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Phosphoranes. 3. New Tris(trifluoromethyl)phosphoranes $(CF_3)_3PXY$ with Monofunctional [F, Cl, $N(CH_3)_2$, OCH_3, SCH_3, $OSi(CH_3)_3$] Substituents

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New five-coordinate molecular phosphoranes of the types $(CF_3)_3PY_2$ (Y = OCH_3) and $(CF_3)_3P(F)Y$ (Y = $N(CH_3)_2$, OCH_3, SCH_3, $OSi(CH_3)_3$) have been prepared from $(CF_3)_3PF_2$ and the trimethylsilyl reagent $(CH_3)_3SiY$ or dimethylamine. An improved synthesis of $(CF_3)_3P(Cl)N(CH_3)_2$ is also described. Formulation of the monofluoro- and disubstituted phosphoranes as the isomeric phosphonium salts can be clearly ruled out by NMR spectroscopic studies. At low temperatures, ^{19}F, ^{31}P, and, in the case of $(CF_3)_3P(Cl)N(CH_3)_2$, ^{13}C NMR spectra of the phosphoranes show the presence of different CF_3 environments consistent with substitution at axial or equatorial positions of the (assumed) trigonal-bipyramidal framework. The former are characterized by relatively small $^2J_{PF}$ and the latter by relatively large $^2J_{PF}$ values. Ground-state structures are consistent with the preferential location of halogen (F, Cl) in the axial positions and of OCH_3, SCH_3, or $N(CH_3)_2$ groups in the equatorial positions. The CF_3 groups which occupy the remaining axial and equatorial sites are, in most cases, distinguishable by ^{19}F NMR with only moderate cooling of the sample. New ^{31}P NMR data for $(CF_3)_3P[N(CH_3)_2]_2$ strongly support the location of both $N(CH_3)_2$ groups in the equatorial plane as suggested earlier. The barrier to the averaging of CF_3 environments appears to decrease in the order $N(CH_3)_2 > SCH_3 > OCH_3$. The presence of a halogen substituent appears to lower the barrier to the averaging process compared to the doubly substituted molecules and a chlorophosphorane appears to have a lower barrier than the corresponding fluorophosphorane.

Introduction

Various substituted trifluoromethyl(dialkylamino)phosphoranes have been previously obtained[1,2] from the well-known tris(trifluoromethyl)chloro- and -fluorophosphoranes $(CF_3)_3PX_2$ (X = F,[3] Cl[4]) by means of simple substitution reactions. It appears that the barriers to positional interchange processes[5] such as Berry pseudorotation or Turnstile rotation which render CF_3 environments indistinguishable are relatively high in these derivatives and distinct axial and equatorial CF_3 environments in the trigonal-bipyramidal framework can be readily resolved. The relative preferences for axial and equatorial substitution can therefore be deduced from the resultant ground-state structures.[1,2,6] In some cases, exemplified by the very low-temperature NMR spectra of $(CF_3)_3P[N(CH_3)_2]_2$[1] and $(CF_3)_3P[OSi(CH_3)_3]_2$,[7] the ^{19}F NMR spectra become very complex presumably because additional averaging processes such as P–N or P–O bond rotation, inversion at nitrogen, etc. cease, destroying the averaged magnetic environments in the molecule and creating detectable inequivalencies. In an effort to understand the chemical and stereochemical properties of five coordinate phosphorus compounds, we have embarked on a study of variously substituted phosphoranes[8] and report herein the properties of several derivatives of tris(trifluoromethyl)phosphorane, $(CF_3)_3PXY$, containing a combination of monofunctional substituents such as F, Cl, OCH_3, SCH_3, $N(CH_3)_2$, and $OSi(CH_3)_3$.

Results and Discussion

A. Synthesis and Characterization. Trimethyl(dimethylamino)silane gave only the monosubstituted chlorophosphorane $(CF_3)_3P(Cl)N(CH_3)_2$ when treated with $(CF_3)_3PCl_2$ (eq 1)

$$(CH_3)_3SiN(CH_3)_2 + (CF_3)_3PCl_2 \rightarrow (CF_3)_3P(Cl)N(CH_3)_2 + (CH_3)_3SiCl \qquad (1)$$

regardless of reacting ratio in contrast to the behavior of dimethylamine which gave both $(CF_3)_3P(Cl)N(CH_3)_2$ and $(CF_3)_3P[N(CH_3)_2]_2$ according to the conditions employed.[1] The silylamine therefore provides the superior synthetic route to $(CF_3)_3P(Cl)N(CH_3)_2$.[1]

Controlled aminolysis of the difluorophosphorane $(CF_3)_3PF_2$ in the gas phase at ordinary temperatures gave the monofluoroaminophosphorane, $(CF_3)_3P(F)N(CH_3)_2$, in 55% yield assuming[9] eq 2 is obeyed. The reaction is, however, clearly more complex because a small amount of fluoroform which indicates loss of CF_3 substituents was formed and also because some $(CF_3)_3PF_3^-$, which presumably arises from a competitive addition of the unreacted fluorophosphorane to F^- during the course of the aminolysis, was observed (see eq 3). In addition,

$$2(CF_3)_3PF_2 + 3(CH_3)_2NH \rightarrow 2(CF_3)_3P(F)N(CH_3)_2 + (CH_3)_2NH_2^+HF_2^- \qquad (2)$$

$$(CF_3)_3PF_2 + F^- \rightarrow (CF_3)_3PF_3^- \qquad (3)$$

the appearance of a species tentatively identified as $(CF_3)_3PN(CH_3)_2^+$ in the solid residues suggests that part of the reason for the low yield may be ascribed to the formation of the involatile isomeric phosphonium salt $(CF_3)_3PN(CH_3)_2^+F^-$, which may be further stabilized by the large substituted trifluoromethylfluorophosphate anion also present.

Trimethylmethoxysilane and -methylthiosilane, ($(CH_3)_3SiOCH_3$ and $(CH_3)_3SiSCH_3$), provided efficient conversion of the halogenophosphoranes to methoxy or methylthio derivatives under mild (i.e., room temperature or below) reaction conditions. In general, the reactions proceeded similarly to the analogous reactions of these reagents and PF_5 or organofluorophosphoranes as described by Schmutzler et al.[10,11] Thus $(CH_3)_3SiOCH_3$ converted $(CF_3)_3PCl_2$ to the disubstituted phosphorane $(CF_3)_3P(OCH_3)_2$ (eq 4, X = Cl)

$$(CF_3)_3PX_2 + 2(CH_3)_3SiOCH_3 \rightarrow (CF_3)_3P(OCH_3)_2 + 2(CH_3)_3SiX \quad (X = F, Cl) \qquad (4)$$

and no partially substituted product was obtained. If equimolar reactant proportions were employed, the difluorophosphorane was efficiently converted to the monoalkoxyfluorophosphorane

$$(CF_3)_3PF_2 + (CH_3)_3SiOCH_3 \rightarrow (CF_3)P(F)OCH_3 + (CH_3)_3SiF \qquad (5)$$

and the use of a twofold molar ratio of $(CH_3)_3SiOCH_3$ resulted in complete conversion of the difluorophosphorane to the dimethoxyphosphorane according to eq 4 (X = F). Iodine appears to play a catalytic role in these reactions since in the presence of I_2 both mono- and disubstituted methoxyphosphoranes were formed from an equimolar ratio of $(CH_3)_3SiOCH_3$ and $(CF_3)_3PF_2$ in contrast to iodine-free systems which obeyed eq 5.

