tallization from *n*-hexane/dichloromethane yielded the bis(cyclotriphosphazene) (VIII) in ~60% yield. The spectra of this compound were identical to those previously reported.[3] The cupriophosphazene was found not to react with 2-bromo-1,1-diethoxyethane.

c. Reactions with 2-Methoxyallyl Bromide. i. The cupriophosphazene (0.014 mol) was generated as described above. The alkyl halide (0.60 mol) was added, and the mixture was stirred for 48 h at room temperature. The solvent was then removed under reduced pressure, and the products were dissolved in toluene (250 mL). This organic layer was washed with aqueous HCl (~10% solution, 250 mL) and dried over magnesium sulfate, and the solvent was removed under reduced pressure to leave the crude product (VII), which was recrystallized from *n*-hexane/dichloromethane.

ii. The lithiophosphazene (0.014 mol) was generated at −80 °C as described above. The 2-methoxyallyl bromide (0.015 mol) was added slowly, and the mixture was allowed to stir for 16 h, during which time the temperature was allowed to rise to ~25 °C. The solvent was then removed under high vacuum, and *n*-hexane was distilled onto the residues. The resultant solution was filtered through infusorial earth by using Schlenk techniques, and the solvent was again removed under high vacuum to leave a crude product. Recrystallization from freshly distilled *n*-hexane yielded compound X.

Rearrangement/Hydrolysis Reactions. All of the reactions described in this section of the work were initially monitored by ^1H NMR. The solvent, $CDCl_3$, was freshly distilled from P_4O_{10}, and the rearrangement or hydrolysis was accomplished with the use of either H_2O, D_2O, H_2O/HCl, or D_2O/DCl.

a. Rearrangement of Compound X to Compound IX. The 2-methoxyprop-2-enyl-substituted compound (X) was dissolved in dichloromethane. Two or three drops of water were introduced into the solution, and the mixture was stirred for 1 h. The solution was then dried over magnesium sulfate, and the solvent was removed under reduced pressure to leave compound XI, which was recrystallized from *n*-hexane.

b. Hydrolysis of Compound XI to Compound VII. The 2-methoxyprop-1-enyl-substituted compound (XI) was dissolved in dichloromethane and treated with ~5 drops of HCl (0.01 M solution). This mixture was allowed to stir for 16 h and was then dried over magnesium sulfate. The solvent was then removed under reduced pressure to leave the acetonyl-substituted phosphazene (VII), which was recrystallized from *n*-hexane.

c. Rearrangement/Hydrolysis of Compound X to Compound VII. This reaction was accomplished by treatment of a dichloromethane solution of compound X with aqueous HCl in an identical manner to that described above for compound XI.

d. Attempted Rearrangement of Compound XII. i. The prop-2-enyl-substituted phosphazene (XII) (3.0 g, 0.009 mol) (synthesized as previously reported[15]) was dissolved in THF (100 mL) and cooled to −80 °C. Then, *n*-butyllithium (0.5 mL of a 2.0 M solution in *n*-hexane) was introduced, and the mixture was allowed to stir for 16 h, during which time the temperature was allowed to rise to ~25 °C. After removal of the solvent under reduced pressure, a subsequent analysis of the ^1H NMR spectrum of the product indicated that no rearrangement of compound XII had occurred.

ii. The prop-2-enyl compound (XII) was treated with dilute HCl in a manner identical with that described above for compound XI. Inspection of the ^1H NMR of the product indicated that no rearrangement of compound XII had occurred.

