Phosphoranes. 6. Determination of Ground State Structures of Trifluoromethylphosphoranes by Means of Carbon-13 Nuclear Magnetic Resonance Spectroscopy. The Correlation of $^1J_{PC}$ with the Trigonal-Bipyramidal Site and the Relation between $^1J_{PC}$ and $^2J_{PF}$ of CF_3 Substituents in Phosphoranes

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Abstract: Fluorine decoupled ^{13}C NMR spectra of an extensive series of phosphoranes containing one or more axially and/or equatorially substituted trifluoromethyl groups can be consistently assigned by associating the small value of the $^{31}P-^{13}C(F)$ coupling constant with the axial CF_3 groups and the larger couplings to equatorial environments. The same trend has been previously observed for $^2J_{PF}$ couplings in these and similar compounds. The trend of $^{31}P-^{13}C(F)$ coupling constants can be ascribed to the variation of "s" character in the bond and the dominant effect observed herein is the difference in "s" character between axial and equatorial P-C(F) bonds. Except in one case, $(CF_3)_2P(CH_3)_3$, where $^1J_{PC(F)}$ (axial only) appears to be negative, $^1J_{PC(F)}$ (axial) is probably positive. Relating the observed values of $^1J_{PC(F)}$ to cases where rapid intramolecular exchange or more ambiguous ground states are possible leads to an "apicophilicity" series: $F > Cl > Br > CF_3 > OR, SR, NR_2, R$ which follows the order of σ_I of the substituent rather than the electronegativity. These results, when combined with our previous $^2J_{PF}$ studies, suggest that the ground state structures of monofunctionally substituted phosphoranes can be predicted from the σ_I values of the substituents, those with the largest values preferring axial locations. A new bromophosphorane, $(CF_3)_2PFBr_2$, has been prepared and characterized. $(CF_3)_3P$ and Br_2 establish a reversible oxidative equilibrium. CF_3PBr_4 appears to be best described as the phosphonium salt $CF_3Br_3^+Br^-$ in solution. In addition to the phosphorane data, ^{13}C NMR parameters for nine trifluoromethylphosphines are reported.

The study of the fluxional behavior of substituted fluorophosphoranes and related molecules[1,2] requires a knowledge of the site preferences of the various substituent groups.[3] A qualitative "apicophilicity" series conveniently describes the relative tendency of a specified group to reside in the axial position in the ground state. It is obvious that the use of such a series presupposes a knowledge of the geometry of the phosphorane since a structural change from, say, trigonal bipyramid to square pyramidal renders the application of the rules of "axial preference" meaningless. Such structural studies are beyond the scope of the present work. We can, however, make the reasonable assumption that the trigonal-bipyramidal molecular structure, which has been established for several related phosphoranes,[4] prevails throughout a series involving only halogen, CF_3, CH_3, $N(CH_3)_2$, OCH_3, SCH_3, and similar monofunctional substituents. In fact square-pyramidal phosphorane structures have to date been established only in cases with bidentate substituents.[5]

We have suggested,[3,6-11] on the basis of $^2J_{PF}$ coupling constant values obtained for an extensive series of monofunctionally substituted trifluoromethylphosphoranes, that the previously proposed electronegativity rule of apical substitutional preference,[12a] which states that the most electronegative group will preferentially occupy the axial position in a trigonal bipyramid, must be modified to give the halogens axial preference over other, possibly formally more electronegative, substituents. Furthermore, it appeared[3] that σ_I values[13] were better predictors of axial preference than electronegativity values. Ambiguity remained in those cases in which the CF_3 groups, which provided the $^2J_{PF}$ values, were expected to be stereochemically equivalent exclusively in either axial or equatorial environments, because the spectra were then expected to be temperature independent. Unfortunately, apparent temperature independence may also falsely arise from a very low barrier to permutational interchange. Although a clear assignment of axial or equatorial environment for CF_3 groups could be made in general from the magnitude of $^2J_{PF}$ alone, it was desirable to provide independent support for the assignments. The present application of ^{13}C NMR spectroscopy to many of these monofunctionally substituted trifluoromethylphosphoranes has provided additional support for the apical preference series,[3,6-11] based on ^{19}F and ^{31}P NMR data.

Although there have been several ^{13}C NMR studies on three- and four-coordinate organophosphorus compounds,[14,15] little use has been made of this technique in the study of the stereochemistry of phosphoranes. Our work[16] and recent work of others[17-20] has indicated that the technique possesses considerable promise.

Results and Discussion

1. ^{13}C NMR Spectroscopy of Phosphoranes. The results of fluorine decoupled ^{13}C NMR spectroscopic studies on 22 phosphoranes containing one, two, and three trifluoromethyl groups are given in Table I. Relatively high concentrations (0.7-1.0 g samples in 10 mm o.d. tubes) were necessary because of the lack of significant nuclear Overhauser enhancement of the signals because either coupled nuclei (^{31}P, ^1H) remain in the molecule or quadrupolar or scalar relaxation processes[14] broaden the signals appreciably. The latter process appears to be very important in the case of chlorophosphoranes where the poorest quality spectra were obtained even with very high concentrations of the compound. The concentration or temperature dependence of the $^1J_{PC(F)}$ values was not investigated in detail since (with the exception of the effects due to dynamical averaging of environments discussed below) such effects were small, being typically less than 3 Hz over a 50°C range.