Only the mono(methylthio)fluorophosphorane, $(CF_3)_3P(F)SCH_3$, was obtained by treatment of $(CF_3)_3PF_2$ with $(CF_3)_3SiSCH_3$ at low temperatures

$$(CF_3)_3PF_2 + (CH_3)_3SiSCH_3 \rightarrow (CF_3)_3P(F)SCH_3 + (CH_3)_3SiF \qquad (6)$$

This phosphorane was unstable and decomposed at room

Table I. Hydrolysis of Phosphoranes

	Conditions	Quantity of compd, g (mmol)	Yield of CF_3H, g (mmol)	Ions remaining[13] in hydrolysate
$(CF_3)_3P(F)N(CH_3)_2$	Neutral	0.127 (0.42)	0.029 (0.41)	$(CF_3)_2PO_2^-$
	Alkaline	0.147 (0.49)	0.066 (0.94)	$CF_3PO_3^{2-}$
$(CF_3)_3P(OCH_3)_2$	Neutral	0.131 (0.44)	0.031 (0.45)	$(CF_3)_2PO_2^-$
	Alkaline	0.096 (0.32)	0.045 (0.64)	$CF_3PO_3^{2-}$
$(CF_3)_3P(F)OCH_3$	Neutral	0.146 (0.51)	0.035 (0.50)	$(CF_3)_2PO_2^-$
	Alkaline	0.121 (0.42)	0.058 (0.83)	$CF_3PO_3^{2-}$
$(CF_3)_3P(F)SCH_3$	Neutral	0.131 (0.43)	0.030 (0.42)	$(CF_3)_2PO_2^-$
	Alkaline	0.091 (0.30)	0.041 (0.58)	$CF_3PO_3^{2-}$

temperature to $(CF_3)_3P$, $(CF_3)_3PS$, $(CF_3)_3PF_2$, and CH_3SSCH_3 plus some as yet unidentified solid. Attempts to prepare $(CF_3)_3P(SCH_3)_2$ were unsuccessful and no evidence was found for the formation of this compound in a reacting system of $(CF_3)_3PF_2$ and $(CH_3)_3SiSCH_3$ followed by ^{19}F NMR spectroscopy. Reaction of $(CH_3)_3SiSCH_3$ with $(CF_3)_3PCl_2$ gave only $(CF_3)_3P$, $(CH_3)_3SiCl$, and CH_3SSCH_3. The observed products suggest that the desired bis(thiomethyl)phosphorane may have been formed but subsequently decomposed at the reaction temperature. It is interesting to note that the methylthiofluorophosphoranes seem to be more stable than methoxyfluorophosphoranes[11] whereas the reverse order of stability appears to prevail in the trifluoromethylphosphorane system. The trifluoromethylphosphoranes are however more easily reduced than fluorophosphoranes and this may influence the relative stabilities. In this connection it is also worth noting that none of the disulfides $(RS)_2$ (R = CF_3, CH_3, C_6H_5) react with $(CF_3)_3P$ under reasonable conditions suggesting that they are not capable of oxidizing $(CF_3)_3P$ to a phosphorane.[12]

The treatment of $(CF_3)_3PF_2$ with $[(CH_3)_3Si]_2O$ gave tris(trifluoromethyl)fluorotrimethylsiloxyphosphorane, $(CF_3)_3P(F)OSi(CH_3)_3$, which was unstable and was only identified spectroscopically. This compound decomposed quickly to give as the ultimate products of the reaction, $(CF_3)_3PO$ and $(CH_3)_3SiF$. The reaction probably proceeds in two steps according to eq 7 and 8. No evidence for the

$$(CF_3)_3PF_2 + (CH_3)_3SiOSi(CH_3)_3 \rightarrow (CF_3)_3P(F)OSi(CH_3)_3 + (CH_3)_3SiF \qquad (7)$$

$$(CF_3)_3P(F)OSi(CH_3)_3 \rightarrow (CF_3)_3PO + (CH_3)_3SiF \qquad (8)$$

formation of the known bis(trimethylsiloxy)phosphorane $(CF_3)_3P[OSi(CH_3)_3]_2$[7] was obtained although this compound might have been expected by analogy with the reactions of $(CH_3)_3SiOCH_3$ discussed above. It seems reasonable to suggest that the phosphorane $(CF_3)_3P[OSi(CH_3)_3]_2$ can only be obtained if the phosphorus atom possesses no halogen substituents; otherwise inter- or intramolecular halogen transfer to form trimethylsilyl halide and the phosphoryl derivative is favored.[7]

Alkaline hydrolysis of the stable new phosphoranes gave, in general, 2 molar equiv of fluoroform, leaving the $CF_3PO_3^{2-}$ anion[13] in solution (eq 9). Neutral hydrolysis yielded 1 molar equiv of fluoroform leaving the $(CF_3)_2PO_2^-$ anion[13] in solution (eq 10). Both reactions are characteristic[4] of pentavalent trifluoromethylphosphorus compounds and provide quantitative characterization. Data are given in Table I.

$$(CF_3)_3P(X)(Y) + 3H_2O \rightarrow CF_3PO_3^{2-} + 2CF_3H + 2H^+ + HX + HY \qquad (9)$$

$$(CF_3)_3P(X)(Y) + 2H_2O \rightarrow (CF_3)_2PO_2^- + CF_3H + H^+ + HX + HY \qquad (10)$$

(a) $X = F$; $Y = OCH_3, SCH_3, N(CH_3)_2$

(if $Y = N(CH_3)_2$, $H_2N(CH_3)_2^+$ is formed)

(b) $X = Y = OCH_3$

Table II. Mass Spectral Data

	Intensity[a]				
m/e	$(CF_3)_3P(OCH_3)_2$	$(CF_3)_3P(F)(OCH_3)$	$(CF_3)_3P(F)(SCH_3)$	$(CF_3)_3P(F)N(CH_3)_2$	Assignment[b]
261	6.41	1.76			$(CF_3)_3POCH_3$
257		8.81		0.20	$(CF_3)_3PF$
254			0.32		$(CF_3)_2PF_2(SCH_3)$
251				0.10	$(CF_3)_2PF_2[N(CH_3)_2]$
238		0.34			$(CF_3)_3P$
235			0.06		$(CF_3)_2PF(SCH_3)$
232				2.46	$(CF_3)_2PF[N(CH_3)_2]$
231	10.03				$(CF_3)_2P(OCH_3)_2$
219	2.22	13.35			$(CF_3)_2PF(OCH_3)$
218				1.08	$(CF_3)_2PF[N(H)CH_3]$
207		6.57		2.12	$(CF_3)_2PF_2$
200	0.29				$(CF_3)_2P(OCH_3)$
182				12.79	$(CF_3)F_2PN(CH_3)_2$
181	4.55				$CF_2(CF_3)POCH_3$
169	2.80	17.79			$(CF_3)PF_2(OCH_3)$, $(CF_3)_2P$
166	0.45		0.75		$CF_2(CF_3)PO$, $CF_3P(F)SCH_3$
162				1.08	$CF_3PNC_2H_5$
157				6.89	CF_3PF_3
150				1.08	CF_3PCF_2
147		0.51			C_2F_4PO
135	0.58	1.12	0.63		$CF_3P(F)O$, F_3PSCH_3
132				15.49	$F_3PN(CH_3)_2$
131	5.48				CF_3POCH_3
119	4.00	12.22	4.01	2.31	CF_3PF
112				1.52	C_2F_3P
100	2.22		4.01	1.13	CF_3P
97	0.80				CF_2PO
94				1.87	$FPN(CH_3)_2$
93	1.98				$P(OCH_3)_2$
81	11.31	9.66			CF_2P, $FPOCH_3$
78				0.89	$FPNCH_2$
77	5.48		4.30		$CFPCH_3$, PO_2CH_2, $PSCH_2$
73	1.46				POC_2H_2
69	13.30	17.61	18.35	28.63	CF_3, F_2P
63	1.41				$HPOCH_3$
51				1.43	HPF, HCF_2
50	1.62	1.79	1.75	1.43	CF_2, PF
49			1.75		SCH_5
48			18.35		$HSCH_3$
47	9.10	6.82	13.76	3.15	$HPCH_3$, PO, HPNH
46			3.15		SCH_2
45			12.33		SCH
44			2.64		SC
43				2.16	NC_2H_5
42				8.85	NC_2H_4
33			1.23		SH
32	5.71	0.85	7.17		PH, HCF
31	8.16	2.93		2.41	P, CF, OCH_3

[a] Intensities are expressed as percent total ionization based on the sum of the intensities of ions with *m/e* greater than 30. [b] Assignments of some ions are given in terms of the structural formula for ease of recognition only.

