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Phosphoranes. 5. Chemistry and Stereochemistry of Tetraalkylphosphoranes, $CH_3(CF_3)_3PX$, with One Methyl Group and Monofunctional [F, Cl, OCH_3, SCH_3, $N(CH_3)_2$] Substituents[1]

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Methylation of $(CF_3)_3PF_2$ with tetramethyltin or $(CF_3)_3PX_2$ (X = F, Cl) with tetramethyllead gave the tetraalkylphosphoranes, $CH_3(CF_3)_3PX$, which, according to the NMR spectra, are best formulated as five-coordinate phosphoranes rather than isomeric phosphonium salts. NMR (^{19}F, ^{31}P, and ^{13}C) spectroscopic studies at low temperatures consistently indicate that the halogen, F or Cl, occupies an axial position in an assumed trigonal-bipyramidal structure and that the methyl group resides in the trigonal plane giving a ground-state structure with one axial and two equatorial CF_3 groups. Metathetical substitution of the halogen with groups Y (Y = OCH_3, SCH_3, $N(CH_3)_2$) using $(CH_3)_3SiY$ reagents or $(CH_3)_2NH$ gives the derivative phosphoranes $CH_3(CF_3)_3PY$ which, according to NMR (^{19}F, ^{31}P) spectroscopic studies at appropriate temperatures, have ground-state structures in which Y and CH_3 reside in the equatorial plane of the trigonal bipyramid placing one CF_3 group in an equatorial position and two CF_3 groups in axial positions. In general CF_3 environments are averaged by an exchange process with barriers, as indicated by coalescence temperatures, decreasing in the order $N(CH_3)_2$ > SCH_3 > OCH_3 >> F > Cl. The different CF_3 environments in $CH_3(CF_3)_3PN(CH_3)_2$ are observed at normal room temperatures. Other mass, ^1H NMR, and infrared spectroscopic data are reported as well as the hydrolytic behavior of the phosphoranes.

Introduction

While many derivatives of five-coordinate phosphorus are known, there are few examples in which more than three carbon atoms are bound to phosphorus and, of these, alkyl substituents are very rare.[2] In contrast, fully alkylated three- and four-coordinate phosphorus derivatives are well-known.[3] As part of a study of the substitutional chemistry and dynamic stereochemistry of five-coordinate phosphorus we have now prepared and studied a series of tetraalkylphosphoranes[4] containing one CH_3 group, three CF_3 groups, and one of the monofunctional substituents F,[5] Cl,[5] OCH_3,[5] SCH_3, or $N(CH_3)_2$.

Although the usual methylation reagents[6] (CH_3Li, CH_3MgX, and $Hg(CH_3)_2$) have been employed on occasion to methylate phosphines,[7,8] widespread application of these reagents to produce methylphosphoranes has not been undertaken. One potential source of difficulty is the reactivity of the methylation reagent as exemplified by the formation of the ylide $(CH_3)_3PCH_2$ with $LiCH_3$.[9] Another constraint of particular importance to the chemistry of (fluoroalkyl)phosphorus derivatives is the possibility of halogen abstraction by the electropositive metal atom of the alkylating reagent. This latter potential difficulty can be avoided by the use of tetramethyltin and tetramethyllead wherein the metal possesses a reasonably high electronegativity. Tetramethyllead, which is a more reactive methylating agent than the tin compound as a result of the weaker Pb–C bond, has not been extensively used as a methylation agent although it has been shown to be an effective reagent in the case of boron.[10] Both of these reagents are effective but relatively mild methylation reagents which are volatile and easily handled by standard vacuum techniques. Furthermore, the reactions with these reagents are assisted by the involatility and insolubility of the trimethyltin or the lead halide by-product formed in the reaction.

Tetramethyltin has previously been used to prepare methylated fluoro- and (trifluoromethyl)phosphoranes such as CH_3PF_4,[11] $CF_3(CH_3)PF_3$,[12] $(CF_3)_2CH_3PF_2$,[12] and related derivatives of these compounds, but tetramethyllead has not been previously used to methylate pentacoordinate phosphorus. Until the present study,[5] reported in detail herein, no pentacoordinate (trifluoromethyl)phosphorane containing more than three P–C bonds had been reported.

Results and Discussion

Tetramethyltin was found to be without effect on $(CF_3)_3PCl_2$. In parallel with the previous use of this reagent to prepare CH_3PF_4,[11] $CH_3(CF_3)PF_3$,[12] and $(CH_3)(CF_3)_2PF_2$,[12] however, tetramethyltin converted tris(trifluoromethyl)difluorophosphorane, $(CF_3)_3PF_2$, to methyltris(trifluoromethyl)fluorophosphorane, $CH_3(CF_3)_3PF$, in 82% yield according to eq 1. Equimolar proportions of tetramethyllead (80% in toluene) and the dichlorophosphorane gave, after several days at room temperature, $CH_3(CF_3)_3PCl$ in 69% yield (eq 2), and, under the same conditions, $CH_3(CF_3)_3PF$ was obtained from $(CF_3)_3PF_2$ and a stoichiometric quantity of tetramethyllead. In addition $CH_3(CF_3)_3PCl$ was readily converted to $CH_3(CF_3)_3PF$ in good yield by reaction with SbF_3 at room temperature.

$$(CF_3)_3PF_2 + (CH_3)_4Sn \rightarrow CH_3(CF_3)_3PF + (CH_3)_3SnF \quad (1)$$

$$(CF_3)_3PCl_2 + (CH_3)_4Pb \rightarrow CH_3(CF_3)_3PCl + (CH_3)_3PbCl \quad (2)$$

Reaction of the tetraalkylhalogenophosphoranes with trimethylmethoxysilane or -methylthiosilane[13] gave the corresponding methoxy- or methylthiophosphorane in quantitative yield:

$$\begin{gathered} CH_3(CF_3)_3PX + (CH_3)_3SiE(CH_3) \rightarrow CH_3(CF_3)_3PE(CH_3) + (CH_3)_3SiX \quad (3) \\ [E = O;\ X = F, Cl;\ E = S,\ X = F] \end{gathered}$$

The oxygen derivative formed readily from either the chloro- or the fluorophosphorane. The sulfur derivative was obtained only from the fluorophosphorane and only after several hours of reaction at room temperature. In general, the methoxy derivatives of (trifluoromethyl)phosphoranes appear to be more

Table I. Hydrolysis of Tetraalkylphosphoranes

Compd	Reaction condition	Quantity, g (mmol)	Wt of CF_3H obtained, g (mmol)	Identity of ions in soln[14,15]
$(CF_3)_3CH_3PF$	Neutral	0.166 (0.61)	0.0827 (1.18)	$(CF_3)CH_3PO_2^-$
	Alkaline	0.164 (0.60)	0.0857 (1.32)	$(CF_3)CH_3PO_2^-$
$(CF_3)_3CH_3PCl$	Neutral	0.168 (1.58)	0.0787 (1.12)	$(CF_3)CH_3PO_2^-$
	Alkaline	0.164 (0.57)	0.0800 (1.14)	$(CF_3)CH_3PO_2^-$
$(CF_3)_3CH_3POCH_3$	Neutral	0.142 (0.50)	0.0702 (1.00)	$(CF_3)CH_3PO_2^-$
	Alkaline	0.103 (0.36)	0.0740 (1.06)	$CH_3PO_3^{2-}$
$(CF_3)_3CH_3PSCH_3$	Neutral	0.183 (0.61)	0.0870 (1.24)	$(CF_3)CH_3PO_2^-$
	Alkaline	0.132 (0.44)	0.0926 (1.32)	$CH_3PO_3^{2-}$
$(CF_3)_3CH_3PN(CH_3)_2$	Neutral	0.294 (0.99)	0.1403 (2.00)	$(CF_3)CH_3PO_2^-$
	Alkaline	0.130 (0.44)	0.0920 (1.31)	$CH_3PO_3^{2-}$

easily formed and to be more stable than their fluorophosphorane analogues.[13,14] The thiomethyl derivatives exhibit the reverse trend in that phosphoranes appear to be more stable and more readily formed than the (trifluoromethyl)phosphoranes.