Table I. ^{13}C NMR Parameters of Phosphoranes[a]

Compd	Temp behavior of CH_3 portion of spectrum	Temp of measurement, °C	$^1J_{PC(F)}$[b]		$\delta_{^{13}CF_3}$[c] [intensities]		$^2J_{PF}$[d]			$^1J_{PC(H)}$	$\delta_{^{13}CH_3}$[c]
			Ax	Eq	Ax	Eq	Ax	Eq	(lit.[e])		
1 CF_3PF_4		−40		448		+121.3		170	(172^{22a})		
2 CF_3PCl_4		0		288		+123.6		151	(154^{22a})		
3 CF_3PBr_4		+10		138		+116.7		142			
4 $CF_3PF_2Cl_2$		0		327		+123.5		155	(165^{45})		
5 $(CF_3)_2PF_3$[f]		0		418		+121.3		176	($174–175^{12a,22a}$)		
6 $(CF_3)_2PFCl_2$		0		389		+123.0		183			
7 $(CF_3)_2PCl_3$		0		379		+122.3		190	(193^{22bc})		
8 $(CF_3)_2PBr_3$		0		379		+115.5		182			
9 $(CF_3)_2PFBr_2$		0		336		+120.2		179			
10 $(CF_3)_2P(CH_3)_3$		+33	29		+131.3		6.3			102	+8.6
11 $(CF_3)_2P(CH_3)_2Cl$	Dep.[g]	+30	128[g]		+124.4[g]		79[g]			92	+22.4
12 $(CF_3)_3PF_2$		+31		315		+120.8		167	(167^{22a})		
13 $(CF_3)_3PCl_2$		−20		232		+122.6		139			
14 $(CF_3)_3PBr_2$[h]		−13		201		+120.6		127	(128^{21})		
15 $(CF_3)_3P(CH_3)_2$		+33	<8 (2)	205 (1)	+128.8 [2]	+124.4 [1]	23.5 (2)	114 (1)		88	+8.8
16 $(CF_3)_3P(CH_3)F$	Dep.	−108	17 (1)	258 (2)	+127.4 [1]	+121.1 [2]	35 (1)	135 (2)		100	+27.5
17 $(CF_3)_3P(CH_3)Cl$	Dep.	−70	39 (1)	223 (2)	+124.4 [1]	+121.9 [2]	101[i]			72	+21.1
18 $(CF_3)_3P(CH_3)OCH_3$	Dep.	−70	115 (2)	169 (1)	+126.9 [2]	+123.1 [1]	62 (2)	108.5 (1)		71	+11.4
19 $(CF_3)_3P(CH_3)$-$N(CH_3)_2$		+33	49 (2)	197 (1)	+131.2 [2]	+125.2 [1]	36 (2)	110 (1)		87	+11.7
20 $(CF_3)_3P(CH_3)SCH_3$	Dep.	−90	21.5 (2)	176 (1)	+126.2 [2]	+123.5 [1]	34 (2)	106 (1)		72	+12.5
21 $(CF_3)_3PClN(CH_3)_2$	Dep.	−103	83 (1)	237 (2)	+125.4 [1]	+122.9 [2]	53 (1)	130 (2)			
22 $(CF_3)_3P(CH_3)CN$	Dep.[g]	+33	153[g]		+123.4[g]		69[g]			80	+15.8

[a] Measured in CD_2Cl_2 solution at 22.6 MHz unless otherwise specified. [b] Coupling constant in hertz; numbers in brackets indicate the relative intensities of the signal with indicated $^1J_{PC}$ and $^2J_{PF}$ values. [c] Parts per million from ^{13}C of $(CH_3)_4Si$, positive values indicating shifts to low field of standard. [d] Coupling constants in hertz obtained from ^{31}P and ^{19}F spectra measured in our laboratory. [e] From literature sources as given. [f] 40% $CFCl_3$, 60% CD_2Cl_2. [g] Average of equatorial and axial environments, intramolecular exchange not stopped. Only limited temperature studies were possible because of poor solubilities in common solvents. Not plotted in Figure 1. [h] 30% $CFCl_3$, 70% CD_2Cl_2; compound was immiscible in pure CD_2Cl_2. [i] Average of axial and equatorial environments because averaging process was not stopped in ^{19}F spectrum at lowest accessible temperature.

Many of the compounds listed in Table I can be expected to possess fluxional character typical of five-coordinate trigonal-bipyramidal molecules. In any system there may be a number of stereoisomers suffering permutational interchange and only one structure can be regarded as the most probable ground state structure. At elevated temperatures, if rapid interchange of magnetic environment occurs, only averaged values of parameters are obtained. At reduced temperatures unique magnetic environments may be observed and, if limiting spectra are obtained, parameters typical of each magnetic environment may be assigned. Although the observed parameters may not be exclusively those of the ground state, it is reasonable to assume that the parameters will reflect the dominant contribution from the ground state in all but the most unusual circumstances; hence the observed trends can be used empirically to deduce the ground state geometry of the molecule in the solution state within the lifetime requirements of the NMR experiment.

The barriers to CF_3 permutational exchange are generally higher than those encountered in fluorophosphoranes[12] with