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Registry No. I, 940-71-6; II, 71332-21-3; III (R = H), 82056-02-8; III (R = CH_3), 85319-90-0; III (R = C_6H_5), 82056-06-2; IV (R = H), 85319-91-1; IV (R = CH_3), 85319-92-2; IV (R = C_6H_5), 85319-93-3; V, 77217-61-9; VI, 75083-25-9; VII (R = CH_3), 85319-94-4; VII (R = C_6H_5), 85319-95-5; VIII, 80241-37-8; IX, 77589-25-4; X, 85319-96-6; XI, 85319-97-7; XII, 72474-22-7; lithium ethenolate, 2180-63-4; lithium 2-propenolate, 67863-40-5; lithium 1-phenylethenolate, 35249-09-3; α-bromoacetophenone, 70-11-1; 2-bromo-1,1-diethoxyethane, 2032-35-1; 2-methoxyallyl bromide, 26562-24-3.

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Phosphoranes. 12. Synthesis and Dynamic NMR Study of Methyltris(trifluoromethyl)phosphorane, $CH_3(CF_3)_3PH$

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The fluxional phosphorane $CH_3(CF_3)_3PH$ has been obtained from the reaction of $CH_3(CF_3)_3PCl$ with $RSiH_3$ (R = CH_3, H). Above room temperature $CH_3(CF_3)_3PH$ is thermally unstable, forming $CH_3(CF_3)_2P$ and CF_3H. Low-temperature limiting ^{19}F and ^{31}P NMR spectra suggest that the ground-state geometry has two axial CF_3 groups on a trigonal-bipyramidal framework. Line-shape analysis of the variable-temperature $^{31}P\{^1H\}$ NMR spectra yielded a barrier ($\Delta G^{\ddagger}_{298} = 14.2 \pm 0.8$ kcal) to the intramolecular exchange process that equilibrates the two CF_3 environments. This barrier is compared to those already known for related molecules $CH_3(CF_3)_3PY$ (Y = F, Cl, OCH_3, SCH_3, $N(CH_3)_2$, CH_3). Infrared and mass spectral data of the new hydride are reported.

Introduction

In series of similar phosphoranes, comparison[1-3] of the barrier height to intramolecular rearrangement has provided some insight into the relative contribution of an individual substituent. The simplest substituent Y = H in the two series Y_2PF_3[2] and YPF_4[3] alters the value of the barrier substantially having an effect comparable to a methyl group, but when barriers are ordered[2,3] the relative positions of H and CH_3 appear to vary inexplicably, especially the low barrier for CH_3PF_4. Earlier[1] we showed that the barrier to intramolecular exchange of CF_3 groups in the phosphoranes $CH_3(CF_3)_3PY$ increases for Y in the order F < Cl < OCH_3 < SCH_3 < $N(CH_3)_2$ < CH_3. Reported here is the synthesis of another member of this series, $CH_3(CF_3)_3PH$, and a determination of its barrier to rearrangement that permits inclusion of Y = H in the above order. Application of a parameterized estimation of barriers to the hydrides is discussed.

Experimental Section

Standard vacuum-line techniques were used for all manipulations. Stopcocks were lubricated with Apiezon N grease. Silane, CH_3SiH_3, and $(C_4H_9)_3SnH$ were purchased from Matheson, Columbia, and Alfa Products, respectively. The phosphoranes $CH_3(CF_3)_3PX$ (X = Cl, F)[4] were prepared by reported procedures.

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Routine ^{19}F and ^{1}H NMR spectra of samples, as approximate 5% solutions in CCl_3F, were obtained with a Varian A56/60A spectrometer. The ^{19}F NMR parameters reported in Table III were obtained with a Varian HA-100 spectrometer on similar solutions. Temperature-dependent phosphorus-31 NMR spectra were recorded at 36.43 MHz in the pulsed FT mode with a Bruker HFX-90 spectrometer equipped with a Nicolet 1085 computer and a Bruker temperature controller regulating the probe temperature to within ±0.1 °C. Calibration of the temperature control system has established the precision of the values quoted and in addition has established that no detectable thermal gradients exist within the sample tube. The temperature values quoted are reliable to ±1 °C.

Infrared data on gas-phase samples (pressures of 1.4, 10, and 70 torr) contained in a cell of 9-cm path length with KBr windows were collected with a Nicolet 7199 FT-IR spectrometer. The sample was kept frozen at −196 °C until immediately before measurement.