Direct gas-phase aminolysis of $CH_3(CF_3)_3PCl$ sufficed to form the (dimethylamino)phosphorane $CH_3(CF_3)_3PN(CH_3)_2$ in 81% yield.

$$CH_3(CF_3)_3PCl + 2(CH_3)_2NH \rightarrow CH_3(CF_3)_3PN(CH_3)_2 + (CH_3)_2NH_2^+Cl^- \qquad (4)$$

Some secondary reactions occurred as indicated by the formation of a trace amount of fluoroform; however no other identifiable phosphorus compound was obtained.

The halides $CH_3(CF_3)_3PF$ (mp 20–21 °C), $CH_3(CF_3)_3PCl$ (mp 56–57 °C), and $CH_3(CF_3)_3PN(CH_3)_2$ (mp 115–116 °C) are volatile solids; the remaining compounds, $CH_3(CF_3)_3POCH_3$ and $CH_3(CF_3)_3PSCH_3$, are liquids. The compounds are soluble in nonpolar solvents and behave as molecular phosphoranes rather than phosphonium salts, a formulation strongly supported by NMR spectroscopic studies (vide infra).

Neutral hydrolysis of all compounds resulted in the quantitative evolution of 2 mol of fluoroform and the formation of the $CH_3(CF_3)PO_2^-$ ion in solution:[14]

$$CH_3(CF_3)_3PY + 2H_2O \rightarrow 2CF_3H + CH_3(CF_3)PO_2^- + H^+ + HY \qquad (5)$$
$$[Y = F, Cl, SCH_3, OCH_3, N(CH_3)_2]$$

(In the last case $H_2N(CH_3)_2^+$ is formed.) Alkaline hydrolysis of $CH_3(CF_3)_3PY$ (Y = F, Cl) also obeys eq 5 (except of course the H^+ is neutralized) forming 2 mol of CF_3H and the $CH_3(CF_3)PO_2^-$ [14] ion in solution. The remaining substituted phosphoranes (Y = OCH_3, SCH_3, $N(CH_3)_2$), however, liberated 3 mol of CF_3H according to eq 6. The $CH_3PO_3^{2-}$ ion

$$CH_3(CF_3)_3PY + H_2O + 2OH^- \rightarrow 3CF_3H + CH_3PO_3^{2-} + HY \qquad (6)$$

remaining in solution was identified by ^1H NMR.[15] All of the hydrolyses (Table I) were quantitative within the limits of error and provide analytical support for the formulations given.

Mass Spectra. Mass spectral fragmentation patterns are given in Table II and mass measurement data in Table III. No parent ions were observed in the mass spectra of the phosphoranes, a characteristic which is consistent with other five-coordinate phosphorus systems.[1,16] Ions observed were however consistent with the phosphorane formulas. In addition to CF_3 (or PF_2) at *m/e* 69, a prominent ion in the mass spectra of $CH_3(CF_3)_3PY$ [Y = F, OCH_3, $N(CH_3)_2$] was $(CF_3)_3PY^+$ arising from the loss of CH_3. In the cases Y = Cl, $N(CH_3)_2$, and SCH_3 loss of Y gave $CH_3(CF_3)_3P^+$. Relative abundances of $CH_3(CF_3)_3P^+$ were relatively high (Y = Cl (7.22%), Y = OCH_3 (7.0%), Y = $N(CH_3)_2$ (14.3%)) and demonstrated the presence of three CF_3 and one CH_3 group on phosphorus. The identity of each of these ions was confirmed by mass measurement (Table III). The very large relative abundance of $CH_3(CF_3)_2PF^+$ (confirmed by mass measurement) arising from $CH_3(CF_3)_3PF$ (11.4%) relative to the much lower proportions of this ion in the spectra of Y = Cl, OCH_3, SCH_3, and $N(CH_3)_2$ derivatives (5.36, 5.64, 8.50, and 2.5%, respectively) suggests but does not unambiguously confirm the presence of F attached to P in $CH_3(CF_3)_3PF$ because phosphorus bonds are also formed by CF_2 elimination from P–CF_3 compounds.[17] The phosphoranes $CH_3(CF_3)_3PY$ [Y = F, Cl, OCH_3, $N(CH_3)_2$] except Y = SCH_3 also showed prominent ions derived from this loss process. The low relative yields of CF_2 observed in all cases except that in which the parent contained the P–F unit suggests that it is not unreasonable to consider that the prominence of $CH_3(CH_3)_2PF^+$ in the spectrum of $CH_3(CF_3)_3PF$ supports the formulation of the parent molecule as a fluorophosphorane. Supporting the phosphorane formulation of $CH_3(CF_3)_3PCl$ is the prominent peak due to $CH_3(CF_3)_2PCl^+$ (9.55%), and similarly the prominence of $CH_3(CF_3)_2PN(CH_3)_2^+$ (5.9%) in the mass spectrum of $CH_3(CF_3)_3PN(CH_3)_2$ strongly suggests that the parent phosphorane formulation is correct.

Infrared Spectra. Characteristic bands due to the substituents can be readily identified in the gas-phase infrared spectra of the phosphoranes by comparison with other phosphorus compounds containing similar features.[18] Detailed data are given in Table IV. Characteristic of all compounds is the pattern of CF stretching frequencies in the 1230–1100-cm^{-1} region, the CF_3 deformation frequencies in the 750–730- and 575–560-cm^{-1} region and P–C(F) stretching bands in the 515–470-cm^{-1} region. The CH stretch region (3020–2840 cm^{-1}) is complex in most cases due to the variety of CH_3 environments. The presence of a methyl group attached to phosphorus is characterized by absorption bands near 1420, 1300, and 900 cm^{-1} assigned respectively to the P–CH_3 antisymmetric and symmetric stretching motions and CH_3 rocking.[18] Specific molecules may also be identified by their individual characteristic features; $CH_3(CF_3)_3PF$ possesses an intense band at 885 cm^{-1} which is best assigned to ν(P–F),[18] obscuring the much weaker methyl rocking motion. The chloro analogue, $CH_3(CF_3)_3PCl$, has a strong band at 580 cm^{-1}, best assigned to ν(PCl).[18] The methoxyphosphorane $CH_3(CF_3)_3POCH_3$ has a strong band at 1070 cm^{-1} due to P–O–C stretching[18] and the band at 1095 cm^{-1} in $CH_3(CF_3)_3PN(CH_3)_2$ is probably due to $\nu(PNC_2)$[18] although its proximity to the CF stretching frequencies introduces some uncertainty of assignment. The group shift assignments in these rather complicated molecules are only crude approximations since the considerable mixing of the motions which may occur is neglected.

NMR Spectroscopic Studies and the Stereochemistry of Phosphoranes. NMR spectral behavior of these tetraalkylphosphoranes is most satisfactorily interpreted in terms of a basic trigonal-bipyramidal molecular structure analogous to that established[19] for prototypes of these simple molecules. Considerable evidence supports this assumption[1,5,14,19-28] although a recent electron diffraction[28] study of some (trifluoromethyl)chlorophosphoranes suggests that distortions toward square-pyramidal structures may be important in crowded molecules.