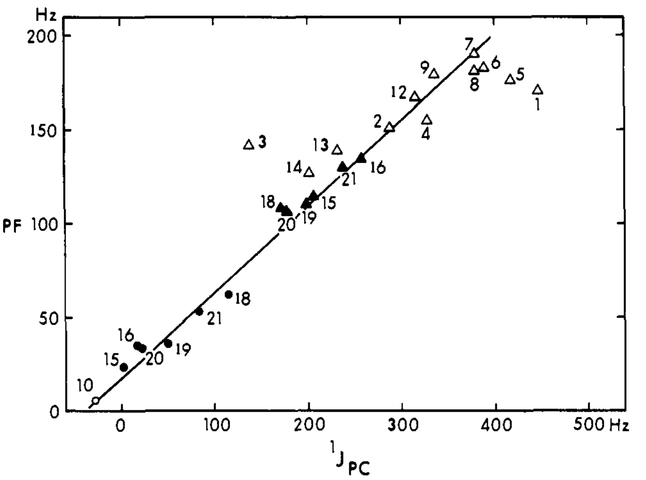
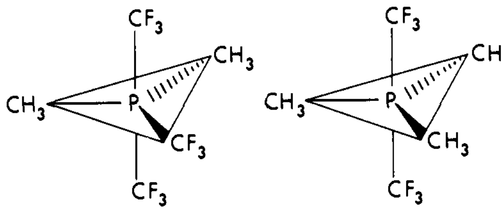
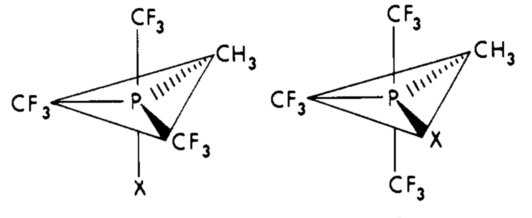


Figure 1. Correlation of ${}^{2}J_{PF}$ with ${}^{1}J_{PC}$ for trifluoromethylphosphoranes. The numbers beside the points correspond to the compounds as listed in Table 1. Axial CF_3 (○ or ●) and equatorial CF_3 (△ or ▲) parameters are deduced as described in the text and correspond to the assignments in Table 1. Filled symbols indicate compounds which provide *both* axial and equatorial CF_3 signals; open symbols indicate that only one CF_3 environment was observed for the compound. The sign of ${}^{1}J_{PC}$ for **10** is taken to be opposite that of all of the remaining ${}^{1}J_{PC}$ values as discussed in the text. Data for compounds **11**, **17**, and **22** were not plotted.[23]



15 **10**

Figure 2. Ground state structures for $(CF_3)_3P(CH_3)_2$ (**15**) and $(CF_3)_2P(CH_3)_3$ (**10**).



A **B**

Figure 3. Alternative ground state structures for $CH_3(CF_3)_3PX$ compounds.

the consequence that relatively modest cooling of the sample is required to distinguish potentially unique CF_3 environments. In view of the ease with which CF_3 permutational exchange can generally be stopped we are confident that we have achieved the necessary limiting spectra to support the identification of the dominant ground state structure. Those dominant ground state structures which were previously tentatively assigned in agreement with our apical preference rules on the basis of the magnitude of the ${}^{2}J_{PF}$ values in cases where the CF_3 portion of the spectrum did not show any apparent temperature dependence now appear to be supported by the present set of ${}^{1}J_{PC(F)}$ values.

2. Correlation of Coupling Constants and Ground State Structures of Phosphoranes. The observed ${}^{1}J_{PC(F)}$ values fall into two distinct ranges: a group of ${}^{1}J_{PC(F)}$ values less than 90 Hz and a group of ${}^{1}J_{PC(F)}$ values greater than 170 Hz with only a few exceptions which can be readily understood. The ${}^{1}J_{PC(F)}$ values can be compared with ${}^{2}J_{PF}$ measurements on the same compound which have been obtained both from the present study and from literature sources.[3,6-12,21,22] It is notable that both parameters exhibit a consistent, generally linear, interdependence as shown in Figure 1 with the serious discrepancies occurring only for those compounds with the highest ${}^{1}J_{PC(F)}$ and ${}^{2}J_{PF}$ values[23] and in the case of **3** (vide infra). It is also notable that averaged ${}^{1}J_{PC(F)}$ and ${}^{2}J_{PF}$ values obtained at ordinary temperatures for fluxional molecules also fall on the line. Following our previous suggestion,[3,6-11] that large ${}^{2}J_{PF}$ values in trifluoromethylphosphoranes arise from equatorially positioned trifluoromethyl groups and small ${}^{2}J_{PF}$ values arise from axially positioned groups, we note that the ${}^{1}J_{PC(F)}$ values parallel this trend and reinforce this association. Similar considerations apply to the few alkylphosphoranes studied by ${}^{13}C$ NMR spectroscopy.[17,20]

We assume that the ${}^{1}J_{PC}$ coupling constant of 128 Hz[20] for $(CH_3)_3PF_2$ is typical of an equatorial CH_3 group. This assumption is supported by electron diffraction studies[4] which have established that, in the gas phase, the related compounds CH_3PF_4 and $(CH_3)_2PF_3$ have trigonal-bipyramidal structures with equatorial CH_3 groups. The ${}^{13}C$ NMR data for methoxytetramethylphosphorane[17] were satisfactorily interpreted in terms of a trigonal-bipyramid molecular structure with three equatorial methyl groups (${}^{1}J_{PC} = 116$ Hz) and one axial methyl group (${}^{1}J_{PC} = 7.3$ Hz). The methoxy group occupied the other axial site. Considering the magnitude of ${}^{1}J_{PC}$ coupling constants to reflect the proportion of "s" character in the P-C bond[14,15,18,24] we suggest that the larger equatorial ${}^{1}J_{PC}$ values indicate a concentration of "s" character in the equatorial molecular plane (i.e., predominant sp^2 hybrid bonding) with concomitantly smaller "s" character in the axial bonds. Additional convincing support is provided by normal temperature ${}^{19}F$, ${}^{31}P$, and ${}^{1}H$ NMR spectra of tris(trifluoromethyl)dimethylphosphorane[16] (**15**), which are best analyzed in terms of a trigonal-bipyramidal molecular structure with two axial CF_3 groups (${}^{1}J_{PC(F)} < 8$ Hz) and one equatorial CF_3 group (${}^{1}J_{PC(F)} = 205$ Hz). The presence of one axial CF_3 environment (${}^{1}J_{PC(F)} = (-)29$ Hz) in bis(trifluoromethyltrimethylphosphorane (**10**), also supported by ${}^{19}F$, ${}^{1}H$, and ${}^{31}P$ NMR spectroscopy,[16] is consistent with this interpretation (Figure 2).