B. Mass Spectra. In common with other pentacoordinate phosphorus compounds,[14] the mass spectra (Table II) of all of the phosphoranes reported herein showed no parent ions. The identities of the largest mass fragments, which were confirmed by accurate mass measurement (Table III), leave no doubt, however, that these fragments arise from the appropriate parent ion through loss of OCH_3 or CF_3 from $(CF_3)_3P(OCH_3)_2$, loss of F or OCH_3 from $(CF_3)_3P(F)OCH_3$, loss of CF_3, CF_2,[15] or F from $(CF_3)_3P(F)SCH_3$, and loss of $N(CH_3)_2$ or CF_2[15] from $(CF_3)_3P(F)N(CH_3)_2$. In all of these phosphorane spectra the most intense peak was that observed

Table III. Mass Measurement Data

Compd	Ion[a]	Calcd *m/e*	Found *m/e*
$(CF_3)_3P(OCH_3)_2$	$(CF_3)_3POCH_3^+$	268.9778	268.9791
	$(CF_3)_2P(OCH_3)_2^+$	231.0009	231.0012
	$(CF_3)_2P(F)(OCH_3)^+$	218.9810	218.9811
$(CF_3)_3P(F)(OCH_3)$	$(CF_3)_3POCH_3^+$	268.9778	268.9778
	$(CF_3)_3PF^+$	256.9578	256.9585
	$(CF_3)_3P^+$	237.9594	237.9594
$(CF_3)_3P(F)(SCH_3)$	$(CF_3)_2P(F)_2(SCH_3)^+$	253.9565	253.9570
	$(CF_3)_2P(F)(SCH_3)^+$	234.9581	234.9572
$(CF_3)_3P(F)N(CH_3)_2$	$(CF_3)_3PF^+$	256.9578	256.9585
	$(CF_3)_2P(F)_2N(CH_3)_2^+$	251.0108	251.0118

[a] A reasonable structural formula rather than the molecular formula is given for each fragment ion for convenience only.

at *m/e* 69 which was principally the CF_3^+ ion with small proportions of the PF_2^+ ion.[15]

The intensity distribution of the ions in the spectrum of $(CF_3)_3P(OCH_3)_2$ suggests that the major fragmentation processes involve cleavage of P–O and P–C bonds to give $(CF_3)_3POCH_3^+$ and $(CF_3)_2P(OCH_3)_2^+$ species. Similarly fragmentation of $(CF_3)_3P(F)OCH_3$ involves preferential loss of OCH_3 and CF_3 rather than loss of the single fluorine atom. In both of the methoxy derivatives, CF_2 elimination was a prominent process.[15] In contrast, ions arising from loss of CF_3 and SCH_3 from $(CF_3)_3P(F)SCH_3$ were either not detectable or were present only in very low abundance. In this spectrum the smaller fragments were dominant reflecting the less stable character of this compound. The more stable fluorophosphorane $(CF_3)_3P(F)N(CH_3)_2$ gave a significant proportion of the ion $CF_3P(F)_2N(CH_3)_2^+$ (*m/e* 182, 12.79%) by means of CF_2 elimination.[15] The ions $CF_3PF_3^+$ (*m/e* 157, 6.9%) and $F_3PN(CH_3)_2^+$ (*m/e* 132, 15.5%) which can also arise from a CF_2 elimination process were similarly abundant in this spectrum.

C. Infrared Spectra. Bands typical of CH_3 and $(CF_3)_3P$ structural units are found in the infrared spectra (Table IV) of the phosphoranes. Assignments indicated therein support the presence of these and other (e.g., C–O–(P) at 1080 cm^{-1} and P–O–(C) at 810 cm^{-1})[16] structural units in the compounds. The latter assignment is somewhat more speculative than the former. In these complicated molecules with low symmetry such group shift analysis must be regarded with caution because of the possibility of extensive mixing of the vibrational modes in the molecule. A particular example of this is presented by $(CF_3)_3P(F)N(CH_3)_2$ which has bands at 750, 720, and 700 cm^{-1} which can be tentatively assigned to the symmetric CF_3 deformation, the P–N stretch, and the P–F stretch (or some other permutation of these assignments), respectively, but each band may well contain elements of all three motions. The assignments given in Table IV, based on qualitative group shift arguments derived from related molecules,[1,16] must be regarded as very tentative.

D. NMR Spectra, Ground-State Structures, and Stereochemical Preferences of Substituents. The ground-state structures of these phosphoranes have been revealed by means of temperature-dependent NMR spectroscopy. In some cases the spectra also confirm the molecular formulas and permit a distinction between the phosphorane and the isomeric phosphonium salt. We assume that the basic structure of these relatively simple molecules is a trigonal bipyramid in keeping with the few examples[17] of this structure in analogous molecules and in agreement with the extensive NMR[18,19] and vibrational[20] spectroscopic studies of closely related molecules. It is worth noting that the only established square-pyramidal phosphorane[21] structures involve bidentate chelate ligands and that characteristic NMR parameters have yet to be established for square-pyramidal geometry.[22]

Table IV. Infrared Spectral Data[a]

$(CF_3)_3P$-$(OCH_3)_2$	$(CF_3)_3$-P(F)-(OCH_3)	$(CF_3)_3$-P(F)-(SCH_3)	$(CF_3)_3$-P(F)[N-$(CH_3)_2$]	Assignment
3040 vw	3020 w			
2990 m	2970 m	2950 m	2960 m	ν(C–H)
2930 vw	2900 vw	2920 w, sh	2940 w, sh	
			2890 w	
2880 w	2860 w	2840 w	2840 w	
		2280 w		
1470 w	1470 w	1440 m	1470 w	$\delta_{asym}(CH_3)$
1360 vw				
1330 w		1330 w	1290 m	$\delta_{sym}(CH_3)$
1215 vs	1225 vs	1220 vs	1210 vs	ν(C–F)
1200 vs	1190 vs	1200 vs	1190 s, sh	
1170 vs	1170 vs		1160 vs	
1130 vs	1145 vs	1100 vs	1130 vs	
			1065 m	
			1010 s	$\nu(PNC_2)$
1085 m	1075 vs			ν(P–O–C)
810 m	820 s			
		850 vw		
760 vw				
740 vw		760 sh	760 sh	
680 m	765 s	745 m	750 s	$\delta_{sym}(CF_3)$(?)
	740 m			
			720 s	ν(PN)(?)
	705 s	690 s	700 s	ν(PF)
		640 s		
610 s	610 s	590 s	600 s	$\delta_{asym}(CF_3)$(?)
		530 m, sh		ν(PS)(?)
520 m	520 m	510 s	515 w	$\nu(PCF_3)$
455 w	425 m	420 m		

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

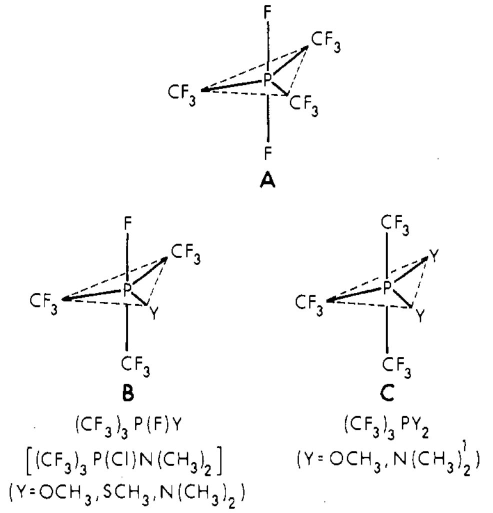

Figure 1. Ground-state structures of the phosphoranes $(CF_3)_3PXY$.