Table II. Mass Spectra of Tetraalkylphosphoranes[a]

m/e	$CH_3(CF_3)_3PF$	$CH_3(CF_3)_3PCl$	$CH_3(CF_3)_3POCH_3$	$CH_3(CF_3)_3PSCH_3$	$CH_3(CF_3)_3PN(CH_3)_2$	Assignment[b]
282					0.61[c]	$(CF_3)_3PN(CH_3)_2$
269			0.12[c]			$(CF_3)_3POCH_3$
257	0.6[c]					$(CF_3)_3PF$
254			0.27			$(CF_3)_3PO$
253	4.1[c]	7.22[c]	7.00[c]	3.5[c]	14.33[c]	$(CF_3)_3PCH_3$
252	1.8					$C_4H_2F_9P$
231				4.2[c]		$(CF_3)_2P(CH_3)SCH_3$
228					5.91	$(CF_3)_2P(CH_3)N(CH_3)_2$
221		3.46				$(CF_3)_2P(CH_3)^{37}Cl$
219		9.55[c]	0.63			$(CF_3)_2P(CH_3)^{35}Cl$, $C_3F_7H_3PO$, C_3F_8P
216			1.13			C_3F_7PO
215			10.83			$(CF_3)_2P(CH_3)OCH_3$
207	2.0	1.13	0.23	1.5		$(CF_3)_2PF_2$
204			0.18	0.3		C_2F_7OP
203	11.4[c]	5.36	5.64	8.5	2.48	$(CF_3)_2P(CH_3)F$
200				0.2		$C_3H_6F_5PS$
199		1.13				$C_3F_5H_2P^{35}Cl$
185				0.4		$C_2H_3F_5PS$
184		1.52	0.90	0.4		$(CF_3)_2PCH_3$
183	1.6	0.76		0.8		$(CF_3)_2PCH_2$
181				1.0		C_3F_6HP
178					1.81	$C_4H_9F_3PN$
171		0.38				$C_2H_3F_4P^{37}Cl$
169		1.52	0.45			$C_2H_3F_4P^{35}Cl$, C_2F_6P
165		.38	7.22	0.3		$C_3H_6F_4OP$
157	1.6	0.76				CF_3PF_3
154				0.2		$C_2H_4F_5P$
153	13.4	6.46	5.41	8.2	3.49	$C_2H_3F_5P$
147				0.8		$C_2H_3F_3SP$
146			0.23			$C_3H_6F_3OP$
142					1.20	$C_3H_4F_3PN$
134	0.3	1.13	0.90	0.8		$C_2H_3F_4P$
131				2.0	1.09	C_2F_4P
128					4.94	$C_4H_9F_2PN$
121		0.38				$CH_3PF_2{}^{37}Cl$
119		1.52	0.90	0.5		$CH_3PF_2{}^{35}Cl$, CF_3H_3PO
115			7.67	0.5		$C_2H_6F_2OP$
103	17.6	7.22	2.48	8.0	2.65	CH_3F_3P
101		1.52	0.68	0.5		$POF^{35}Cl$, CH_4OF_2P
100		1.13	0.45	0.6	1.09	CF_3P
99		0.38				$C_2H_6F_2P$
97				1.0		CH_3FPS, $C_2H_4F_2P$
95						$C_2H_2F_2P$, CHFPS
94					4.64	C_2H_6FPN
93				0.5		C_2H_6PS
91					0.88	C_2H_3FPN
90					13.86	$(CH_3)_2NPCH_3$
87		0.38				$FP^{37}Cl$
85		1.87				$FP^{35}Cl$,
84	0.5			1.0		CH_3F_2P, H_2PSF
81		2.29	3.86	1.5	1.30	PCF_2
77			2.93	2.0		C_2H_3FP
73				1.0	2.18	C_2H_3PO, C_2H_4NP
69	26.0	20.71	11.28	11.0[d]	13.04	CF_3, PF_2
65	9.3	6.84	9.02	7.1	4.70	CH_3FP
64			0.90	0.5		CH_2FP, CH_5PO
63			0.45	0.7		CH_4OP
61			1.13	0.2		CH_2OP
60					2.29	C_2H_5P,
57				0.2		CPN, C_2H_2P, C_2HS
51		1.52	1.35	1.5	1.49	FPH
50	2.4	1.91	1.35	1.5	0.75	CF_2, PF
48				7.0		CH_4S
47		1.50	5.41	9.2	1.12	CH_4P, PO, CH_3S
46			1.35	1.9		CH_3P, C_2H_6O, CH_2S
45	6.0	4.49	4.51	7.0	1.31	CH_2P, C_2H_5O, C_2H_7N
44		1.52	1.35		1.83	CHP, C_2H_6N
43					3.49	C_2H_5N
42					6.02	C_2H_4N
41					1.44	C_2H_3N
32				0.8		S
31	1.0	2.25	1.80			P, CF

[a] Expressed as percent of total ionization which is the Σ_n of all ions with $m/e \geqslant 30$, with intensity >1% of base peak. [b] Molecular formulas are written for some ions merely for convenience of recognition. [c] Identity confirmed by mass measurement. [d] Ratio CF_3:PF_2 ≈ 2.5:1.

Table III. Mass Measurement Results for Tetraalkylphosphoranes

Compd	Ion	Mass	
		Calcd	Found
$CH_3(CF_3)_3PF$	$(CF_3)_3PF^+$	256.9578	256.9592
	$CH_3(CF_3)_3P^+$	252.9829	252.9843
	$CH_3(CF_3)_2PF^+$	202.9861	202.9850
$CH_3(CF_3)_3PCl$	$CH_3(CF_3)_3P^+$	252.9829	252.9824
	$CH_3(CF_3)P^{35}Cl^+$	218.9565	218.9574
$CH_3(CF_3)_3POCH_3$	$(CF_3)_3POCH_3^+$	268.9778	268.9786
	$CH_3(CF_3)_3P^+$	252.9829	252.9836
$CH_3(CF_3)_3PSCH_3$	$CH_3(CF_3)_3P^+$	252.9829	252.9843
	$CH_3(CF_3)_2PSCH_3^+$	230.9832	230.9844
	$(CF_3)_2PF_2^+$	206.9610	206.9610
	$CH_3(CF_3)_2PF$	202.9861	202.9860
$CH_3(CF_3)_3P[N(CH_3)_2]$	$(CF_3)_3PN(CH_3)_2^+$	282.0094	282.0091
	$CH_3(CF_3)_3P^+$	252.9829	252.9825

A considerable reduction of the number of possible permutational isomers resulting from relative positioning of the substituents in either axial or equatorial positions of the trigonal-bipyramidal framework is achieved if, in agreement with other work,[19-22] which is also supported by recently obtained ^{13}C NMR data on alkyl(trifluoromethyl)phosphoranes[23] and $(CH_3)_4POCH_3$,[24] we consider only those structures in which the CH_3 substituent is constrained to the equatorial plane of the trigonal bipyramid. In the present case, then, only two reasonable alternative ground-state structures for the $CH_3(CF_3)_3PY$ molecules remain (Figure 1) in which the substituent (Y) occupies either an axial (A) or an equatorial (B) location in the molecule according to its relative preference for the axial location. As in related systems[1,22,25-27] dynamic ^{19}F, ^1H and ^{31}P NMR spectroscopy can be used to determine the ground-state structures of the present series of molecules and hence the apical preference of the substituent Y. A summary of the NMR parameters is given in Table V.