3. Tetraalkylphosphoranes. If we exclude those structures in which the CH_3 group resides in the axial location, there remain two probable molecular structures A and B (Figure 3) for the tetraalkylphosphoranes $CH_3(CF_3)_3PX$ differentiated by the postion of the substituent X. The exclusion of alternative axial CH_3 substituted forms is justified on the grounds that there is no evidence in either our data or that of others to suggest that CH_3 groups can preferentially occupy axial positions where two or more CF_3 or halogen substituents are present in the molecule. Note also that the ${}^{1}J_{PC}$ value arising from the CH_3 group in compounds **10**, **11**, **15–20**, and **22** is more in keeping with equatorial CH_3 substitution than axial CH_3 substitution.[17,20]

The compounds X = F (**16**)[19] and X = Cl (**17**)[10] show temperature dependent ${}^{13}C$ NMR spectra which yield, at low temperatures, two ${}^{13}C$ signals from the CF_3 groups with the relative intensity ratio of 1:2. The former is characterized by a small ${}^{1}J_{PC(F)}$ value and may be assigned to an axial CF_3 group and the latter, characterized by a large ${}^{1}J_{PC(F)}$ value, can be assigned to two equatorial CF_3 groups in the ground state structure A. Arguments based on ${}^{2}J_{PF}$ values reached the same conclusions.[3,10] Limiting spectra obtained at reduced temperatures yielded ${}^{1}J_{PC(F)}$ values for the compounds[10] X = OCH_3 (**18**), X = SCH_3 (**20**), and X = $N(CH_3)_2$ (**19**) and indicated that the ground state structure is B, an assignment which is also supported by analysis of the ${}^{2}J_{PF}$ values.[3,10] More

Table II. ^{13}C NMR Data of Trifluoromethylphosphines[a]

Compd	Temp, °C	$^1J_{PC}$, Hz	δ_C[b]	$^2J_{PF}$, Hz	$^2J_{PF}$, Hz	Lit.[c] ϕ_F[d]	Ref
$(CF_3)_3P$	+31	14	+126.4	83[e]	85.5	+50.8	22b
$(CF_3)_2PF$	0	30	+125.5	89.5[f]	89.6	+66.5	22b
$(CF_3)_2PCl$	+27	38	+126.3	85[f]	85.1	+61.4	22b
$(CF_3)_2PBr$	0	43	+124.6	78[e]	80.6	+59.5	22b
$(CF_3)_2PI$	+30	45	+122.6	73[f]	73.2	+55.4	22b
CF_3PF_2	−20	48	+123.2	87[f]	87.2	+80.7	22d
CF_3PCl_2	0	75	+126.1	75[e]	79.9	+72.1	22d
CF_3PBr_2	0	77	+122.9	68[f]	69.6	+67.8	22d
CF_3PI_2	+25	87	+118.7	52[f]	52.1	+61.0	22d

[a] ^{13}C at 22.6 MHz with ^{19}F decoupling, measured in CD_2Cl_2 solutions, ^{19}F at 94.2 or 56.4 MHz. [b] Parts per million vs. ^{13}C signal of Me_4Si, positive values indicating resonance to low field of the standard. [c] Literature values of ϕ_{CF_3} and $^2J_{PF}$. [d] Parts per million vs. $CFCl_3$, positive values indicating resonance to high field of the standard CF_3 signals only. [e] From ^{31}P spectra. [f] From ^{19}F spectra.

detailed analysis of the temperature dependence of the spectra arising from the permutational process which averages CF_3 environments will be reported elsewhere. Unambiguous consistent assignments of ground state structures A or B can therefore be obtained from $^1J_{PC(F)}$ and $^2J_{PF}$ values for the series $CH_3(CF_3)_3PX$. The assignment of the structure A to the compound X = F and the structure B to the compounds X = OCH_3, SCH_3, and $N(CH_3)_2$ is consistent with the electronegativity rule enunciated elsewhere;[12] however, the rule is apparently violated in the case where X = Cl which clearly possesses structure A, although the generally accepted electronegativity[25] of the CF_3 group is greater than that of Cl.

4. The Simple Trifluoromethylhalogenophosphoranes. It is notable that all the trifluoromethylhalogenophosphoranes involving two or more halogens that are listed in Table I have large $^1J_{PC}$ values suggesting exclusive equatorial CF_3 substitution. In the case of halogens other than F, the electronegativity rule[12a] appears to be consistently violated.

(a) The Fluorophosphoranes. Magnitudes of $^1J_{PC(F)}$ and $^2J_{PF}$ for CF_3PF_4 (**1**), $(CF_3)_2PF_3$ (**5**), and $(CF_3)_3PF_2$ (**12**) suggest consistent equatorial CF_3 substitution, a prediction which is in agreement with the electronegativity rule but at variance with structures initially suggested on the basis of ^{19}F NMR chemical shift data.[12a] The vibrational spectroscopic study[26] of CF_3PF_4 also suggested equatorial placement of the CF_3 group; however, a microwave study[27] suggested a C_{3v} structure for CF_3PF_4. The $^1J_{PC(F)}$ values obtained for **1** (448 Hz) and **5** (418 Hz) are among[28] the largest $^1J_{PC}$ coupling constants that have been measured and we think that these values are strongly indicative of equatorial CF_3 substitution.