Preparation of $CH_3(CF_3)_3PH$. Three attempts to prepare $CH_3(CF_3)_3PH$ by treating $CH_3(CF_3)_3PF$ with $(C_4H_9)_3SnH$, $CH_3(CF_3)_3PF$ with $(CH_3)_3SiH$, and $CH_3(CF_3)_3PCl$ with $(CH_3)_3SiH$ on a small scale in NMR tubes showed that only a trace of the fluorophosphorane had been consumed after 1 week at 80 °C, 70% of the fluorophosphorane had been consumed after 2 weeks at 60 °C, and complete consumption of the chlorophosphorane had occurred in 1 week at 80 °C, respectively. The only products observed by NMR, $CH_3P(CF_3)_2$ ($\phi_F = 58.1$, $^2J_{PF} = 76$ Hz) and CF_3H ($\phi_F = 78.5$, $J_{HF} = 80$ Hz), were those resulting from decomposition of the unstable $CH_3(CF_3)_3PH$, which indicated that milder conditions with a more effective hydriding reagent were required.

In a typical successful preparation about 1 g (3.5 mmol) of $CH_3(CF_3)_3PCl$ was cocondensed with SiH_4 or CH_3SiH_3 (ca. 5.5 mmol) in a sealed tube of 25-mL volume. The tube was then shaken for 18 h at room temperature. The conversion of chlorophosphorane to $CH_3(CF_3)_3PH$ was better than 90% under these conditions, but decomposition to $CH_3P(CF_3)_2$ and CF_3H did not permit more than a 40% isolated yield. In the dynamic vacuum-line fractionation of the reaction mixture, unreacted $CH_3(CF_3)_3PCl$ was trapped at −45 °C and $CH_3(CF_3)_3PH$ slowly passed a trap at −56 °C and was trapped as a liquid at −63 °C. Unreacted SiH_4 (or CH_3SiH_3) and H_3SiCl (or CH_3SiClH_2) as well as $CH_3P(CF_3)_2$ and CF_3H were trapped at −196 °C. The deuterated analogue was prepared in the same fashion from SiD_4 (Merck) and $CH_3(CF_3)_3PCl$.

Mass Spectral Results. Mass spectral data were collected with an AEI MS-50 spectrometer operating at an ionizing voltage of 70 eV. The sample was kept frozen at −196 °C until immediately before measurement. The data are as follows [*m/e* (%), identity]: 185 (10.19), $CH_3(CF_3)_2PH$; 184 (100.00), $CH_3(CF_3)_2P$; 165 (11.37), $CH_3(CF_3)PCF_2$; 135 (2.36), $CH_3(CF_3)PFH$; 134 (30.97), $CH_3(CF_3)PF$; 130 (2.12), $(CH_2)_2CF_3P$; 119 (2.69), CF_3PF; 116 (4.85), $CH_3(CF_3)PH$; 115 (3.18), $CH_3(CF_3)P$; 101 (10.54), CF_3PH; 100 (2.22), CF_3P; 96 (4.30), CH_3PCF_2; 95 (1.22), CH_2PCF_2; 94 (4.15), $CHPCF_2$; 85 (2.49), CH_3PHF_2; 84 (20.39), CH_3PF_2; 81 (1.65), CF_2P; 77 (4.85), $C_3H_3F_2$; 69 (39.58), PF_2 and CF_3; 66 (3.22), CH_3PHF; 65 (6.17% as $C_2H_3F_2$ and 84.35% as CH_3PF); 64 (1.50), CH_2FP; 51 (1.88), FHP (for those ions with $m/e > 50$ and an intensity >1.0% of the base peak). A structural formula is given only for ease of recognition.