The present series of phosphoranes can be assigned to either structure B (X = F, Y = OCH_3, SCH_3, $N(CH_3)_2$; X = Cl, Y = $N(CH_3)_2$[1]) or structure C (X = Y = OCH_3) (Figure 1). With the exception of $(CF_3)_3P(Cl)N(CH_3)_2$ the ground-state structures of the phosphoranes are those predicted by application of the rule that the most electronegative substituents preferentially occupy the axial positions in the trigonal bipyramid as first proposed by Muetterties et al.[19] We have proposed[6] that Cl, although less electronegative than CF_3,[23] also preferentially occupies the axial position in chlorophosphoranes and that a superior indicator[6] of positional preference is the σ_I value[24] of the substituent. Thus all halogens[25] preferentially occupy the axial positions whereas

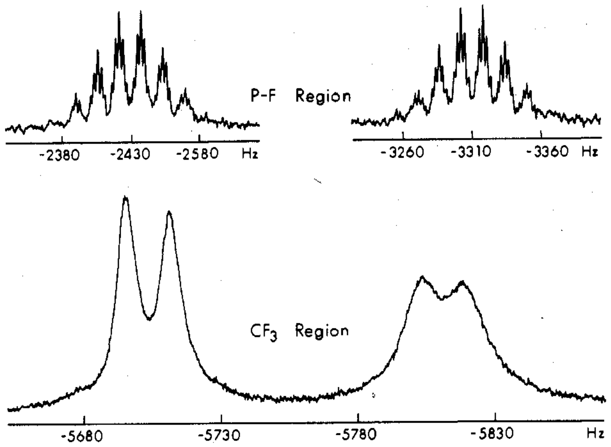

Figure 2. ^{19}F (94.2 MHz) normal-temperature (+33 °C) spectrum of $(CF_3)_3PF[N(CH_3)_2]$ obtained on a solution in CCl_3F. Scale values refer to shifts from CCl_3F in Hz.

substituents such as OCH_3, SCH_3, and $N(CH_3)_2$ prefer equatorial locations[1,2,6] either as a result of their low inductive character (i.e., σ_I is relatively small) or as a result of stronger π interactions between these substituents and phosphorus in the equatorial plane.[26] CF_3 groups, which appear to possess no strong preference for either location, occupy the remaining positions in the five-coordinate molecular framework.

In almost all cases the ground-state structure can be clearly deduced from low-temperature ^{19}F (and ^{31}P) NMR spectroscopy. At normal probe temperatures the ^{19}F NMR spectra of the $(CF_3)_3P(F)Y$ [Y = OCH_3, SCH_3, $N(CH_3)_2$] series of phosphoranes show only two distinct fluorine atom environments due to the three equivalent CF_3 groups and the single fluorine, respectively. The latter signal comprises a doublet of multiplets (see Figure 2) characterized by a large coupling constant (~900 Hz) due to $^1J_{PF}$. The magnitude of $^1J_{PF}$ clearly indicates that the fluorine is directly bound to phosphorus[18] even in the solution state at ordinary temperatures and confirms the phosphorane[8] formulation. Small couplings within each component of the doublet arise from coupling of this single fluorine to the fluorine atoms of equivalent CF_3 groups ($^3J_{FF}$) and to the protons ($^4J_{FH}$) of the fifth substituent. The more intense ^{19}F signal which arises from the equivalent CF_3 groups comprises a major doublet due to $^2J_{PF}$ (~100 Hz) coupling with phosphorus plus smaller couplings to the single fluorine ($^3J_{FF}$) and to the protons. The expected correspondences of coupling constant values are observed in both regions of the spectrum.

Fluorine NMR spectroscopy of the compounds $(CF_3)_3P(F)Y$, (Y = OCH_3, NMe_2, SCH_3) at progressively lower temperatures showed that the signal due to the single fluorine atom was essentially unaffected except for loss of the multiplet fine structure within each component of the major doublet, most probably as a result of increased multiplicity and some broadening due to solvent effects. The signal due to CF_3 resonances collapsed completely at intermediate temperatures to resolve eventually (−80 °C for Y = OCH_3 and −40 °C for Y = $N(CH_3)_2$; see Figure 3) into two chemically shifted regions with 2:1 relative intensity. In both of the above spectra the more intense signal appears as a doublet of quintets due to the equality of $^4J_{FF}$ coupling to the axial CF_3 group and $^3J_{FF}$ (both 15–16 Hz) coupling to the single fluorine. The relatively large value of $^2J_{PF(eq)}$ is clearly shown by the major doublet structure in the stronger signal. The weaker signal is poorly resolved or unresolved in the ^{19}F spectrum at the illustrated and lower temperatures due to the relatively small value of $^2J_{PF(ax)}$; however, even in the less favorable cases of $(CF_3)_3P(F)SCH_3$ and $(CF_3)_3P(F)N(CH_3)_2$ (Figure 4), this value can be unambiguously obtained from the low-temperature ^{31}P spectrum. In general all of the required $^2J_{PF}$ coupling constant data which could not be obtained by ^{19}F NMR spectroscopy alone were provided by proton-decoupled ^{31}P NMR spectroscopy at similar temperatures placing the stereochemical assignments on a relatively firm uniform foundation.

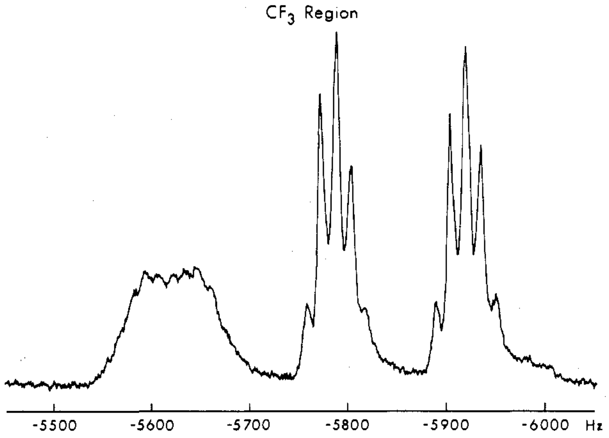

Figure 3. CF_3-region (^{19}F, 94.2 MHz) NMR spectrum of $(CF_3)_3P(F)N(CH_3)_2$ at −40 °C obtained on a solution in CCl_3F. The scale gives shifts from CCl_3F in Hz.

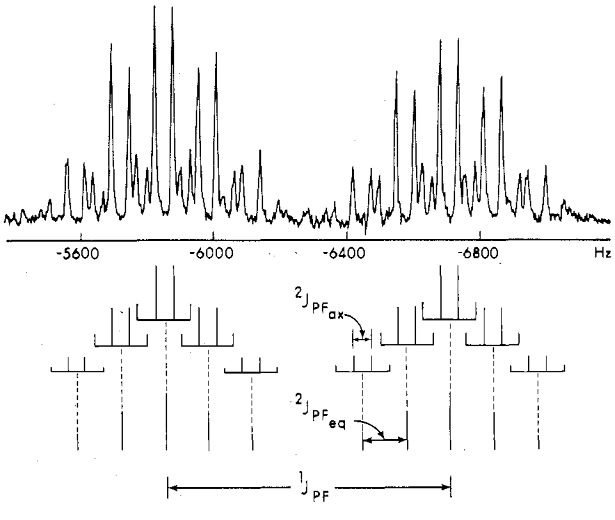

Figure 4. Low-temperature $^{31}P\{^1H\}$ spectrum (36.4 MHz) of $(CF_3)_3P(F)N(CH_3)_2$ obtained at −50 °C on a solution in CCl_3F. The frequency scale gives the shift relative to P_4O_6 but was measured by heteronuclear lock techniques relative to ^2H of CD_2Cl_2. The stick diagram shows the axial and equatorial $^2J_{PF}$ values and the expected pattern arising from the central five lines of the septet.

The low-temperature (−70 °C) ^{19}F NMR spectrum of $(CF_3)_3P(F)SCH_3$ showed overlapping axial and equatorial signals with the latter appearing as a doublet of doublets of quartets superimposed on the broad and poorly resolved signal arising from the axial CF_3 group. Additional complexity in the spectrum arises from this accidental chemical shift coincidence.