Fast intramolecular exchange processes[29] involving fluorine ligands also influence the observations. For example, we have examined the ^{19}F spectrum of CF_3PF_4 to temperatures as low as −150 °C in $CFCl_3/CF_2Cl_2$ but we were unable to observe changes consistent with stopping of intramolecular F exchange. The simplest intramolecular exchange mechanism, Berry pseudorotation[29a] with an equatorial CF_3 pivot, is compatible with the proposed ground state structure of this molecule with an equatorial CF_3 group based on $^1J_{PC(F)}$ and $^2J_{PF}$ values and supported by the vibrational spectroscopic results.[26] The alternative structure suggested by the microwave study[27] does not alleviate the problem posed by equivalent F environments in CF_3PF_4 except perhaps to suggest that alternate structures may be energetically similar to the ground state structure which in turn leads to a low rearrangement barrier. In this context we have also reexamined the ^{19}F spectrum of PF_5 in the FT mode to temperatures of −135 °C in carefully dried isopentane and do not observe even noticeable line broadening at this temperature indicating that the averaging mechanism, compatible with either Berry, turnstile, or similar processes, is very fast.

Less understandable is the behavior of $(CF_3)_2PF_3$, which also failed to show the distinct axial-equatorial F atom environments which are expected for the favored ground state structure with two equatorial CF_3 groups even when examined at very low temperatures (^{31}P to −160 °C, ^{19}F NMR to −125 °C, ^{13}C NMR to −125 °C). While such evidence could support the argument that the generally accepted diequatorially CF_3 substituted C_{2v} ground state structure is incorrect, we believe that the $^1J_{PC(F)}$ data reported herein and our previous interpretation of $^2J_{PF}$ data on these and related compounds[3,6,7] support the C_{2v} structure and the lack of axial-equatorial F atom distinction arises from a fast permutational process with an undefined mechanism.

(b) The Chlorophosphoranes. Vibrational[30] and NQR[31] spectroscopic studies of CF_3PCl_4 and a vibrational study[32] of $(CF_3)_2PCl_3$ were interpreted in terms of axial CF_3 ground state structures which are at variance with the conclusions derived from the present ^{13}C and previous[3,6-11] ^{19}F NMR data. A recent electron diffraction[33] study of $(CF_3)_2PCl_3$ and $(CF_3)_3PCl_2$ also suggests preferential axial substitution of CF_3 groups in a regular or distorted (respectively) trigonal bipyramid. We have, in view of this result, attempted, without success, to detect different CF_3 environments in the case of $(CF_3)_3PCl_2$ by means of ^{13}C (to −130 °C, the limit imposed by the solubility of the compound), ^{19}F (to −160 °C), and ^{31}P NMR (to −160 °C) spectroscopy. The resonance lines did not broaden significantly even at these low temperatures except in the case of the ^{19}F spectrum, where spinning of the sample ceased. If the gas phase structure prevails in solution the barrier to CF_3 permutational exchange must be unusually small. Alternatively and perhaps more likely the solution structure may involve axial Cl atoms and equivalent equatorial CF_3 groups. The reasons for these discrepancies are not clear but it is worth noting that the different spectroscopic techniques evaluate compounds in different physical states at different temperatures and also the techniques have different characteristic measurement lifetimes.

(c) The Bromophosphoranes. The bromophosphoranes were prepared by the oxidation of the corresponding phosphines by elemental bromine according to the method of Burg et al.[34] and additional NMR spectral parameters are given in Table III.

Tris(trifluoromethyl)phosphine formed a reversible temperature-dependent oxidative equilibrium (eq 1, $K \sim 2\ L^{-1}$ at 260 K) with bromine in $CD_2Cl_2/CFCl_3$ solution which was observed by ^{31}P, ^{19}F, and ^{13}C NMR spectroscopy.

$$(CF_3)_3P + Br_2 \rightleftharpoons \underset{\mathbf{14}}{(CF_3)_3PBr_2} \qquad (1)$$

Cooled solutions showed no evidence of the decomposition to CF_3Br and other trifluoromethylphosphines which was reported by Burg et al.[34] under more severe conditions. Only two products were observed in the ^{13}C NMR spectra, tris(trifluoromethyl)phosphine ($^1J_{PC(F)}$ = 14 Hz, $\delta(^{13}C)$ +126.4 ppm)

Table III. ^{19}F and ^{31}P NMR Parameters of Bromophosphoranes

Compd[a]	ϕ_F[d]	δ_P[e]	$^1J_{PF}$, Hz	$^2J_{PF}$, Hz	$^3J_{FF}$, Hz
9 $(CF_3)_2PFBr_2$	78.6 (CF_3) 101.5 (P-F)	153	1255	179	13.0
3 CF_3PBr_4[b]	66.8	86		142	
8 $(CF_3)_2PBr_3$	81.4	163		182	
14 $(CF_3)_3PBr_2$[c]	65.6[f]	177		127[f]	