Results and Discussion

A. Synthetic Considerations. The reaction of $CH_3(CF_3)_3PCl$ with either silane or methylsilane at room temperature produced the phosphorane $CH_3(CF_3)_3PH$ in about 90% yield in 18 h (eq 1). However, the recovered yield was only about

$$CH_3(CF_3)_3PCl + RSiH_3 \rightarrow CH_3(CF_3)_3PH + RSiH_2Cl \quad (1)$$

$$R = CH_3 \text{ or } H$$

40% because the phosphorane is unstable with respect to the formation of CF_3H and $CH_3P(CF_3)_2$ according to reaction 2.

$$CH_3(CF_3)_3PH \rightarrow CH_3P(CF_3)_2 + CF_3H \quad (2)$$

Table I. Infrared Spectral Data[a,b] for $CH_3(CF_3)_3PH$

	assignt		assignt
3055 vw	ν(C–H)	1282 m	ν(C–F)
2955 vw		1207 vw	
2415 vw	CF overtones	1174 vs	
2380 vw		1173 s, sh	
2340 vw		1132 m	
2320 vw		1102 s	
2261 w, sh	ν(P–H)	1055 m	
2278 w[c]		956 m	
2200 vw	CF overtones?	887 m[d]	ρ(P–CH_3)
2100 vw		776 m	
1500 vw		735 m	δ(CF_3(sym))
1430 w	ν(C–H) asym	695 vw	
1375 w		650 vw	
1340 w		607 w	
1313 w		558 m	
1282 m		525 w	
		490 w	
		457 s	ν(P–C(F))
		409 w	

[a] Values in cm^{-1} from gas-phase spectra. [b] Abbreviations: w, weak; m, medium; s, strong; sh, shoulder; v, very; ν, stretching; δ, deformation; ρ, rocking; sym, symmetric; asym, asymmetric. [c] Shifts to 1647 cm^{-1} in $CH_3(CF_3)_3PD$. [d] The deuterio analogue shows three bands in this region: 852 cm^{-1} (m) (tentatively assigned to P-H bend), 876 cm^{-1} (m) (ρ(P–CH_3)?), and 921 cm^{-1} (w). All other band positions are essentially identical.

At 40 °C the half-life of a 10% solution of $CH_3(CF_3)_3PH$ in $CFCl_3$ is about 1 h. Other CF_3-containing phosphorus(V) hydrides have been noted[5] to be thermally unstable, but the decomposition products were not identified. Although the more easily handled $(CH_3)_3SiH$ and $(C_4H_9)_3SnH$ also reacted with $CH_3(CF_3)_3PX$ (X = Cl, F), presumably to form first $CH_3(CF_3)_3PH$, the longer reaction time and higher temperatures resulted in the isolation of only the decomposition products CF_3H and $CH_3P(CF_3)_2$. These results contrast the ready room-temperature gas-phase reactions[5-7] of $(CF_3)_nPF_{5-n}$ (n = 0–3) with $(CH_3)_3SiH$ in which phosphorus(V) hydrides were produced in good yield by exchange of one or two of the fluorine atoms bound to phosphorus.

B. Spectral Characterizations. The infrared spectrum of $CH_3(CF_3)_3PH$ (Table I) showed many bands similar to those observed in $CH_3(CF_3)_3PY$ (Y = F, Cl, OCH_3, SCH_3, $N(CH_3)_2$). Major differences are due to the nature of Y. For Y = H, a band centered at 2278 cm^{-1}, assigned to the P–H stretching frequency, supports the formulation of the present compound. The ν(P–H) band occurs at a lower wavenumber than that observed for HPF_4 (2485 cm^{-1}), H_2PF_3 (2545 and 2465 cm^{-1}), CH_3PF_3H (2460, 2445, 2435 cm^{-1}),[8] and $C_2H_5PF_3H$ (2430 cm^{-1}),[8] and our identification was hampered by the possibility of interfering ν(CF) overtones in the same region. Deuteration shifts the P–H frequency to 1647 cm^{-1}, confirming our identification. We can assign the extra band, which appeared at 852 cm^{-1} upon deuteration, to the P–D bending motion, but the appropriate band due to P–H bending could not be seen because this value for the P–D bend indicates that the P–H bend will lie under the very much stronger CF_3 stretching vibrations between 1000 and 1200 cm^{-1}. Additional complexity in the 800–900-cm^{-1} region of the spectrum of the deuterated species suggests that further complications may be present.