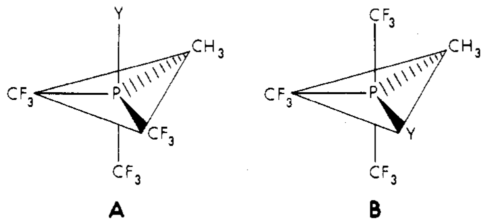

Figure 1. Most probable ground-state structures for $CH_3(CF_3)_3PY$ molecules.

The normal-temperature (+33 °C) ^{19}F NMR spectrum[5] of $CH_3(CF_3)_3PF$ (Figure 2) shows clearly the equivalent CF_3 groups and the unique F. The pattern in each half of the major doublet consists of the central 16–18 lines of a nominal 22-line pattern due to coupling of the single fluorine with nine equivalent fluorine atoms in CF_3 groups and with the methyl protons as a result of a simple relationship between $^3J_{FF}$ and $^3J_{FH}$. The presence of $^1J_{PF}$ and $^3J_{FF}$ coupling constants shows that the single F atom is bound to P thereby supporting the phosphorane structure.

At −90 °C the CF_3 portion of the ^{19}F spectrum of $CH_3(CF_3)_3PF$ (Figure 2) consisted of an overlapping doublet of septets of unit intensity which, according to the relatively small[1,22,25-27] value of $^2J_{PF}$ (35.0 Hz), arises from an axial CF_3 group coupled to P and to six equivalent fluorines of the equatorial CF_3 groups. In contrast to our earlier assignment[5] of a zero value to the $^3J_{FF}$(trans) coupling between the axial

Table IV. Infrared Spectral Data for Tetraalkylphosphoranes[a]

$CH_3(CF_3)_3PF$	$CH_3(CF_3)_3PCl$	$CH_3(CF_3)_3POCH_3$	$CH_3(CF_3)_3PSCH_3$	$CH_3(CF_3)_3P[N(CH_3)_2]$	Assignment
3040 w	3040 vw	3010 w	2900 br, w	3020 vw	
2990 w	2995 vw	2960 w		2960 w	
2930 vw	2910 vw			2930 w	ν_{C-H}
				2880 vw	
				2840 vw	
2300 w					CF overtone
1425 w	1410 vw	1460 w	1450 vw	1460 w	$\nu_{(P)CH}(as)$
				1385 w	δ_{CH}
	1310 vw			1290 w	$\nu_{(P)C-H}(sym)$
1230 vs	1220 vs	1215 sh	1225 s		
1215 vs	1210 vs	1210 vs		1200 s	
	1170 sh	1180 sh	1210 vs		
1170 vs	1160 s	1170 vs	1185 vs	1160 vs	ν_{C-F}
1140 sh		1160 sh	1160 vs	1110 m	
1110 m	1135 vs	1120 vs	1120 w		
	1090 sh		1100 m		
				1095 s	ν_{PNC_2}
			1085 sh		
		1070 m			ν_{PO-C}
980 s	965 s	960 m	965 m	980 m	
	880 m	875 m	865 m, br	870 m	ρ_{P-CH_3}
885 s					ν_{P-F}
		785 m			
785 s	760 m	750 w	750 w	770 m	
760 m					
735 s	730 s		730 m	740 m	$\delta_{C-F}(sym)$
680 vs		655 m	675 m	640 m	$\nu_{P-C(H)}(sym)$
555 m					
575 s		580 m	575 m	560 m	$\delta_{C-F}(as)$
			560 sh		
	570 s				ν_{P-Cl}
515 s	510 m	500 m	510 m		
	490 m		465 m	485 m	$\nu_{P-C(F)}$
			455 sh		
450 s	460 s				
	420 m	445 m	450 m		
410 s	410 m		410 m		

[a] Gas-phase spectra; all values in cm^{-1}: s, strong; m, medium; w, weak; v, very; sh, shoulder; ν, stretching; δ, deformation; e, rocking; sym, symmetric; as, asymmetric; ?, a very tentative assignment.

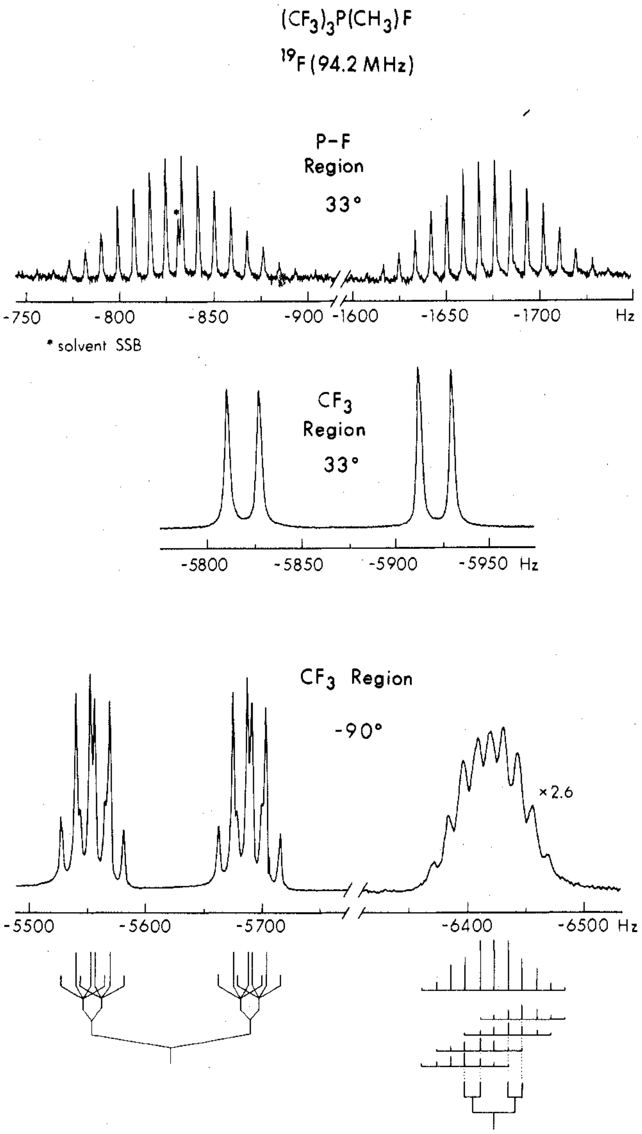

Figure 2. Fluorine-19 NMR spectra of $CH_3(CF_3)_3PF$ at +33 and −90 °C. The scale gives chemical shifts in Hz from CCl_3F, negative values indicating resonance to high field of standard. The band marked with an asterisk in the uppermost spectrum is a solvent spinning sideband. All vertical scales are arbitrary. At −90 °C the vertical scale of the right-hand member due to axial CF_3 is 2.6 times that of the left-hand group due to equatorial CF_3. The origin of the splitting pattern in the −90 °C spectrum is illustrated by the stick diagram at the bottom of the figure.

CF_3 and axial F, a more detailed examination of the axial CF_3 signal suggests that this coupling should be assigned a value of approximately 12 Hz, largely on the grounds of the improved agreement of the calculated[29] and experimental spectra which resulted when this value was included. This is the first reasonable assignment of $^3J_{FF}$(trans) in the (trifluoromethyl)phosphorane system. In previous cases[1,25,27] the axial CF_3 signal has been much too broad and featureless to reveal this minor coupling although there is no a priori reason for trans coupling to be zero.