[a] CD_2Cl_2 solutions except where indicated. [b] Toluene-d_8 solvent. This compound appears to be a phosphonium salt; see text. [c] Solvent: 40% $CFCl_3$, 60% CD_2Cl_2. [d] Relative to $CFCl_3$; positive values indicate resonance to high field of standard. [e] Relative to P_4O_6; positive values indicate resonance to high field of standard. [f] Fluorine-19 spectrum unchanged to −140 °C.[21]

and a second product ($^1J_{PC(F)} = 201$ Hz, $\delta(^{13}C)$ +120.6 ppm) which was presumed to be the phosphorane, **14**, principally because the high value of $^1J_{PC(F)}$ suggests that the molecule has equatorial CF_3 groups. The ^{31}P spectra showed, in addition to signals attributable to $(CF_3)_3P$, a decet, $\delta(^{31}P)$ +177 ppm, $^2J_{PF} = 127$ Hz, and the fluorine spectrum showed a doublet, ϕ +65.6 ppm, $^2J_{PF} = 127$ Hz, demonstrating that the molecule contained three CF_3 groups and that cleavage of trifluoromethyl groups by bromine had not occurred. The magnitudes of $^1J_{PC(F)}$ and $^2J_{PF}$ suggest equatorial CF_3 substitution with the halogen apparently occupying the axial sites in spite of its lower relative electronegativity. It is also worth noting that the ^{19}F NMR spectrum of $(CF_3)_3PBr_2$ was unchanged[21] to −140 °C further suggesting that the CF_3 groups occupy equivalent equatorial sites in the molecule.

The reaction of $(CF_3)_2PBr$ with bromine produced $(CF_3)_2PBr_3$ (**8**) (mp 7 °C, lit.[34] 6.0–9.4 °C). This bromophosphorane (**8**) appeared to be stable at, or just below, room temperature provided that a small excess of the phosphine was present, suggesting that the presence of a small quantity of free bromine catalyzes the disproportionation reported previously.[34] The $^1J_{PC(F)}$ value of 379 Hz for **8** suggests equatorial substitution of the CF_3 group placing Br in the axial site again contrary to the electronegativity prediction.[12a] The $^2J_{PF}$ value (127 Hz) supports this conclusion.

A compound of the formula CF_3PBr_4 (**3**) was formed by bromine oxidation of the corresponding phosphine. This bright orange compound was stable in the presence of small quantities of the free phosphine, and had a melting point of 27 °C (lit.[34] 28 °C). This compound provides the only serious anomaly in the list of $^1J_{PC(F)}$ values given in Table I because the value is unexpectedly small. Also this $^1J_{PC(F)}$ value does not correlate with $^2J_{PF}$. This anomaly can be readily explained by considering **3** to be more properly described as a phosphonium salt (e.g., $CF_3PBr_3^+$ Br^-) and not as a phosphorane. This interpretation is supported by the low value of the phosphorus chemical shift for **3** (+86 ppm vs. P_4O_6[35]), which is consistent with a phosphonium salt formulation.[36] Alternatively it is possible that the four bulky bromine substituents cause a distortion toward a square pyramidal phosphorane structure with presumably an axial CF_3 group thus relieving the 90° steric strain which exists in the trigonal-bipyramidal structure. The likely $^1J_{PC}$ or ^{31}P chemical shift values which would be expected for the square pyramidal species are not predictable.

The most stable bromophosphorane synthesized in this study was the new compound formed by the oxidation of $(CF_3)_2PF$ with bromine

$$\underset{}{(CF_3)_2PF} + Br_2 \rightarrow \underset{\mathbf{9}}{(CF_3)_2PFBr_2} \qquad (2)$$

with close to quantitative yield of **9** being obtained as colorless crystals at −78 °C. The phosphorane nature of **9** was indicated by mass spectrometry where M − F and M − CF_3 (M = parent) ions were both observed, the former in proportions suggestive of its initial presence rather than the result of processes such as the elimination of CF_2.[37] As usual the parent ion was not observed; however, the mass spectra clearly indicate the presence of two Br atoms bound to P and since the most likely phosphonium salt would be $(CF_3)_2PFBr^+Br^-$, this latter evidence strongly supports the phosphorane formulation. A neat sample of **9** was less than 30% decomposed after 40 h at 45 °C, making it the most thermally stable bromophosphorane of the series considered here. The principal mode of decomposition appeared to be halogen redistribution:

$$\underset{\mathbf{9}}{2(CF_3)_2PFBr_2} \rightarrow (CF_3)_2PF_2Br + \underset{\mathbf{8}}{(CF_3)_2PBr_3} \qquad (3)$$

The $^1J_{PC(F)}$ (336 Hz) and $^2J_{PF}$ values for **9** also suggest that CF_3 groups occupy equatorial sites; thus the axial positions are occupied by F and presumably one of the Br atoms. Halogens, even those which are less electronegative[25] than CF_3, therefore preferentially occupy the axial site. Further support is provided in the case of **9** by the fact that neither the ^{13}C spectrum nor the CF_3 portion of the ^{19}F spectrum exhibits any temperature dependence which can be ascribed to CF_3 positional interchange.

5. Signs of the Coupling Constants in Trifluoromethylphosphoranes. It is notable that the averaged $^1J_{PC(F)}$ values obtained at ordinary temperatures for those systems which suffer intramolecular CF_3 exchange correspond to the weighted average of the $^1J_{PC(F)}$ values obtained at low temperatures for the specific axial and equatorial coupling; therefore we can conclude that axial and equatorial P–CF_3 couplings have the same sign. A similar conclusion follows from $^2J_{PF}$ averaging. We cannot a priori obtain signs from the present data but a curious anomaly is provided by **10** in that poor fit is obtained in Figure 1 if we assume that $^1J_{PC(F)}$ and $^2J_{PF}$ signs are unchanged within the entire present series. On the other hand, if we allow $^1J_{PC(F)}$ to have the opposite sign in **10** to all other compounds, then the point for **10** falls on the straight line which correlates the coupling constant data points. Thus if $^1J_{PC(F)}$ is usually positive in agreement with the few measured values[20] we suggest that $^1J_{PC(F)}$ is negative in **10**. The signs of $^2J_{PF}$ appear to be the same in the present series and are probably positive[38] throughout.