The mass spectrum showed no parent ion, as is generally the case for phosphoranes.[9] The observed ions were consistent with the molecular formula of $CH_3(CF_3)_3PH$, and in view of

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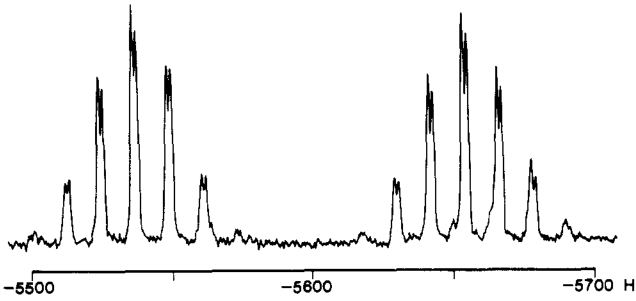
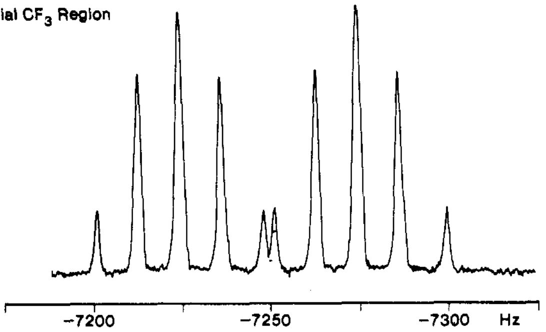
(a) Equatorial CF_3 Region



(b) Axial CF_3 Region



(c) $^{31}P\{^1H\}$

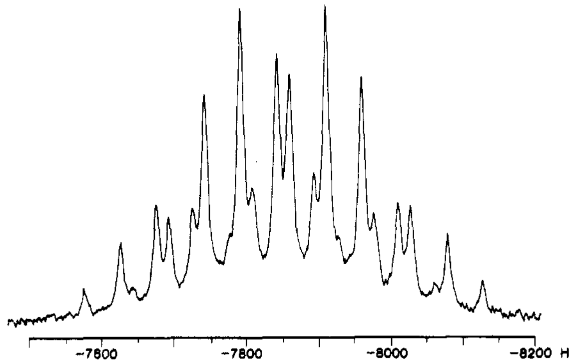


Figure 1. (a, b) Fluorine-19 continuous-wave (94.2 MHz) NMR spectra of $CH_3(CF_3)_3PH$ at -50 °C. The spectra were obtained in CCl_3F solution, and the scale gives chemical shift in hertz from solvent reference. Note that the scales are different for each region. Intensity is arbitrary, and integrated intensity of the equatorial region (a) is half that of the integrated intensity of the axial region (b). (c) Proton-decoupled ^{31}P Fourier transform (36.4 MHz) limiting NMR spectrum of $CH_3(CF_3)_3PH$ at -50 °C. The spectrum was obtained in CCl_3F solution with $(CD_3)_2CO$ lock. The scale gives chemical shift in hertz from the reference P_4O_6.