All $(CF_3)_3P(F)Y$ (except Y = $OSi(CH_3)_3$ which was not investigated) compounds therefore show two CF_3 environments with a relative intensity ratio of 1:2 at low temperatures as expected for structure B. The weaker signal, characterized by a relatively small value of $^2J_{PF}$, arises from the axial CF_3 group and the stronger signal, characterized by the larger value of $^2J_{PF}$, is associated with the equatorial CF_3 substituents. Note (Table V) that the relative chemical shifts of axial and equatorial groups do not display a consistent relationship to

Table V. NMR Data of Tris(trifluoromethyl)phosphoranes

	Temp, °C	τ^a	ϕ_F,^{b} ppm	ϕ_{CF_3},^{b} ppm (rel intens)	$\sigma_{^{31}P}$,^{c} ppm	$^1J_{PF}$, Hz	$^2J_{PF}$, Hz	$^3J_{PH}$, Hz	$^4J_{FH}$ ($^5J_{FH}$), Hz	$^3J_{FF}$, Hz	$^4J_{FF}$, Hz
$(CF_3)_3P(OCH_3)_2$	+30	6.19^g		63.4^h	+187.0^{f,j}		96.0	13.6	0.8		
	−80			61.7 (1)^{e,h,k}			108.0^k				13.5
				63.6 (2)^{e,i,l}			88^l				
$(CF_3)_3P(F)OCH_3$	+30	6.03^m	50.2^{f,n}	64.4^m	+169.0^{f,n}	912	112.5	13.9	1.2	14.0	
	−80		51.4	63.0 (2)^{e,k,o}	+170.9^{d,q}	909	133.0^k			15.5	12.0
				67.0 (1)^{e,l,p}			72.0^l				
$(CF_3)_3P(F)SCH_3$	+30	7.92^m	1.0^{f,n}	61.7^m	161.5^{f,n}	980	103.7	19.2	2.5 (0.5)	16.5	
	−70		1.1	60.3^{k,o}	161.5^{d,f,q}	973	134.0^{d,k}			r	13.0
				~59.9^r			33.8^{d,l}			r	
$(CF_3)_3P[N(CH_3)_2]_2$	−40			55.6 (1)^z	+152.5^{d,f,x}		107.0^{k,y}				
				57.0 (2)^z			50.8^{l,y}				
$(CF_3)_3P(F)[N(CH_3)_2]$	+30	7.00^{m,s}	30.5^{f,t}	61.1^m	174.7^{f,t}	857	109.0	10.6	2.8 (0.4)	16.0	
	−40		32.3	62.3 (2)^{e,k,o}	175.9^{d,f,q}	849	130.0^k			16.0	16.0
				59.6 (1)^{e,l,p}			54.0^l				
$(CF_3)_3P(Cl)[N(CH_3)_2]$	+30	7.20^g		59.0^{h,z}	156.5^{d,u}		107.0	14.0	0.7		
$(CF_3)_3P(F)OSi(CH_3)_3$^{v}	+30	9.56^w	45.5^{f,g}	66.7^m		979	120.5			13.5	

[a] τ relative to internal tetramethylsilane (τ 10.0). [b] ϕ relative to internal (solvent) CCl_3F standard with positive values indicating resonance to high field of standard. [c] Versus P_4O_6[30] as external standard (capillary), positive values indicating resonance to high field of standard. [d] Obtained from $^{31}P\{^1H\}$ NMR spectra. [e] Relative intensity in arbitrary units. [f] Outermost unit intensity lines not observed, but observed intensity ratio is correct for first-order pattern given. [g] Doublet of decets. [h] Doublet of septets. [i] Doublet of quartets. [j] Decet of septets. [k] CF_3 equatorial. [l] CF_3 axial. [m] Doublet of doublets. [n] Doublet of decets of quartets. [o] Doublet of overlapping doublet of quartets (approximate quintet). [p] Broad doublet (see text). [q] Doublet of septets of quartets. [r] Axial signal is broad and unresolved, and, because of accidental chemical shift equivalence, the signal lies under the equatorial signal. Therefore relative intensities and some coupling constants cannot be obtained from the ^{19}F spectrum. [s] Additional fine structure observed but not resolved clearly. [t] Doublet of decets of septets. [u] Decet. [v] Identified spectroscopically; not isolated. [w] Singlet. [x] Quartet of septets. [y] Values which give best fit of experimental and calculated (NUMARIT[36]) ^{31}P spectrum. [z] Reference 1.

one another even within this limited series. For example the axial CF_3 resonances of unit intensity appear to higher field of equatorial CF_3 resonances of twofold relative intensity in $(CF_3)_3P(F)OCH_3$ whereas the reverse is true in the case of $(CF_3)_3P(F)N(CH_3)_2$; thus no consistent association of CF_3 chemical shift with substituent position is possible. The value of $^2J_{PF}$ however appears to consistently indicate the substituent position in all of the compounds studied herein and previously.[1,2,6]

The $^2J_{PF}$ values assigned to axial and equatorial CF_3 environments in the $(CF_3)_3P(F)Y$ series of compounds are consistent with our suggestion[1] that the structures of the trifluoromethylfluorophosphoranes agree with the electronegativity rule having only equatorial CF_3 groups rather than the inconsistent proposed structures[19] with axial CF_3 substitution for $(CF_3)_2PF_3$ and $(CF_3)_3PF_2$ and an equatorial CF_3 group in CF_3PF_4. The similarity of $^2J_{PF}$ values within the series (CF_3PF_4, 172 Hz; $(CF_3)_2PF_3$, 175 Hz; $(CF_3)_3PF_2$, 167 Hz)[1] and the agreement of these values with the relatively large $^2J_{PF}$ values found both herein and earlier[2] in a series of compounds in which equatorial environments appeared to be clearly distinguished strongly support the proposed assignment of exclusive equatorial CF_3 substitution in the ground-state structures of all three trifluoromethylfluorophosphoranes. The chemical shift arguments used previously[19] appear to be unreliable. The apparent inability of distinguishing axial and equatorial F environments particularly in CF_3PF_4, also used to support the earlier proposed structures,[19] can be understood in terms of a fast positional interchange process with a low barrier, which averages these F environments.

Although further study of $(CF_3)_3P(Cl)N(CH_3)_2$[1] with low-temperature ^{19}F and ^{31}P NMR spectroscopy failed to add any more conclusive evidence to that reported previously,[1] new $^{13}C\{^{19}F\}$ NMR data have provided convincing evidence to support the suggestion that this molecule adopts the ground-state structure B at low temperatures.[25] At 163 K the $^{13}C\{^{19}F\}$ spectrum of the CF_3 groups in $(CF_3)_3P(Cl)N(CH_3)_2$ consists of a pair of doublets with a relative intensity ratio of 2:1. The more intense doublet with the larger coupling constant ($^1J_{PC}$ = 237 Hz) can be confidently assigned to two equatorial CF_3 groups and the doublet of lesser intensity with the smaller coupling constant ($^1J_{PC}$ = 83 Hz), to the single axial CF_3 group since the $^1J_{PC}$ values appear to correlate linearly with $^2J_{PF}$ values[25]. At 233 K, the distinction between axial and equatorial environments is lost and the resultant average value of the coupling constant ($^1J_{PC}$ = 186 Hz) is in good agreement with the weighted average of the above axial and equatorial $^1J_{PC}$ values. Thus Cl appears to occupy the axial position in preference to a CF_3 group, in violation of the electronegativity rule,[19] as we tentatively suggested earlier,[1] and this behavior appears to persist for the chlorophosphoranes[1] and bromophosphoranes[25] supporting our proposed[6] apicophilicity series indicated by σ_I. Also notable is the fact that the barrier to the positional interchange process affecting $(CF_3)_3P(X)N(CH_3)_2$ molecules appears to be significantly lower in the case of X = Cl than for X = F.