The remaining and more intense portion of the ^{19}F (CF_3) signal at −90 °C consisted of a double doublet of quartets due to two equatorial CF_3 groups (according to the relatively large value[1,22,25-27] of $^2J_{PF}$ (135 Hz)) split by $^3J_{FF}$(cis) (16.0 Hz) and $^4J_{FF}$ (12.5 Hz) interactions with the axial fluorine and the axial CF_3 group.

The ground-state structure of $CH_3(CF_3)_3PF$ is therefore A (Figure 1), a conclusion which is supported by $^{31}P\{^1H\}$ NMR spectra at −90 °C which clearly showed the expected major doublet due to $^1J_{PF}$ and a septet of quartets in each portion of the doublet due to $^2J_{PF_{ax}}$ and $^2J_{PF_{eq}}$ (Figure 3) confirming the presence of magnetically nonequivalent CF_3 groups in the ratio of 2:1 and confirming the magnitudes of $^2J_{PF}$ coupling constants obtained from the ^{19}F spectrum.

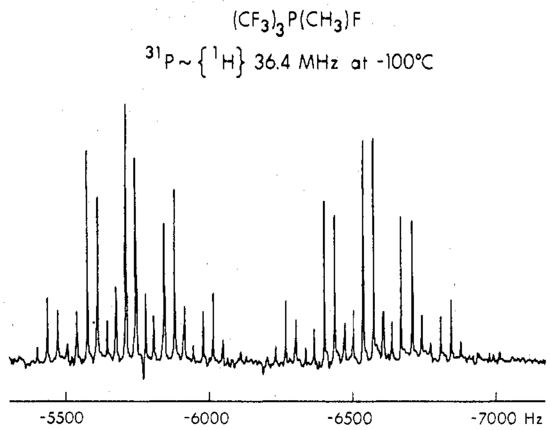

Figure 3. Fourier-transform phosphorus-31 (proton-decoupled) NMR spectrum of $CH_3(CF_3)_3PF$ at −100 °C. The frequency scale gives the shift in Hz (negative offset values indicating resonance to high field) relative to a P_4O_6 reference as calculated from actual heteronuclear lock signals. The spectrum consists of a doublet ($^1J_{PF}$) of septets (due to two equatorial CF_3 groups) of quartets (due to the axial CF_3 group) and the coupling constants are given in Table V.

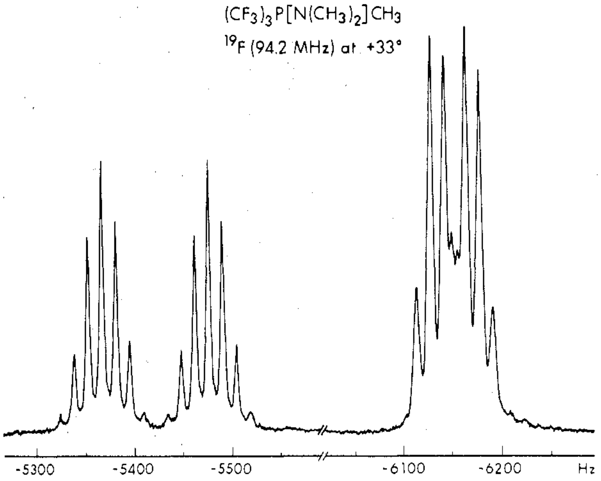

Figure 4. Fluorine-19 NMR spectrum of $CH_3(CF_3)_3PN(CH_3)_2$ at +33 °C. The frequency scale gives chemical shift in Hz, negative offset values indicating resonance to high field of CCl_3F reference.

The normal-temperature (+33 °C) ^{19}F spectrum of $CH_3(CF_3)_3PN(CH_3)_2$ (Figure 4) consisted of two chemically shifted regions with a relative intensity ratio of 2:1. The more intense signal is due to two axial CF_3 groups coupled to phosphorus with a relatively small value of $^2J_{PF}$ (36.5 Hz) and to the fluorine atoms of the unique (equatorial) CF_3 group. Proton coupling was not resolved either because it was complex or because the values were smaller than the resolving capability of the instrument under the conditions employed. The larger $^2J_{PF}$ coupling constant (110.0 Hz) is found in the unit intensity signal and is ascribed[1,22,25-27] to the equatorial CF_3 group. The ground-state structure of the molecule at +33 °C is therefore B (Figure 1). It is notable that the ground-state structure of this molecule is discernible at ordinary temperatures implying a relatively high barrier to the CF_3 averaging process in contrast to the halides where the barrier to the averaging process appears to be much lower.

As might be expected, intermediate behavior was observed for $CH_3(CF_3)_3POCH_3$ and $CH_3(CF_3)_3PSCH_3$ which showed only broad unresolved doublets ($^2J_{PF}$(av)) in the ^{19}F spectra at normal temperatures. Cooling samples of these compounds

Table V. NMR Data

		Chem shifts			Coupling const, Hz		
	Temp, °C	τ^{a}	ϕ^{b}	δ^{c}	$^{2}J_{PF}$	J_{PH}	Other
$CH_3(CF_3)_3PF$	+33	7.89^{d}	$62.3^{e,g}$ $(6)^{h}$	$+164.1^{i}$	102.6	15.4	
			13.3^{f} $(1)^{h}$				$^{1}J_{PF} = 843$, $^{3}J_{FH} = 8.7$, $^{3}J_{FF} = 17.3$
	−90		$59.7^{j,k}$ $(2)^{h}$	$+166.4^{n,o}$	135.5^{j}		$^{3}J_{FF} = 16.0^{p}$
			$68.2^{l,m}$ $(1)^{h}$		35.5^{l}		$^{4}J_{FF} = 12.5$
$CH_3(CF_3)_3PCl$	+33	7.48^{q}	63.3^{r}	$+165.8^{s}$	101.0	12.8	$^{4}J_{FH} = 0.8$
$CH_3(CF_3)_3POCH_3$	+33	$8.10^{q,t}$		$+171.3^{w}$	75.5	11.2^{t}	$^{4}J_{FH} = 0.9$
		$5.97^{q,u}$				12.8^{u}	$^{5}J_{PH} = 0.9$
	+80		67.0^{v}				
	−40		$60.0^{j,x}$ $(1)^{h}$	$+169.9^{n,y}$	108.5^{j}		
			$66.9^{l,r}$ $(2)^{h}$		62.0		
$CH_3(CF_3)_3PSCH_3$	+33	$7.84^{q,t}$	*aa*			11.8^{t}	$^{4}J_{FH} = 0.9$
		$7.76^{q,z}$				20.0^{z}	$^{5}J_{FH} = 1.4$
	−10		$58.9^{j,x}$ $(1)^{h}$	$+167.1^{n,y}$	106.0^{j}		
			$63.5^{l,r}$ $(2)^{h}$		33.5^{l}		
$CH_3(CF_3)_3PN(CH_3)_2$	+33	8.01^{t} $(1)^{h}$	$57.6^{j,x}$ $(1)^{h}$	$+177.3^{n,y}$	110.0^{j}	12.5	$^{4}J_{FH} = 1.0$
		7.10^{bb} $(2)^{h}$	$65.3^{l,r}$ $(2)^{h}$		36.5^{l}	13.3	$^{5}J_{FH} = 1.1$