Table II. NMR Parameters of $CH_3(CF_3)_3PH^a$

	shifts, ppm	coupling constants, Hz
$^{31}P^b$ (δ)	215.7	$J_{PH} = 607.9$
		$J_{PCH} = 14.5$
$^{19}F^c$ (ϕ)	77.0^e	$J_{PCF} = 50.3^e$
	59.4^f	$J_{PCF} = 116.8^f$
		$J_{FCPF} = 11.6$
$^1H^d$ (τ)	8.25^g	$J_{HPCF} = 11.6^e$
		$J_{HPCF} = 1.5^f$
	3.60^h	$J_{HPCH} = 4.0$

[a] At -50 °C in $CFCl_3$. [b] Relative to P_4O_6, positive values indicate resonance to high field of standard. [The chemical shift of 85% H_3PO_4 is +112 ppm (to high field) of P_4O_6: Chapman, A. C.; Horner, J.; Mowthorpe, D. J.; Jones, K. T. *Chem. Commun.* 1965, 121.] [c] Relative to $CFCl_3$, positive values indicate resonance to high field of standard. [d] Relative to external Me_4Si (τ = 10). [e] Axial CF_3 group. [f] Equatorial CF_3 group. [g] CH_3 group. [h] PH.

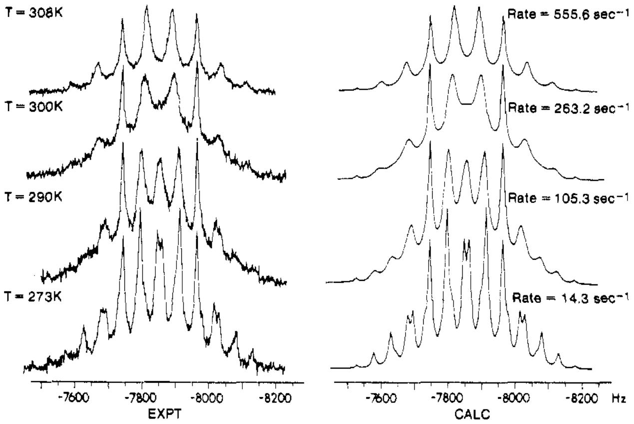


Figure 2. Representative $^{31}P\{^1H\}$ (FT, 36.4 MHz) NMR spectra of $CH_3(CF_3)_3PH$ at various temperatures compared to spectra calculated with appropriate rates of exchange. The solution and scale are as in Figure 1c.

its thermal instability the presence of the base peak at m/e 184 assigned to $CH_3P(CF_3)_2$ is not surprising. Other prominent fragments are those due to $CH_3(CF_3)PF$, CH_3PF_2, CH_3, PF_2, and CH_3PF, which have been commonly observed for similar phosphoranes.[9]

From earlier arguments[9] that CH_3 occupies an equatorial position in the trigonal-bipyramidal framework of phosphoranes in the presence of more electronegative substituents and that H also preferentially occupies an equatorial position in (trifluoromethyl)phosphoranes,[5,6] we expect a trigonal-bipyramidal structure with H, CH_3, and one CF_3 in equatorial sites and with both axial sites occupied by CF_3 groups. The NMR parameters (Table II) are consistent with this structure. At -50 °C, the ^{19}F NMR spectrum revealed (Figure 1) a doublet of quintets (intensity 2) for two equivalent CF_3 groups coupled to phosphorus ($^2J_{PF}$ = 50.3 Hz) with the quintet pattern arising from interaction of the equatorial hydrogen and CF_3 ($^3J_{HF}$ = $^4J_{FF}$ = 11.6 Hz) and a doublet of septets of doublets (intensity 1) arising from coupling with phosphorus ($^2J_{PF}$ = 116.8 Hz), two axial CF_3 groups ($^4J_{FF}$ = 11.6 Hz), and the equatorial hydrogen ($^3J_{HF}$ = 1.5 Hz). Assignment of the larger and smaller $^2J_{PF}$ values to the equatorial and axial couplings, respectively, is consistent with previous findings[9,10] and suggests, if no unusual effects are operative, that P 3s orbital contributions are greatest in the equatorial bonds.[11] Increasing the temperature to +31 °C resulted only in very broad resonances, and the thermal instability of the compound prevented recording a high-temperature limiting ^{19}F NMR spectrum. The $^{31}P\{^1H\}$ NMR spectrum at -50 °C (Figure 1) showed the expected quartet of septets while the proton-coupled ^{31}P NMR spectrum showed in addition the doublet of this splitting pattern due to the large P–H coupling (607.9 Hz). The observance of a broad doublet with the same large P–H coupling in the ^1H NMR spectrum supports the formulation of the compound as $CH_3(CF_3)_3PH$.