The ^{19}F NMR spectrum of $(CF_3)_3P(OCH_3)_2$ (Figure 5) is also temperature dependent and consists, at normal temperatures, of a doublet of septets. The spectrum was transformed into two chemically shifted regions with a 2:1 relative intensity ratio at −80 °C. The twofold intensity region consisted of a well-resolved doublet of quartets, characterized by a relatively smaller value of $^2J_{PF}$, which can be assigned to the axial CF_3 signals. The unit intensity region, which consisted of a doublet of septets (with a slightly skewed intensity distribution within the multiplet pattern) with a relatively larger value of $^2J_{PF}$, can be assigned to the equatorial CF_3 groups. The two OCH_3 groups, which have a low apical preference[1,2,6] or, equivalently, a pronounced preference for location in the equatorial plane, are expected to reside in the equatorial plane forcing two CF_3 groups into the axial positions. The expected ground-state structure is therefore C. Again we consider that positional indication is only reliably provided by $^2J_{PF}$ values and we associate the largest $^2J_{PF}$ values with equatorial CF_3 substituents. In this context, the appearance of the smaller $^2J_{PF}$ value in the most intense ^{19}F signal of $(CF_3)_3P(OCH_3)_2$ in contrast to the $(CF_3)_3P(F)Y$ series where the smaller $^2J_{PF}$ value was found in the least intense ^{19}F (CF_3 portion) resonance signal is consistent with the proposal that the structures consist of two and one axial CF_3 group(s), respectively, in the two systems suggesting that F (and Cl) is preferentially located in the axial position

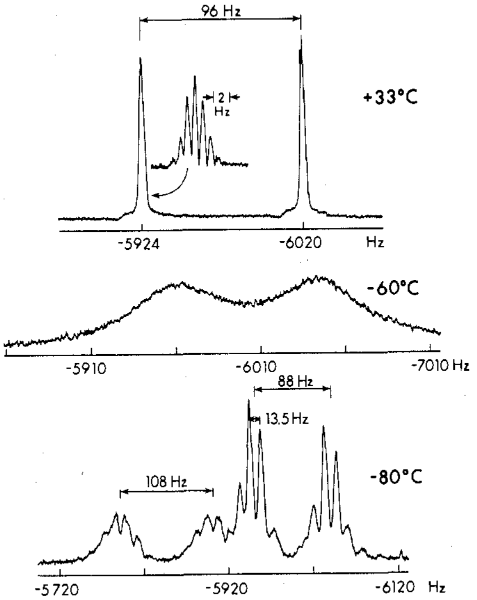

Figure 5. ^{19}F (94.2 MHz) NMR spectra of $(CF_3)_3P(OCH_3)_2$ at +33, −60, and −80 °C obtained on a solution of the compound in CCl_3F. The frequency scale gives shifts (in Hz) from the CCl_3F reference. The inset at +33 °C shows the fine structure present in the peaks at higher resolution.

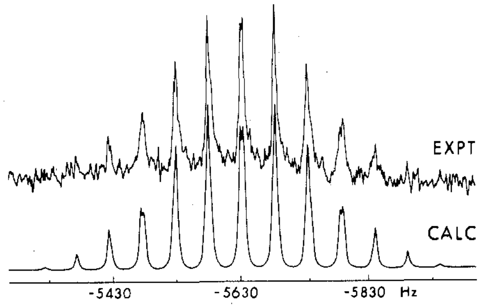

Figure 6. Observed and calculated[36] ($^{31}P\{^1H\}$, 36.4 MHz) NMR spectra of $(CF_3)_3P[N(CH_3)_2]_2$ at −40 °C. The frequency scale gives chemical shift values relative to P_4O_6 (actually measured by heteronuclear lock reference system). The pattern consists of an overlapping septet of quartets due to two axial CF_3 groups ($^2J_{PF}$ = 50.8 Hz) and one equatorial CF_3 group ($^2J_{PF}$ = 107.0 Hz) attached to phosphorus.

whenever it is present in the molecule.

It is unfortunate that solubility and solvent limitations prevented the observation of the $^{31}P\{^1H\}$ NMR spectrum of $(CF_3)_3P(OCH_3)_2$ which would provide additional confirmation of the ^{19}F spectral behavior. We have, however, now obtained the $^{31}P\{^1H\}$ NMR spectrum of $(CF_3)_3P[N(CH_3)_2]_2$[1] at −40 °C (Figure 6) which completely supports the previous conclusions[1] derived from the ^{19}F spectrum in which the ground-state structure C was suggested. The behavior of $(CF_3)_3P(OCH_3)_2$ is similar to that of $(CF_3)_3P[N(CH_3)_2]_2$ including a similar pattern of relative $^2J_{PF}$ values and intensities in both cases. In both molecules, additional effects are observed in the ^{19}F NMR spectra at temperatures below that required to distinguish CF_3 environments. These effects were more readily discernible in the amino compound because of the higher barrier to CF_3 averaging present therein[1] and for this reason further analysis of the ^{19}F spectrum of $(CF_3)_3P(OCH_3)_2$ has not been completed at this time.

Similar additional complexities in the ^{19}F spectra of $(CF_3)_3P(F)Y$ molecules were observed upon cooling the samples to temperatures well below those required to clearly distinguish the CF_3 environments (i.e., <−100 °C). Notable was the broadening of the lines and loss of coupling constant structure in the portion of the spectrum assigned to the axial CF_3 groups, whereas the equatorial portions of the spectrum remained relatively unaffected. At very low temperatures, occasional resolution of the axial signal into a complex multiplet spread over nearly 1000 Hz having similar appearance to the ^{19}F spectra of $(CF_3)_3P[N(CH_3)_2]_2$[1] and $(CF_3)_3P[OSi(CH_3)_3]_2$[7] occurred. We suggest that additional averaging processes such as P–O, P–S, or P–N bond rotation or nitrogen inversion etc. are stopped at these very low temperatures with concomitant cessation of the rotation of the axial CF_3 groups creating, thereby, inequivalent F atoms within the CF_3 group. For steric reasons, the axial CF_3 groups are the more likely to be affected by these restricted rotational processes and this is reflected in the observed collapse of the axial CF_3 portion of the spectrum while the equatorial CF_3 portion is relatively unaffected. Further studies of this phenomenon and of related intramolecular exchange behavior are in progress on simpler systems.[25]

In the absence of detailed line shape analyses and quantitative information establishing the intramolecular character (which we think likely, particularly in the case of disubstituted derivatives such as $(CF_3)_3P(OCH_3)_2$) of the exchange processes, it is premature to speculate further on the nature of the permutational exchange process. Either a Berry or a Turnstile process can account for the observed spectral behavior but at this time we cannot distinguish between these mechanisms or verify their validity.

The ^{1}H NMR spectra of the compounds $(CF_3)_3P(F)Y$ [Y = OCH_3, SCH_3, $N(CH_3)_2$] at normal instrument temperatures (+33 °C) showed a doublet of doublets due to coupling of the protons with ($^3J_{PH}$) and with the single fluorine ($^4J_{FH}$) directly bound to the phosphorus atom. The ^{1}H NMR spectrum of $(CF_3)_3P(OCH_3)_2$ under similar conditions showed a major doublet due to $^3J_{PH}$ coupling. In all cases, each component was further split into decets as a result of coupling of the protons to nine equivalent fluorine nuclei of the three CF_3 groups, thus confirming the presence of three CF_3 groups in the molecules. Very low-temperature ^{1}H NMR spectroscopy of these molecules also suggested onset of inequivalencies arising from frozen molecular conformations as discussed above; however, no clear interpretation could be obtained from these spectra.

Summary and Conclusions

NMR spectra of $(CF_3)_3P(F)X$ derivatives show in all cases a signal due to the single fluorine with a large coupling to phosphorus strongly suggesting that the compounds are correctly formulated as five-coordinate phosphoranes rather than phosphonium salts.

At ordinary temperatures, the CF_3 environments are equivalent. Axial and equatorial CF_3 environments were detected by low-temperature ^{19}F and ^{31}P NMR or, in the case of $(CF_3)_3P(Cl)N(CH_3)_2$, only by very low-temperature (160 K) ^{13}C NMR spectroscopy. The barrier to the CF_3 averaging process increases roughly in the order $(CF_3)_3P(Cl)N(CH_3)_2$ < $(CF_3)_3P(F)(OCH_3)$ ~ $(CF_3)_3P(OCH_3)_2$ < $(CF_3)_3P(F)SCH_3$ ~ $(CF_3)_3P[OSi(CH_3)_3]_2$ < $(CF_3)_3P(F)N(CH_3)_2$ < $(CF_3)_3P[N(CH_3)_2]$[1] as indicated by the approximate coalescence temperatures. At very low temperatures, other dynamic averaging processes cease which further complicates the spectra. In some cases these effects are evident at temperatures required to resolve CF_3 environments so that the axial signals, which are more susceptible to the effects of a conformational interaction, may not be as clearly resolved as equatorial CF_3 enviroments.