[a] τ relative to $(CH_3)_4Si$; $\tau = 10.0$. [b] ϕ in ppm from internal CCl_3F, with positive values indicating resonance to high field of standard. [c] δ in ppm vs. P_4O_6;[36] positive values indicate resonance to high field of standard. The chemical shift of 85% H_3PO_4 is +112 ppm vs. P_4O_6. [d] Doublet of doublet of decets. [e] CF_3 resonance. [f] F resonance; predicted 22-line pattern in each component of the doublet due to $^{3}J_{FF}$ and $^{3}J_{FH}$ $(\simeq {}^{1}/_{2}(^{3}J_{FF}))$. [g] Doublet of doublets. [h] Relative intensity. [i] Doublet of decets (central 8 lines observed) of quartets. [j] CF_3 equatorial. [k] Double doublet of quartets. [l] CF_3 axial. [m] Overlapping doublet of septets. [n] $^{31}P\{^{1}H\}$ spectrum. [o] Doublet of septets of quartets. [p] Value for $^{3}J_{FPCF_e}$. An additional value of 12.0 Hz for $^{3}J_{FPCF_a}$ gave much better agreement of the calculated and observed spectra but this value was not clearly revealed in the complex overlapping multiplet. [q] Doublet of decets. [r] Doublet of quartets. [s] Decet of quartets (central 8 lines observed in decet). [t] CH_3 on phosphorus. [u] CH_3O group. [v] Doublet. [w] Decets of septets. [x] Doublet of septets. [y] Septet of quartets. [z] CH_3S group. [aa] Broad doublet; see text. [bb] $(CH_3)_2N$ group.

to −10 and −40 °C, respectively, revealed, in both cases, a signal of unit intensity possessing a septet structure characterized by a relatively large value of $^{2}J_{PF}$ (108.5 and 106.0 Hz, respectively) indicative[1,22,25-27] of an equatorial CF_3 group and a more intense signal which was essentially a doublet of quartets characterized by a relatively small value of $^{2}J_{PF}$ (62.0 and 33.5 Hz, respectively) indicative[1,22,25-27] of axial CF_3 groups. The ground-state structure of both of these molecules is therefore also B (Figure 1). The axial CF_3 signals in both of these compounds have first-order spin-splitting patterns but the small values of $^{2}J_{PF}$ and the similar couplings exhibited by these axial CF_3 groups with the equatorial CH_3 group create either broadened spectra (Y = OCH_3) or a complex group of many overlapping lines. $^{31}P\{^{1}H\}$ spectra at temperatures appropriate for the distinction of axial and equatorial CF_3 environments in particular molecules were easily assigned on a first-order basis assuming that the larger $^{2}J_{PF}$ value could be attributed to the single (equatorial) CF_3 environment and the smaller $^{2}J_{PF}$ value was associated with the equivalent pair of axial CF_3 groups in keeping with the assignments utilized for ^{19}F spectra. Ambiguities arising from the assignment of ^{19}F NMR spectra were resolved by the ^{31}P data. The ground-state structures assigned to the molecules $CH_3(CF_3)_3PY$ (i.e., B) (Y = $N(CH_3)_2$, OCH_3, SCH_3) are consistent with both ^{31}P and ^{19}F NMR spectra. We have also obtained $^{13}C\{^{19}F\}$ NMR spectra of the series $CH_3(CF_3)_3PY$ (Y = $N(CH_3)_2$, OCH_3, SCH_3) which support the assignment of the ground-state structure B. Carbon-13 NMR also clearly supports the assignment of $CH_3(CF_3)_3PF$ to the ground-state structure A.

The consistent relationship between the relative magnitude of $^{2}J_{PF}$ and position in these and all other[1,22,23,25-27] CF_3 phosphoranes so far investigated in which relatively larger values of $^{2}J_{PF}$ are ascribed to equatorially located CF_3 groups and the relatively smaller $^{2}J_{PF}$ values to axial groups seems to be generally obeyed. Location of F in the axial position is of course in keeping with the rule proposed by Muetterties et al.[21] which places the most electronegative group in the axial position. Thus we expect only one axial CF_3 group in this molecule (structure A, Figure 1) and it is notable that the single CF_3 group has a small value of $^{2}J_{PF}$ in this compound. In the compounds in which CF_3 is the most electronegative substituent (Y = OCH_3, SCH_3, $N(CH_3)_2$) the proposed structures are also in keeping with the electronegativity rule[21] and $^{2}J_{PF}$ values are consistent with previously suggested rules.[22,23,25-27] Also in this series the chemical shift values exhibit a regular trend with those values arising from axial CF_3 groups consistently falling to low field of the equatorial CF_3 group signals. Chemical shift trends are not always dependable[22,23,25-27] and the present trend is probably coincidental.

The ground-state structure of $CH_3(CF_3)_3PCl$ was not clearly revealed by either ^{19}F or $^{31}P\{^{1}H\}$ NMR spectroscopic studies because of solubility limitations at low temperatures and yet this is the most interesting member of the series because CF_3 is more electronegative than Cl.[30] The normal-temperature ^{19}F spectrum of $CH_3(CF_3)_3PCl$ showed only the CF_3 doublet with quartet $^{4}J_{HF}$ splitting. Only partial resolution of the ^{19}F spectrum into two very broad overlapping bands with relative intensity 2:1 was achieved at −100 °C, the lowest accessible temperature, which however suggested the presence of distinguishable axial and equatorial environments in the molecule. Because no coupling constant data were obtained, the different chemical shift regions could not be firmly connected to particular CF_3 environments in contrast to the other members of the present series. If the chemical shift trend exhibited by this limited series of molecules prevails for $CH_3(CF_3)_3PCl$, in spite of the generally poor predictability of substituent position by means of CF_3 chemical shift generally found for (trifluoromethyl)phosphoranes,[1,22,23,25,27] we could associate the unit intensity signal which appears to low field of the stronger signal with an axial CF_3 group to tentatively support the reasonable assignment of ground-state structure A (Figure 1) $CH_3(CF_3)_3PCl$. This assignment was strongly supported by the ^{13}C NMR spectrum (Figure 5) at −70 °C which clearly showed two CF_3 regions in a 2:1 intensity ratio, the former characterized by a large $^{1}J_{PC}$ (223 Hz) and the latter by a small $^{1}J_{PC}$ (39 Hz) coupling constant suggesting equatorial and axial environments,[23,24] respectively. Thus the ground-state structure of $CH_3(CF_3)_3PCl$ is A (Figure 1) and Cl appears to prefer an axial position as suggested earlier.[1,22,23,25-27] The electronegativity rule[21] may therefore require modification. The situation is not totally unambiguous however in view of recent electron diffraction results for gaseous $(CF_3)_2PCl_3$ and

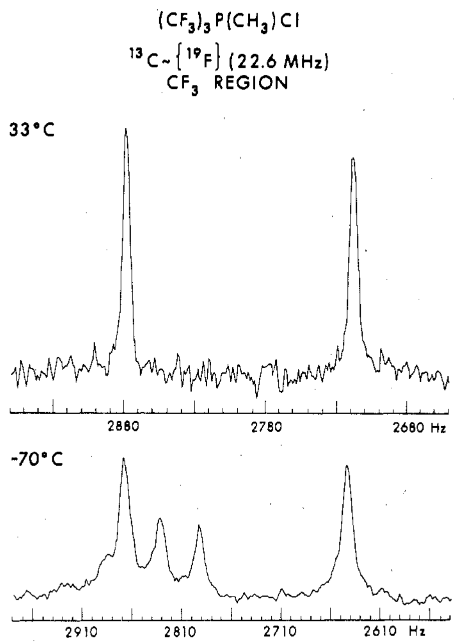

Figure 5. Fourier-transform carbon-13 NMR (fluorine-decoupled) spectrum of the CF_3 portion of $CH_3(CF_3)_3PCl$ at +33 and −70 °C. The former shows an averaged signal whereas the latter shows two groups of peaks with large and small values of ${}^1J_{PC}$ with a relative intensity ratio of 2:1. The scale gives chemical shifts in Hz, positive values indicating resonance to high field, relative to the ${}^{13}C$ signal of the tetramethylsilane reference. Vertical scales are arbitrary, and note that each horizontal scale is different.