C. Barrier to Permutational Rearrangement. The dynamic behavior of $CH_3(CF_3)_3PH$ was clearly demonstrated by the temperature-dependent $^{31}P\{^1H\}$ NMR spectra from -50 to +35 °C. At +35 °C, the limiting spectrum showing 8 of a possible 10 lines was nearly reached, indicating the averaging of the CF_3 groups in the one equatorial and two axial environments. This observable process most likely proceeds via a series of Berry pseudorotations.[12] Nine spectra were matched (Figure 2) with computer-simulated spectra[13] in the temperature range

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Table III. Activation Parameters for Intramolecular Exchange in $CH_3(CF_3)_3PH^{a,b}$

A	$(1.73 \pm 1.6) \times 10^{15}\ s^{-1}$	T_{av}	292 K^c
E_a	17.6 ± 0.5 kcal	$\Delta H^\ddagger_T$	17.0 ± 0.5 kcal
		$\Delta S^\ddagger_T$	9.3 ± 1.8 eu
$\Delta G^\ddagger_{298}$	14.2 ± 0.8 kcal	$\Delta G^\ddagger_T$	14.2 ± 0.8 kcal

[a] The sample composition was a 1:1 mixture of $CFCl_3$ and $CH_3(CF_3)_3PH$. [b] Obtained by unconstrained least-squares fit of rate-temperature data from $^{31}P\{^1H\}$ NMR. The error limits are those derived from statistical analysis. [c] This is not a coalescence temperature but rather the midpoint of the fitted region.

from 0 to +35 °C with rates ranging from 14.9 to 591.5 s^{-1} and a width at half-height maximum of 12.0 Hz. The kinetic magnetization transfer matrix (**K**) is the same as that given as supplementary material elsewhere.[14]

The activation parameters in Table III were obtained by fitting the temperature-rate data to Arrhenius and Eyring equations.[15] In keeping with previous work[1] the more reliable $\Delta G^\ddagger_{298}$ values instead of E_a values are used when barriers of related (trifluoromethyl)phosphoranes are compared.

While a moderate number of acyclic pentavalent hydrides of phosphorus are known, barriers to the permutational rearrangements of these systems have been established for only three compounds: H_2PF_3 ($\Delta G^\ddagger_{218} = 10.2$ kcal),[16] $CF_3(H)PF_3$ ($\Delta G^\ddagger_{133} = 6.3$ kcal),[16] and the present case $CH_3(CF_3)_3PH$ ($\Delta G^\ddagger_{298} = 14.2 \pm 0.8$ kcal). The last value is the largest barrier yet found for any acyclic pentavalent hydride of phosphorus. It is known that the rearrangement process in HPF_4 has ceased at −120 °C in the ^{19}F NMR spectrum,[6] but a numerical value of the barrier has not yet been reported. Judging from the temperature requirement, however, it is likely to be smaller than that for $CH_3(CF_3)_3PH$. The compounds $CH_3(H)PF_3$ and $C_2H_5(H)PF_3$ have been synthesized and the ^{19}F NMR spectra resolved[8] at −60 °C, but again no barrier determination has been reported. It is clear that hydrides are not exceptionally fluxional and that the barriers to permutational processes can be substantial. Comparison of measured barriers shows an increase in the series $CH_3(CF_3)_3PY$ in the order $F < Cl < OCH_3 < H < SCH_3 < N(CH_3)_3 < CH_3$[1] for Y. Except for the position of CH_3, this order compares well with barriers for fluorine interchange in the series F_4PY[3] [F, CH_3 (CF_3?) < Cl < H, SR < $N(CH_3)_2$] and for the series Y_2PF_3[2] [F, CF_3 < Cl, Br < H < CH_3 < C_6H_5 < $N(CH_3)_2$].