All of the ground-state structures are consistent with apical substitutional preferences proposed elsewhere,[6] and the trend appears to be predicted by the σ_I[24] value of the substituent. Since all halogens appear to occupy axial positions in preference to equatorial ones, the compounds $(CF_3)_3P(X)Y$ [X = F, Y = OCH_3, SCH_3, $N(CH_3)_2$ (and presumably $OSi(CH_3)_3$); X = Cl, Y = $N(CH_3)_2$] possess ground-state structures having either F or Cl and one CF_3 in axial positions. The axial CF_3 group is characterized by a relatively low value of $^2J_{PF}$. Two CF_3 groups (characterized by relatively large $^2J_{PF}$ values) are found in the equatorial plane along with the fifth group (Y). When no halogens are present as in $(CF_3)_3P(OCH_3)_2$ (and $(CF_3)_3P[N(CH_3)_2]_2$[1]), two CF_3 groups (with a $^2J_{PF}$ value similar to that of the axial CF_3 group in the above systems) occupy axial positions and the third (with a $^2J_{PF}$ value similar to the equatorial CF_3 groups above) occupies the equatorial plane along with two OCH_3 (or $N(CH_3)_2$[1]) groups. A clear and consistent interpretation of the NMR spectral behavior is obtained for this and related[1,2,6,7] systems if the larger $^2J_{PF}$ values are associated with equatorial CF_3 and the smaller $^2J_{PF}$ values with axial CF_3 substitution. The relative numbers of CF_3 groups can be deduced from the relative intensity of the ^{19}F signal. Chemical shifts vary irregularly and cannot be used to indicate substituent position.

Experimental Section

All reactions were done in sealed tubes using standard vacuum techniques. $(CF_3)_3P$,[4] $(CF_3)_3PCl_2$,[4] $(CF_3)_3PF_2$,[3] $(CH_3)_3SiN(CH_3)_2$,[27] $(CH_3)_3SiOCH_3$,[28] and $(CH_3)_3SiSCH_3$[29] were prepared according to published methods.

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. Proton and ^{19}F NMR spectra were obtained with Varian A56/60 or HA100 spectrometers operating at 56.4 or 94.2 MHz (^{19}F) or at 60 or 100.1 MHz in the case of ^1H. Phosphorus NMR spectra were obtained with a Bruker HFX-90 spectrometer operating at 36.4 MHz in the pulsed FT mode. In general all spectra were obtained on approximately 10% solutions in CCl_3F or CF_2Cl_2 or mixtures of both. Fluorine chemical shifts were measured relative to internal $CFCl_3$ solvent or relative to external (capillary) CCl_3F if other solvents were used. Proton and phosphorus chemical shifts were measured relative to internal tetramethylsilane and an external capillary of P_4O_6 (neat),[30] respectively. Each instrument was equipped with a calibrated variable-temperature controller and quoted temperatures are reliable to ±5 °C.

Hydrolysis. All compounds were hydrolyzed in 10% aqueous NaOH at room temperatures for 48 h and the yields of fluoroform, characterized by infrared and gas-phase molecular weight measurements, are quoted in Table I. Anions remaining in solution were characterized by ^{19}F NMR.[13] The results of neutral hydrolyses are also given in Table I.

Preparation of Tris(trifluoromethyl)chlorodimethylaminophosphorane.[1] Tris(trifluoromethyl)dichlorophosphorane $(CF_3)_3PCl_2$ (0.533 g, 1.73 mmol) and an equimolar quantity of dimethylaminotrimethylsilane $(CH_3)_3SiN(CH_3)_2$ (0.201 g, 1.71 mmoles) were allowed to warm slowly from −196 °C in a sealed tube with agitation. Reaction occurred quickly upon warming to form a white solid at about −10 °C. Separation of the mixture of products under vacuum gave $(CF_3)_3P(Cl)N(CH_3)_2$[1] (0.385 g, 1.21 mmol) trapped at −45 °C and $(CF_3)_3P$[4,31] (0.048 g, 0.20 mmol) trapped at −196 °C. Samples of $(CF_3)_3P(Cl)N(CH_3)_2$ were observed to decompose at room temperatures yielding further amounts of $(CF_3)_3P$ and an unidentified white solid. In a similar fashion $(CF_3)_3PCl_2$ (0.524 g, 1.70 mmol) and an excess of $(CH_3)_3SiN(CH_3)_2$ (0.496 g, 4.24 mmol) gave an undetermined amount of $(CF_3)_3P(Cl)N(CH_3)_2$ collecting in the −45 °C trap, as the only volatile phosphorane product, identified by its ir spectrum, plus an unseparated mixture of $(CH_3)_3SiCl$ and $(CH_3)_3SiN(CH_3)_2$ (0.486 g total, trapped at −78 and −96 °C) in a 1.0:1.5 molar ratio, respectively, according to the integrated ^1H NMR spectrum,[32] and $(CF_3)_3P$[4,31] (0.111 g, 0.47 mmol) which was obtained as the most volatile fraction.

Preparation of Tris(trifluoromethyl)fluorodimethylaminophosphorane. Gaseous dimethylamine (0.162 g, 3.60 mmol) was slowly admitted to a sample of gaseous $(CF_3)_3PF_2$ (0.502 g, 1.82 mmol) contained in a 1-l. gas-phase reactor[9] at room temperature. A white solid formed immediately upon contact of the two vapors. After 1 h at room temperature, separation of the volatile products under vacuum gave tris(trifluoromethyl)fluoro(dimethylamino)phosphorane, $(CF_3)_3P(F)N(CH_3)_2$ (0.301 g, 1.00 mmol), trapped at −45 °C and dimethylamine (0.004 g). The compound $(CF_3)_3P(F)N(CH_3)_2$ was characterized by its spectroscopic properties (ir, Table IV; NMR, Table V; mass spectral data, Tables II and III) and hydrolysis reactions (Table I).

The ^{19}F NMR spectrum of the acetonitrile solution of the remaining white solid showed four multiplets, three of which (centered at 67.0, 90.8, and 99.9 ppm; J_{PF} = 860 Hz) were consistent with those reported[33] for $(CF_3)_3PF_3^-$. The other signal, centered at 54.7 ppm, is tentatively assigned[25] to $(CF_3)_3PN(CH_3)_2^+$.

Preparation of Tris(trifluoromethyl)dimethoxyphosphorane. (a) $(CF_3)_3PCl_2$ (0.264 g, 0.85 mmol) and methoxytrimethylsilane $(CH_3)_3SiOCH_3$ (0.171 g, 1.64 mmol) reacted upon slow warming from −196 °C to room temperature in a sealed tube. Separation of the volatile products gave $(CF_3)_3P(OCH_3)_2$ (0.240 g, 0.80 mmol) trapped at −45 °C, $(CF_3)_3PCl_2$ (0.007 g) trapped at −63 °C, and $(CH_3)_3SiCl$ (0.172 g, 1.58 mmol) trapped at −96 °C. $(CF_3)_3P(OCH_3)_2$ was characterized by its spectroscopic properties (ir, Table IV; NMR, Table V; mass spectral data, Tables II and III) and hydrolysis reactions (Table I).

(b) The reaction of $(CF_3)_3PCl_2$ (0.290 g, 0.94 mmol) with a limited quantity of $(CH_3)_3SiOCH_3$ (0.091 g, 0.87 mmol) gave $(CF_3)_3P(OCH_3)_2$ (0.100 g, 0.33 mmol) and an unseparated, more volatile mixture of $(CF_3)_3PCl_2$, $(CH_3)_3SiCl$, and $(CF_3)_3P(OCH_3)_2$ (0.275 g), all identified by their NMR spectra.[31,32]

(c) $(CF_3)_3PF_2$[3] (0.452 g, 1.64 mmol) and excess $(CH_3)_3SiOCH_3$ (0.406 g, 3.90 mmol) reacted on slow warming from −196 °C to room temperature in a sealed tube. Separation of the volatile products gave $(CF_3)_3P(OCH_3)_2$ (0.489 g, 1.63 mmol) and a fraction which was mainly $(CH_3)_3SiF$[32] contaminated with some unreacted $(CH_3)_3SiOCH_3$ (0.362 g), identified by NMR and ir spectra.