6. ^{13}C Chemical Shift Trends in the Phosphorane Series. The ^{13}C chemical shift of axial CF_3 groups lies consistently downfield of that arising from equatorial CF_3 groups whenever the two kinds of CF_3 environment can be meaningfully compared in the same molecule. In an absolute sense, however, little consistent rationale exists for relative axial or equatorial ^{13}C shifts, and these values cannot be used in support of positional assignments. A similar situation prevails for ^{19}F chemical shift parameters. This lack of consistency presumably arises because the chemical shifts are more highly responsive to the combination of σ and π effects in a molecule whereas coupling constants are dominated by σ effects.

7. ^{13}C NMR Spectra of Trifluoromethylphosphines. The ^{13}C and ^{19}F NMR spectral parameters of the phosphines are reported in Table II. The $^1J_{PC(F)}$ coupling constants increased, without exception, in the order $(CF_3)_3P < (CF_3)_2PF < (CF_3)_2PCl < (CF_3)_2PBr < (CF_3)_2PI < CF_3PF_2 < CF_3PCl_2 < CF_3PBr_2 < CF_3PI_2$. The smooth progression in coupling constants would seem to indicate no change in sign through the series. Within a given subseries, i.e., mono or bis CF_3 substitution, the coupling constant seems to be sensitive to the electronegativity of the other substituents probably reflecting a reduction in "s" character in the P-C bond.[39] There is no linear (or even a smooth) correlation between $^1J_{PC}$ and $^2J_{PF}$ of the phosphines in contrast to the phosphorane data. The only quantitative relationship seems to be a decrease of $^2J_{PF}$ with increasing $^1J_{PC}$ within each of the subseries $(CF_3)_2PX$ and CF_3PX_2, which suggests perhaps that the sign of one or the other of the coupling constants is the reverse of that which exists in the phosphorane series; but the trends, limited as they are to small subseries, are not sufficiently broad to warrant conclusions. The lack of definitive trends within the phosphine series is not altogether surprising because these molecules are more likely to suffer changes in molecular geometry, and hence P-C bond hybridization between substituents, than in the case for the trigonal-bipyramidal phosphoranes.

8. Summary and Conclusions. The data presented in Table I form a self-consistent set allowing the clear deduction of a consistent axial preference series from both $^1J_{PC(F)}$ and $^2J_{PF}$ values. The relative tendency to locate in the axial position decreases in the order F > Cl, Br > CF_3 > OR, SR, NR_2, R. This provides further strong evidence that the electronegativity rule[12a] for axial placement requires replacement by a parameter which can illustrate the overriding tendency of halogens to displace other groups from the axial position. The σ_I inductive parameters, introduced earlier,[3,6-11] seem to provide the necessary indicator of observed order.

The various methods of structure determination employed for the simple halogenophosphoranes have yielded conflicting results. Although previous interpretations of NMR data suggested that the $(CF_3)_{5-x}PF_x$ (x = 2, 3, 4) series on occasion violated the electronegativity rule,[12a] the present new data and their interpretation suggests that this series obeys the electronegativity rule throughout, although the lack of detection of the expected nonequivalence of P-F environments in $(CF_3)_2PF_3$ is puzzling. Our results for CF_3PF_4 are in agreement with the vibrational study[26] but disagree with a microwave study[27] which suggested axial placement of the CF_3 group. The present NMR data for chlorophosphoranes CF_3PCl_4, $(CF_3)_2PCl_3$, and $(CF_3)_2PCl_2$, especially that derived from ^{13}C NMR measurements, suggest that the electronegativity rule[12a] is violated and that Cl preferentially occupies an axial position. In contrast vibrational studies of CF_3PCl_4 and $(CF_3)_2PCl_3$,[30,32] a NQR study of CF_3PCl_4,[31] and electron diffraction studies[33] of $(CF_3)_2PCl_3$ and $(CF_3)_3PCl_2$ have been interpreted in terms of preferential axial substitution of CF_3 groups. Axial Cl substitution is supported by our inability to detect (by ^{13}C NMR as low as −130 °C) the distinct axial and equatorial CF_3 environments of $(CF_3)_3PCl_2$ which would devolve from the structure obtained by electron diffraction.[33] In view of the ease with which CF_3 environments are detected by ^{13}C NMR spectroscopy (vide supra), we think that it is reasonable to consider our lack of resolution of CF_3 environments in the case of $(CF_3)_3PCl_2$ to be significant, although this conclusion is by no means definitive. The basis for the discrepancies in the chlorophosphorane series is not clear but may arise from the differences in state and/or the temperatures involved in the different studies. The bromophosphoranes also appear to involve axial halogen substitution. One compound, CF_3PBr_4, was best described as a phosphonium salt. The greater tendency for Br (and Cl) to dissociate in solution may influence the solution spectral behavior of the heavier halogenophosphoranes.

Experimental Section

Carbon-13 spectra were recorded on samples contained in 10 mm o.d. precision NMR tubes. Solvents were purified by trap to trap fractionation and condensed under vacuum onto the compounds. Spectra were recorded using a Bruker HFX 90-Nicolet 1085 (FT mode) spectrometer operating at 22.6 MHz. Fluorine decoupling frequencies were generated by a HP 5110B frequency synthesizer, multiplied by 3 by the Bruker console prior to amplification by the Bruker broad band decoupler, and further modulated by the imposition of 4167 Hz side bands. Internal ^2D lock was used for field/frequency stability. Typical settings for data acquisition were 4K pulses, pulse width 8 μ, pulse interval 0.8 s. CD_2Cl_2 was the usual solvent; fluorinated or aromatic solvents were avoided wherever possible since they produce signals in the $^{13}CF_3$ region. Spectra were recorded at temperatures which (a) gave an adequate signal to noise ratio (Overhauser enhancement from ^{19}F decoupling is minimal) and (b) lower pressures for the more volatile compounds to prevent explosion of the thin wall NMR tubes. In certain cases the spectra were temperature dependent (see Table I) and cooling to low temperature was necessary to resolve axial and equatorial environments.