Calculation of the barriers to permutational interchange using the parameters given by Holmes,[17] which equates the CF_3 "element effect" to that of fluorine, gave an estimated barrier of 14.9 kcal in excellent agreement with the observed value. Using interpolated CF_3 parameters[14] which reflect the fact that the electronegativity of CF_3 is less than that of F gave a value of 11.5 kcal, poorer agreement but within the expected reliability of these calculations. Similar calculations gave 7.9 and 9.0 kcal, respectively, for $F_3(CF_3)PH$, in reasonable agreement with the experimental value of 6.4 kcal.[16] In this latter case, equating F and CF_3 parameters means that any arrangement of F and CF_3 provides equienergetic ground states and hence the ground-state structure is not fully predictable (H is however predicted to be in an equatorial position). The NMR data seem to clearly indicate that the CF_3 is in the equatorial position.[5,16] Furthermore, in this system all permutational pathways present equal energetic barriers. Using our unique CF_3 parameter obviates these difficulties for $F_3(CF_3)PH$, predicting the correct ground-state structure (**52** where CF_3 (=1) and H (=4) are equatorial and fluorine atoms occupy sites 2, 3, 5)[14,18] and selecting the pathway as either, in the pathway notation of Holmes[14,18]

$$\mathbf{52} \xrightleftharpoons{(4)} \mathbf{31} \xrightleftharpoons{(2)} \mathbf{54} \xrightleftharpoons{(3)} \mathbf{12} \xrightleftharpoons{(4)} \mathbf{35} \qquad (3)$$

or the equally energetic path

$$\mathbf{52} \xrightleftharpoons{(3)} \mathbf{14} \xrightleftharpoons{(2)} \mathbf{35} \qquad (4)$$

In either case the barrier maximum is provided by the square-pyramidal intermediates, which have an apical F atom.

The specific value assigned to the CF_3 element effect is without consequence in the prediction of the ground state of $CH_3(CF_3)_3PH$ because F vs. CF_3 distinctions are not required. Either set of parameters provides correct ground-state prediction (**52** where H (=1) and CH_3 (=4) are predicted to lie in the equatorial plane). The pathway given by eq 3 is slightly more favorable (11.5 kcal) than that given by eq 4 (11.8 kcal). In the former case the barrier maximum arises from the square-pyramidal intermediate with an apical fluorine atom whereas, in the latter, the maximum occurs with the trigonal-bipyramidal isomer **14**, which has H and CH_3 axial and all F atoms equatorial. While, as indicated above, the assignment of equal parameters to F and CF_3 gives a better estimation of the barrier, the unique value for CF_3 also selects ground states correctly and also gives reasonable agreement with the experimental barrier.

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Registry No. $CH_3(CF_3)_3PH$, 85318-50-9; $CH_3(CF_3)_3PF$, 57572-93-7; $(C_4H_9)_3SnH$, 688-73-3; $(CH_3)_3SiH$, 993-07-7; $CH_3(CF_3)_3PCl$, 56420-21-4; $CH_3P(CF_3)_2$, 1605-54-5; SiH_4, 7803-62-5; CH_3SiH_3, 992-94-9; CF_3H, 75-46-7.

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(13) A locally adapted version of the program EXCHSYS was used, described by: Kreiger, J. K; Deutsch, J. M.; Whitesides, G. M. *Inorg. Chem.* **1973**, *12*, 1535. Details of the program are given in: Kreiger, J. K., Ph.D. Thesis, MIT, Cambridge, MA, 1971.

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(18) See Figure 1.11 and Table 1.13 of ref 17. The labeling scheme is consistent with that used in ref 14 and 17.