$(CF_3)_3PCl_2$ which suggest equatorial Cl placement although some distortion in the framework of the latter was apparent.[28] NQR data for[20b] and a gas-phase vibrational study[20e] of CF_3PCl_4 also suggest equatorial Cl substitution.

Proton NMR spectra of the halides $CH_3(CF_3)_3PX$ at +33 °C show in the case of the fluoride (X = F) a double doublet of decets and in the case of the chloride (X = Cl) a doublet of decets arising from the CH_3 group on phosphorus split by interaction with the phosphorus, the nine equivalent CF_3 fluorines, and, in the case of the fluoride only, a further doubling due to the directly bound fluorine atom attached to P. This latter coupling also directly supports the proposed phosphorane structure. The molecules $CH_3(CF_3)_3PY$ (Y = OCH_3, SCH_3) show two doublets of decets of equal intensity due to the methyl group on phosphorus coupling to phosphorus and nine equivalent fluorine atoms and similarly a signal arising from the substituent methyl group coupled to the same nuclei. The ${}^1H$ spectrum of $(CF_3)_3CH_3PN(CH_3)_2$ is similar in nature except that the amino proton signal is twice as intense as that arising from the CH_3 on phosphorus. The lines in the multiplets are relatively broad and show only an averaged value of long-range ${}^4J_{FH}$ or ${}^5J_{FH}$ coupling constants. The $N(CH_3)_2$ group can be readily identified by means of its relative intensity but the OCH_3 and SCH_3 groups are not readily distinguished from the P–CH_3 signal because the coupling constants (${}^2J_{PH}$ and ${}^3J_{PH}$) are similar, the spin-splitting patterns are identical, and, in the case of the SCH_3 derivative, the chemical shift values are also very similar. We think it reasonable to assign the $\tau \sim 6.0$ signal to the OCH_3 group in $CH_3(CF_3)_3POCH_3$ in keeping with the higher electronegativity of oxygen. Synthesis of the SCD_3 analogue of the SCH_3 compound removed the SCH_3 signal and clearly identified the signal at τ 7.84 as belonging to the PCH_3 function. It is notable that ${}^3J_{PH} > {}^2J_{PH}$ in $CH_3(CF_3)_3POCH_3$, $CH_3(CF_3)_3PSCH_3$, and $CH_3(CF_3)_3PN(CH_3)_2$.

Summary and Conclusions

Except therefore for $CH_3(CF_3)_3PCl$, it was possible to observe clearly distinguishable and identifiable axial and equatorial CF_3 environments by means of ${}^{19}F$ and ${}^{31}P$ NMR spectroscopy at appropriate temperatures and to assign therefrom the ground-state structure. The amino derivative $CH_3(CF_3)_3PN(CH_3)_2$ showed these features in the normal-temperature ${}^{19}F$ and ${}^{31}P$ NMR spectra (+33 °C) whereas the remaining members of the series Y = SCH_3 (−10 °C), Y = OCH_3 (−40 °C), and Y = F (−90 °C) revealed their ground-state structures only at reduced temperatures. The chloro derivative, $CH_3(CF_3)_3PCl$, showed by ${}^{19}F$ chemical shift that different CF_3 environments were present at −100 °C but the identity of these environments and an assignment of the ground-state structure were provided only by ${}^{13}C$ NMR spectroscopy.

The molecules $CH_3(CF_3)_3PY$ (Y = F, Cl) possess ground-state trigonal-bipyramidal structures in which the halogen (F or Cl) preferentially occupies an axial position. No evidence contradicting the assumption that the CH_3 group preferentially occupies the equatorial position was found. The CF_3 groups are distributed between the remaining axial and two equatorial sites to give ground-state structure A (Figure 1). In the case of Y = OCH_3, SCH_3, and $N(CH_3)_2$ compounds, the Y groups also preferentially occupy an equatorial site along with CH_3 leaving two axial sites and one equatorial site for the three CF_3 groups thus leading to ground-state structure B (Figure 1). All of these conclusions except that of the relative preference demonstrated by Cl are in accord with the "electronegativity rule".[21]

The temperature dependence of the NMR spectra of these molecules is most likely due to an intramolecular positional interchange mechanism of the Berry or equivalent[31] type which interchanges CF_3 axial and equatorial environments. The barriers to such interchange, according to approximate coalescence temperatures, decrease in the order $N(CH_3)_2 >$ $SCH_3 > OCH_3 \gg F > Cl$. It is not clear why the Cl derivative should have a much lower barrier than the F derivative and it is possible that different mechanisms of interchange are involved in each of the compounds herein although we think this unlikely. The quantitative aspects of the rearrangement barriers will be discussed in a future publication.

Experimental Section

All reactions were done in sealed tubes and standard vacuum techniques were used throughout. $(CF_3)_3P$,[32] $(CF_3)_3PCl_2$,[32] $(CF_3)_3PF_2$,[33] $(CH_3)_3SiOCH_3$,[34] and $(CH_3)_3SiSCH_3$[35] were prepared according to published methods. $(CH_3)_4Sn$ and $(CH_3)_4Pb$, the latter in 80% toluene solution, were purchased from Alfa Inorganics and used without further purification. Infrared spectra were recorded with a Perkin-Elmer 457 spectrometer in a 9-cm gas cell with potassium bromide windows. Mass spectra were recorded with an AEI MS-9 spectrometer operating at an ionizing voltage of 70 eV. A special inlet device allowed volatilization of the compound at room temperature into the source region through the direct-insertion probe port. Proton and fluorine spectra were recorded at 60.0 and 56.4 MHz, respectively, with a Varian A56/60 or at 100.0 and 94.2 MHz, respectively, with a Varian HA 100 instrument. Phosphorus spectra were recorded with a Bruker HFX-90-Nicolet 1085 spectrometer at 36.4 MHz operating in the pulsed FT mode. All spectra were recorded on samples containing an approximate 10% solution of the compound in $CFCl_3$ and CF_2Cl_2. Fluorine chemical shifts were measured relative to internal $CFCl_3$ solvent or external (capillary) $CFCl_3$ in cases where other solvents were used. Proton and phosphorus chemical shifts were measured relative to external tetramethylsilane (Me_4Si, 10% in CCl_3F capillary) and P_4O_6 (capillary),[36] respectively. Each instrument was equipped with a variable-temperature controller which was established as accurate to within ±1 °C of the indicated temperature by calibration.

Preparation of Methyltris(trifluoromethyl)fluorophosphorane. (a) Tris(trifluoromethyl)difluorophosphorane[33] (1.204 g, 4.36 mmol) and tetramethyltin (0.749 g, 4.18 mmol) were condensed under vacuum into a 50-cm³ tube, which was then sealed. A white solid was formed when the reaction vessel was gradually warmed to room temperature. The reaction mixture was then shaken at room temperature for 2 days. Separation of the reaction mixture by vacuum fractionation yielded $CH_3(CF_3)_3PF$ (0.931 g, 3.42 mmol, 82%), mp 20–21 °C (uncor), which was trapped at −63 °C, and a mixture of additional $(CF_3)_3(CH_3)PF$ and $(CF_3)_3PF_2$ (0.223 g), as shown by its NMR spectrum, which passed −63 °C. $(CH_3)_3SnF$ (0.761 g, 4.17 mmol) remained in the reaction tube. A trace amount of noncondensable gas was also produced.