$(CF_3)_3P$, $(CF_3)_2PF$, $(CF_3)_2PCl$, $(CF_3)_2PBr$, $(CF_3)_2PI$, CF_3PF_2, CF_3PCl_2, CF_3PBr_2, and CF_3PI_2 were prepared according to published methods.[40-43] Similarly phosphoranes **1–22** were prepared as described elsewhere[3,6-11,16,34,40,43-48] with the exception of compound **9**, the novel bromofluorophosphorane which is reported below. Purities of all the phosphoranes were checked by IR, ^{19}F NMR, and ^{31}P NMR spectroscopy.

Preparation of Bis(trifluoromethyl)dibromofluorophosphorane (9). Bis(trifluoromethyl)fluorophosphine[41] (0.80 g, 4.26 mmol), bromine (0.64 g, 4.00 mmol), and methylene chloride (1.38 g) were condensed into an NMR tube, sealed under vacuum, and were allowed to warm slowly from −196 to −78 °C. The tube was shaken at −78 °C whereupon a dark, clear solution was produced. A rapid decoloration then took place over a period of approximately 20 s to give a clear, colorless solution. Fine needles slowly separated out from the solvent; they were observed to rapidly dissolve on warming.

The tube was opened to the vacuum line and methylene chloride and excess $(CF_3)_2PF$ (total weight 1.44 g) were trapped at −196 °C while the crude product (1.39 g, 4.0 mmol) was trapped at −45 and −78 °C. The crude product was purified by trap to trap condensation to give a product, mp −8 ± 1 °C (1.29 g, 3.71 mmol, 93% yield).

Hydrolysis and Bromine Analysis. A. Neutral Hydrolysis. The compound (0.300 g, 0.862 mmol) was shaken for 5 days with ~0.3 mL of distilled water. A ^{19}F NMR spectrum of the resulting solution revealed only the $(CF_3)_2PO_2^-$ ion.[49] Trap to trap separation of products yielded only 0.0012 g of CF_3H (0.017 mmol, 0.6% cleavage).

B. Alkaline Hydrolysis. The compound (0.201 g, 0.578 mmol) was shaken with 0.3 mL of 10% NaOH for 5 days. A ^{19}F NMR spectrum of the resulting solution revealed only the $(CF_3)_2PO_2^-$ ion.[49] Trap to trap separation of products yielded only 0.0046 g of CF_3H (0.066 mmol, 1.1% cleavage).

C. Titrimetric bromide analysis was carried out on the above solutions yielding an average result of 47.3% (calculated 46.0%).

Spectral Properties of 9. A. Infrared. The infrared spectrum of bis(trifluoromethyl)dibromofluorophosphorane was recorded in the gas phase with a 9-cm cell fitted with KBr windows on a Perkin-Elmer 457 grating infrared spectrometer. The pertinent features are 1292 (vw), 1191 (vs), 1177 (vs), 1156 (vs), 1117 (vw), 828 (m), 581 (m), 565 (m), 547 (m), 515 (m), 396 cm^{-1} (vw). Sample pressure was 0.2 cm.

B. Mass Spectrum. The following major peaks were observed (*m/e* group (intensity as percent of base peak (*m/e* 69) = 100), assignment): 277, 279, 281 (44.6) CF_4PBr_2; 267, 269 (31.6) C_2F_7PBr; 227, 229, 231 (3.1) PF_2Br_2; 217, 219 (11.0) CF_5PBr; 198, 200 (3.1) CF_4PBr; 188 (2.3) C_2F_7P; 179, 181, (2.5) CF_3PBr; 129, 131 (36.2) CF_2Br or PFBr; 119 (7.0) CF_3PF; 100 (3.1) CF_3P; 79, 81 (22.0) Br. Bromine-containing fragments were easily assigned on the basis of triplet (two bromines present) or their doublet (one bromine present) patterns. The assignment of the ion at *m/e* 267, 269 was confirmed by mass measurement (calcd for $CF_4P^{79}Br_2$, 276.8040; found, 276.8052).

Reaction of Bromine with CF_3PF_2. The attempted bromine oxidation of trifluoromethyldifluorophosphine produced copious quantities of a brown solid, which was apparently only partially soluble in common solvents except toluene in which it dissolved completely, and a second, very volatile, product that was trapped at −196 °C and was identified as CF_3PF_4. The brown solid moved under vacuum and was trapped at −45 and −78 °C. Unreacted bromine was separated by this distillation. A solution of the brown solid in toluene showed, by ^{31}P NMR spectroscopy, a mixture of phosphines and phosphoranes, the lack of separation probably indicating complexation. A trace amount of a compound with a directly bound fluorine on phosphorus was observed in this toluene solution and, from analysis of the splitting patterns, was attributed to $(CF_3)_3PFBr$. The principal products of the reaction suggested the approximate equation

$$4CF_3PF_2 + \tfrac{5}{2} Br_2 \rightarrow CF_3PF_4 + CF_3PBr_2 + (CF_3)_2PBr_3 \quad (4)$$

Since the desired product, $CF_3PF_2Br_2$, was not produced in detectable yield the reaction was not investigated further.

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