Preparation of Tris(trifluoromethyl)fluoromethoxyphosphorane. (a) Tris(trifluoromethyl)difluorophosphorane $(CF_3)_3PF_2$[3] (0.657 g, 2.38 mmol) and slightly less than 1 molar equiv of $(CH_3)_3SiOCH_3$ (0.201 g, 1.93 mmol) reacted on slowly warming from −196 °C to room temperature. Separation of the volatile products gave tris(trifluoromethyl)fluoro(methoxy)phosphorane $(CF_3)_3P(F)OCH_3$ (0.511 g, 1.77 mmol) trapped at −63 °C and an unseparated mixture of $(CH_3)_3SiF$, $(CF_3)_3PF_2$, and $(CF_3)_3P(F)(OCH_3)$ (0.340 g), all identified by their NMR spectra. The methoxyfluorophosphorane $(CF_3)_3P(F)OCH_3$ was characterized by its spectroscopic properties (ir, Table IV; NMR, Table V; mass spectral data, Tables II and III) and hydrolysis reactions (Table I).

(b) A similar reaction of $(CF_3)_3PF_2$ (0.6242 g, 2.26 mmol) with $(CH_3)_3SiOCH_3$ (0.225 g, 2.15 mmol) plus a trace amount of iodine gave $(CF_3)_3P(OCH_3)_2$ (0.0830 g, 0.28 mmol) which was trapped at −45 °C, $(CF_3)_3P(F)(OCH_3)$ (0.490 g, 1.70 mmol) which was trapped at −63 °C, and an unseparated mixture of $(CH_3)_3SiF$ and $(CF_3)_3PF_2$ (0.226 g) also identified by NMR[19] and infrared spectroscopy.

Tris(trifluoromethyl)fluorotrimethylsiloxyphosphorane. The reaction of $(CF_3)_3PF_2$ (0.898 g, 3.25 mmol) and $[(CH_3)_3Si]_2O$ (0.506 g, 3.13 mmol) was followed by NMR spectroscopy. The spectrum of the freshly prepared sample showed the presence of $(CH_3)_3SiF$ (τ 9.74 (doublet), ϕ_F 155 ppm (doublet), J_{FH} = 8.0 Hz),[32] $(CF_3)_3P{=}O$ (ϕ_F 65.8 (doublet), J_{PF} = 113.0 Hz),[31] and a species which is consistent with $(CF_3)_3P(F)OSi(CH_3)_3$ (see Table V). After 4 h at room temperature, the signals attributed to $(CF_3)_3P(F)OSi(CH_3)_3$ had disappeared leaving $(CF_3)_3PO$ and $(CH_3)_3SiF$ as the only ^{19}F-containing species present in solution.

Preparation of Tris(trifluoromethyl)fluoro(thiomethyl)phosphorane. (a) $(CF_3)_3PF_2$ (0.375 g, 1.36 mmol) and trimethylthiomethylsilane, $(CH_3)_3SiSCH_3$ (0.105 g, 0.88 mmol), reacted in a sealed tube when slowly warmed from −196 to −10 °C. The reaction vessel was kept at −10 °C and the volatile products were removed under vacuum to give tris(trifluoromethyl)fluoro(thiomethyl)phosphorane, $(CF_3)_3P(F)(SCH_3)$ (0.256 g, 0.84 mmol), which was trapped at −45 °C and an unseparated mixture of $(CH_3)_3SiF$ and $(CF_3)_3PF_2$ (0.223 g). The compound $(CF_3)_3P(F)(SCH_3)$ was characterized by its spectroscopic properties (ir, Table IV; NMR, Table V; mass spectral data, Tables II and III) and hydrolysis reactions (Table I). A sample of $(CF_3)_3P(F)(SCH_3)$ (0.3440 g, 1.13 mmol) decomposed on standing at room temperature for 1 week in a sealed tube. The volatile products which were only partly separated by vacuum fractionation were identified as a mixture of CH_3SSCH_3 and $(CF_3)_3P{=}S$ (0.133 g)[34] which was trapped at −78 °C and a more volatile mixture of $(CF_3)_3PF_2$ and $(CF_3)_3P$ (0.177 g) identified by their NMR spectra.[19,31,35] An unidentified yellow-brown solid (0.034 g by difference) remained in the reaction vessel.

(b) A sample of $(CF_3)_3PF_2$ (contaminated with a trace of $(CF_3)_3P{=}O$) (0.185 g, ca. 0.67 mmol) and $(CH_3)_3SiSCH_3$ (0.169 g, 1.41 mmol) were combined in an NMR tube. NMR spectra obtained on the mixture after reaction for 15 min at room temperature showed the presence of $(CF_3)_3P(F)(SCH_3)$ and trace amounts of $(CF_3)_3PO$, $(CH_3)_3SiF$, and $(CH_3)_3SiSCH_3$ but showed no signals which could be assigned to the disubstituted phosphorane $(CF_3)_3P(SCH_3)_2$.

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Registry No. $(CF_3)_3P(OCH_3)_2$, 51874-39-6; $(CF_3)_3P(F)OCH_3$, 59888-71-0; $(CF_3)_3P(F)SCH_3$, 51874-42-1; $(CF_3)_3P[N(CH_3)_2]_2$, 51874-38-5; $(CF_3)_3P(F)[N(CH_3)_2]$, 51874-41-0; $(CF_3)_3P(Cl)[N(CH_3)_2]$, 51874-40-9; $(CF_3)_3P(F)OSi(CH_3)_3$, 59888-72-1; $(CF_3)_3PCl_2$, 420-72-4; $(CH_3)_3SiN(CH_3)_2$, 2083-91-2; dimethylamine, 34285-60-4; $(CF_3)_3PF_2$, 661-45-0; $(CH_3)_3SiOCH_3$, 1825-61-2; $[(CH_3)_3Si]_2O$, 107-46-0; $(CH_3)_3SiSCH_3$, 3908-55-2; ^{31}P, 7723-14-0.

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Thiourea Adducts of Dimethylhaloarsines. Cationic Trivalent Arsenic

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The reaction of dimethylhaloarsines (Me_2AsX; X = Cl, Br) with thiourea (tu) in aprotic solvents yields 1:1 and 1:2 addition compounds which are best formulated as $Me_2As(tu)^+X^-$ and $Me_2As(tu)^+X^-\cdot tu$. The cationic nature of the trivalent arsenic is evidenced by the ir and Raman spectra which show the presence of an As–S linkage but the absence of an As–X linkage. These adducts evolve dimethylhaloarsine when exposed to the atmosphere or when subjected to reduced pressure. The quantitative evolution of arsine was followed by differential thermal and thermogravimetric techniques (DTA, TGA). A stepwise loss of arsine is observed only from $Me_2As(tu)^+Br^-$. The enthalpy changes for the decomposition of adduct to yield tu and arsine are 19.1 and 18.0 kcal mol^{-1} for the 1:2 chloro and bromo adducts and 14.7 and 15.5 kcal mol^{-1} for the 1:1 chloro and bromo adducts.

Introduction

The interaction of thiocarbonyl compounds with trivalent arsenic halides has been studied to a very limited extent. Loh and Dehn[1] prepared the adduct $(PhNH)_2CS\cdot AsBr_3$ which they obtained from a methyl ethyl ketone solution of arsenic tribromide and the substituted thiourea. Only elemental analyses were reported by these authors. From aqueous solution Walter[2] obtained a thiourea adduct with arsenic trichloride in which at least one As–Cl bond was replaced with an As–thiourea bond according to eq 1. Another report[3] described

$$2(NH_2)_2CS + AsCl_3 \xrightarrow{H_2O} [(NH)(NH_2)CS]_2AsCl\cdot H_2O + 2HCl \qquad (1)$$