(b) $(CF_3)_3PF_2$[33] (0.665 g, 2.41 mmol) and $(CH_3)_4Pb$ as an 80% solution in toluene (0.669 g) were treated in a similar fashion. Vacuum fractionation of the products gave an inseparable mixture of volatile compounds of which $CH_3(CF_3)_3PF$ and toluene were the major constituents.

(c) $CH_3(CF_3)_3PCl$ (0.676 g, 2.35 mmol) and freshly sublimed SbF_3 gave, after shaking together for 24 h at room temperature, $CH_3(CF_3)_3PF$ (0.618 g, 2.27 mmol, 97%) as the only volatile product. Anal. Calcd for $C_4H_3F_{10}P$: C, 17.64; H, 1.10; F, 69.85; P, 11.40. Found: C, 17.71; H, 1.03; F, 70.09; P, 10.85.

Preparation of Methyltris(trifluoromethyl)chlorophosphorane. $(CF_3)_3PCl_2$[32] (1.437 g, 4.65 mmol) was combined with an 80% solution of $(CH_3)_4Pb$ in toluene (1.842 g) in a sealed tube. Immediately on warming of the mixture to room temperature a white solid formed. After agitation at room temperature for 1.5 h, the mixture was fractionated to yield $CH_3(CF_3)_3PCl$ (0.960 g, 3.33 mmol, 72%), mp 56–57 °C (uncor) which trapped at −45 °C and a mixture of additional unseparated $CH_3(CF_3)_3PCl$, $(CH_3)_4Pb$, and toluene (0.96 g) which passed the −45 °C trap. A solid residue of $(CH_3)_3PbCl$ (1.345 g, 4.67 mmol) remained in the reaction tube.

The Attempted Reaction of Tris(trifluoromethyl)dichlorophosphorane with Tetramethyltin. $(CF_3)_3PCl_2$ (0.239 g, 0.77 mmol) and $(CH_3)_4Sn$ (0.352 g, 1.96 mmol) were found by NMR spectroscopy to be unchanged after 1 week at room temperature.

Preparation of Methyltris(trifluoromethyl)methoxyphosphorane. (a) From Methyltris(trifluoromethyl)fluorophosphorane. $CH_3(CF_3)_3PF$ (0.214 g, 0.79 mmol) and $(CH_3)_3SiOCH_3$ (0.134 g, 1.29 mmol) were combined in a sealed tube and slowly warmed from −196 °C to room temperature. Separation of the totally volatile mixture of products gave $CH_3(CF_3)_3POCH_3$ (0.223 g, 0.79 mmol, 100%) which collected at −45 °C and a mixture of $(CH_3)_3SiF$ and unreacted $(CH_3)_3SiOCH_3$ (0.126 g) which passed −45 °C. Anal. Calcd for $C_5H_6F_9OP$: C, 21.12; H, 2.11; F, 60.21; P, 10.92. Found: C, 21.13; H, 2.14; F, 60.45; P, 11.02.

(b) From Methyltris(trifluoromethyl)chlorophosphorane. $CH_3(CF_3)_3PCl$ (0.336 g, 1.16 mmol) and $(CH_3)_3SiOCH_3$ (0.167 g, 0.61 mmol) were combined in a sealed tube and allowed to react while slowly warming from −196 °C to room temperature. Separation of the volatile products gave $CH_3(CF_3)_3POCH_3$ (0.330 g, 1.16 mmol, 100%) which collected at −45 °C and a mixture of $(CH_3)_3SiCl$ and unreacted $(CH_3)_3SiOCH_3$ (0.168 g) which passed −45 °C.

Preparation of Methyltris(trifluoromethyl)methylthiophosphorane. No significant reaction was observed between $CH_3(CF_3)_3PF$ (0.459 g, 1.69 mmol) and $(CH_3)_3SiSCH_3$ (0.199 g, 1.66 mmol), after standing in contact at room temperature for 30 min. After 4 h of agitation at room temperature however the reaction mixture gave, upon fractionation, $CH_3(CF_3)_3PSCH_3$ (0.501 g, 1.67 mmol, 99%) which was collected at −30 °C and $(CH_3)_3SiF$ (0.154 g, 1.67 mmol, 100%) in the more volatile fraction. Anal. Calcd for $C_5H_6F_9SP$: C, 20.00; H, 2.00; F, 57.00; S, 10.67; P, 10.33. Found: C, 19.99; H, 1.86; F, 56.70; S, 10.80; P, 10.43.

Preparation of Methyltris(trifluoromethyl)dimethylaminophosphorane. The reaction was done in the gas phase in a rector[37] which consisted of a 1-L bulb with two cold fingers, A and B, one of which (B) was separated from the bulb by a tap. With gaseous $CH_3(CF_3)_3PCl$ (0.534 g, 1.85 mmol) in the bulb at room temperature, dimethylamine vapor (0.240 g, 5.32 mmol) was slowly admitted from the cold finger B by means of the tap. A white solid formed immediately upon contact of the two reagents. After 1-h reaction time to ensure complete conversion, separation of the volatile products gave $CH_3(CF_3)_3PN(CH_3)_2$ (0.471 g, 1.59 mmol, 81%), mp 115–116 °C (uncor), which was trapped at −30 °C and unreacted $(CH_3)_2NH$ (0.075 g, 1.66 mmol) which collected in the more volatile fraction.

Neutral and Alkaline Hydrolysis. All of the compounds were subject to neutral and alkaline hydrolysis. In general approximately 0.5–1.0 mmol of the compound was added to 2 mL of distilled water or NaOH (10%) solution and the reaction tube was sealed under vacuum. All reactions were allowed to proceed at room temperature for 48 h and the resultant CF_3H was separated by vacuum fractionation and weighed. Ions remaining in the hydrolysate were identified by NMR (^1H, ^{19}F) spectroscopy.[14,15] The results are given in Table I.

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Registry No. $CH_3(CF_3)_3PF$, 56396-13-5; $CH_3(CF_3)_3PF$ (ionic form), 63715-51-5; $CH_3(CF_3)_3PCl$, 56420-21-4; $CH_3(CF_3)_3PCl$ (ionic form), 63715-48-0; $CH_3(CF_3)_3POCH_3$, 56350-99-3; $CH_3(CF_3)_3POCH_3$ (ionic form), 63715-47-9; $CH_3(CF_3)_3PSCH_3$, 63715-50-4; $CH_3(CF_3)_3PSCH_3$ (ionic form), 63715-46-8; $CH_3(CF_3)_3P[N(CH_3)_2]$, 63715-49-1; $CH_3(CF_3)_3P[N(CH_3)_2]$ (ionic form), 63715-45-7; $(CF_3)_3PF_2$, 661-45-0; $(CF_3)_3PCl_2$, 420-72-4; $(CH_3)_4Sn$, 594-27-4; $(CH_3)_4Pb$, 75-74-1; $(CH_3)_3SiOCH_3$, 3219-63-4; $(CH_3)_3SiSCH_3$, 3908-55-2; $(CH_3)_2NH$, 124-40-3; SbF_3, 7783-56-4; ^{13}C, 7440-44-0.

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