra of the CF_3 groups on pentavalent P are well separated for the two mixtures (Figure 7b). In the major component IX (A), this group is coupled to pentavalent P resulting in a large doublet. These major peaks are further split into doublets of doublets of doublets by F on pentavalent P, by trivalent P, and by F on trivalent P. These coupling constants, although in the expected range relative to the related molecules I–VIII, must be regarded as tentative because of the problems of resolution and assignment in the spectra of the single fluorine atoms and the trivalent phosphorus nucleus. The spectrum of the minor component (IX (B)) shows a similar coupling of the trifluoromethyl groups to pentavalent P. Additional, nearly equal couplings, apparently to F on pentavalent P and to the trivalent phosphorus nucleus, give rise to a triplet structure. A very small coupling to F on trivalent P may also be present but was not resolved.

The NMR spectrum of the pentavalent phosphorus atoms (Figure 8) yields nearly equal chemical shift values for both isomers of IX but the spectra are easily analyzed because fewer couplings are involved and the magnitudes are different from those of P^{III}.

Acknowledgment. We thank Glen Bigam, Tom Brisbane, and Dave Gifford for assistance with the NMR spectra and the National Research Council of Canada for financial support. L.F.D. thanks the National Research Council of Canada for a Studentship.

Registry No. I, 23526-68-3; V, 67478-92-6; VI, 67478-93-7; VII, 67478-94-8; VIII, 67478-95-9; IX, 67478-96-0; $F(CF_3)P(S)SH$, 67478-97-1; $CF_3(F)PN(CH_3)_2$, 3205-95-6; $F(CF_3)P(S)N(CH_3)_2$, 18799-74-1; $(CH_3)_2NH_2{}^+F(CF_3)PS_2{}^-$, 67478-98-2; $(CF_3)_2PN(CH_3)_2$, 432-01-9; $(CH_3)_2NH$, 124-40-3; $(CF_3)_2PS_2H$, 18799-75-2; F_2PS_2H, 20773-09-5; S_8, 18808-47-4; H_2S, 7783-06-4.

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Organo-Substituted Phosphazenes. 10. Reactions of Hexafluorocyclotriphosphazene with Propenyllithium Reagents[1]

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Received April 4, 1978

The interactions of propenyllithium reagents with hexafluorocyclotriphosphazene ($P_3N_3F_6$) hve been investigated. The reaction of either 1-propenyl- or 2-propenyllithium with $P_3N_3F_6$ proceeds with moderate to good yields to give the appropriate monosubstituted phosphazene. The potential for use of these materials as precursors to other organophosphazenes is shown by the occurrence of facile hydrogenation and bromination reactions. Although the addition of 2 equiv of 2-propenyllithium to $P_3N_3F_6$ results in degradation products, the addition of 2 equiv of 1-propenyllithium to $P_3N_3F_6$ results in the production of the geminally substituted phosphazene. Furthermore, the reaction of phenylpentafluorocyclotriphosphazene with 1-propenyllithium also yields a geminal derivative. These results are discussed in terms of the factors which control the substitution pattern observed in the reactions of organolithium reagents with $P_3N_3F_6$. The new propenylfluorophosphazenes are characterized by infrared, NMR (proton and fluorine-19), and mass spectrometry.

Introduction

The reactions of cyclic and polymeric[2] fluorophosphazenes with organolithium reagents have proved to be a valuable method for producing a variety of organophosphazene derivatives. The reactions of alkyl-,[3-6] alkynl-,[7] and aryllithium[2,8-10] reagents have been explored in detail, but, with the exception of a brief report of the synthesis of vinylpentafluorocyclotriphosphazene,[4] the reactions of alkenyllithium reagents have not been reported. An investigation of the reactions of alkenyllithium reagents with hexafluorocyclotriphosphazene ($P_3N_3F_6$) would be of interest in order to establish the factors which are significant in the control of the substitution pathway of the organolithium–fluorophosphazene reaction. Furthermore, the alkenylphosphazenes would be valuable precursors to a wide range of organophosphazenes derived from reactions at the olefinic center. These synthetic transformations would complement those which one could accomplish through reactions of phosphazenes with ketonic functions in the exocyclic group.[11] Therefore, we wish to report the synthesis and characterization of propenyl derivatives of $P_3N_3F_6$.

Experimental Section

Hexachlorocyclotriphosphazene (Ethyl Corp.) was converted to hexafluorocyclotriphosphazene[12] which in turn was converted to