Dimethyltris(trifluoromethyl)phosphorane, Me$_2$P(CF$_3$)$_3$ and Trimethylbis-(trifluoromethyl)phosphorane, Me$_3$P(CF$_3$)$_2$; Stable Monofunctionally Substituted Penta-alkyl Phosphoranes

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Summary The new, stable, penta-alkyl phosphoranes (CF$_3$)$_3$PMe$_2$ and (CF$_3$)$_2$PMe$_3$ are, according to n.m.r. spectral evidence, trigonal bipyramidal molecules, probably non-fluxional, in which CF$_3$ groups are found to be preferentially located in the axial positions.

No simple penta-alkyl phosphorane with five independent carbon-bonded substituents has previously been isolated; alkylation procedures in general yield only ylides such as Me$_3$P=CH$_2$.[1] Recently, stable 'penta-alkyl' phosphoranes were obtained in which two substituent positions were occupied by the bifunctional homocubyl[2] and bicycloheptyl[2] groups, the stability being attributed to the relief of strain provided by the bifunctional substituent.[2] This argument was supported by the stability of the aryl bisphenylene phosphoranes[3] although the stability of pentaphenyl phosphorane[4] suggests that bifunctionality is not a necessary requirement for stability.

We now report the preparation of the new pentacoordinate alkyl phosphoranes, Me$_2$P(CF$_3$)$_3$ (**1**), and Me$_3$P-CF$_3$)$_2$ (**2**), which were obtained in good (**1**, 75%) to moderate yield (**2**, 44%) as stable, unreactive, white solids† [m.p. (**1**), 64—65°; (**2**), 44—46°] from the reaction of (CF$_3$)$_3$PCl$_2$[5] or (CF$_3$)$_2$PCl$_3$[5] with tetramethyl-lead‡ at room temperature in a sealed tube. In addition, Me(CF$_3$)$_3$PF, obtained[6] from (CF$_3$)$_3$PF$_2$[7] and SnMe$_4$, was converted into (**1**) by PbMe$_4$ under the same conditions. N.m.r. spectroscopic studies at normal temperatures provide extensive evidence for a static trigonal bipyramidal structure in both cases. Two CF$_3$ environments in the ratio 2:1 are clearly shown in the ^{19}F n.m.r. (Figure) and ^{13}C n.m.r. spectra at 33 °C of (**1**). The more intense ^{19}F signal is reasonably assigned to two equivalent axial substituents on a trigonal bipyramidal framework, on the basis[8] of the small magnitude of $^2J_{PF}$ reinforced[9] by the value of $^1J_{PC}$. The less intense signal is due to an equatorial CF$_3$ group in keeping[9] with the relatively large magnitude of $^2J_{PF}$ and is similarly reinforced by the relatively large magnitude of $^1J_{PC}$. In all cases these two coupling constants seem to exhibit parallel trends. The ^{1}H and ^{13}C n.m.r. spectra of (**1**) show that the Me environments are equivalent. The expected first-order spin splitting pattern was observed in the ^{19}F and ^{1}H n.m.r. spectra of (**1**)

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† Satisfactory elemental analyses for all elements have been obtained for both compounds.

‡ Used as supplied by Alfa Inorganics as an 80% solution in toluene.

TABLE. N.m.r. data at 33 °C ($CFCl_3$)

		Chemical shifts			Coupling constants/Hz				
		ϕ_F[a]	τ[b]	δ (^{13}C)[c]	$^1J_{PC}$	$^2J_{PH}$	$^2J_{PF}$	$^4J_{FF}$[d]	$^4J_{FH}$
$(CF_3)_3PMe_2$	CF_3 (eq)	59·6[e]	—	127	206	—	114·0	14·0	—
	CF_3(ax)	70·7[f]	—	132	$\leqslant 8$	—	23·5	14·0	—
	Me	—	8·07[g]	7	88	13·4	—	—	—
$(CF_3)_2PMe_3$	CF_3 (ax)	74·4[h]	—	131	29	—	6·3	—	0·7
	Me	—	8·34[i]	8	102	14·0	—	—	—

[a] p.p.m. *vs* CCl_3F, positive values indicating resonance to high field of standard. [b] *vs* Me_4Si, $\tau = 10{\cdot}0$. [c] Measured values (*vs* CD_2Cl_2; $\delta = 53{\cdot}6$ p.p.m.) have been converted to ($^{13}CH_3)_4Si$ reference scale. Positive values indicate resonance downfield of standard. [d] Coupling between axial and equatorial CF_3 groups. [e] Doublet of septets, relative intensity ratio 1. [f] Doublet of quartets, relative intensity ratio 2. [g] Major doublet with complex multiplet arising from CF_3 coupling. [h] Eight lines of decet resolved clearly in each component of major doublet. [i] Doublet of septets.

and all possible coupling constants (Table) have been obtained. Heating the sample of (**1**) to 100 °C resulted in a little increase in the ^{19}F n.m.r. spectral line widths but no loss of fine structure. The simplest spectral assignment is therefore provided by a static trigonal bipyramidal molecular structure for (**1**).

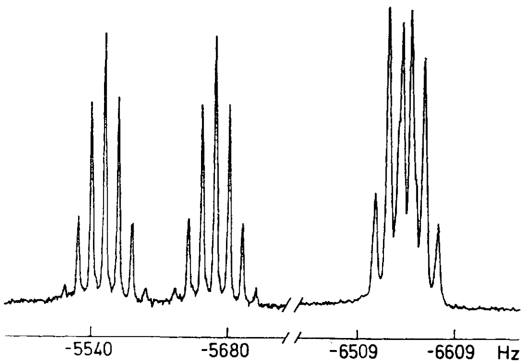

FIGURE. ^{19}F n.m.r. spectrum of $(CF_3)_3PMe_2$ at 33 °C on a solution in $CFCl_3$. The spectrum was obtained at 94·2 MHz.

At 33 °C, the ^{19}F, ^1H and ^{13}C spectra of (**2**) show clearly that all identical groups exist in equivalent environments. Although a completely unambiguous structural conclusion does not follow from these observations, the similarity of $^1J_{PC}$ values for Me and CF_3 substituents in (**2**) to those for Me and axial CF_3 groups in (**1**) suggests that the most reasonable structure of (**2**) is a trigonal bipyramid with exclusively axial CF_3 and exclusively equatorial Me substituents. Alternative assignments involving fluxional character and a square pyrimidal geometry are of course possible; however the above assignment accounts for all spectral data in the simplest and most satisfactory manner.

The very small value of $^2J_{PF}$ observed in the ^{19}F spectrum of (**2**) (6·3 Hz) is the lowest such value yet observed for an axial[8] CF_3 substituent in a trigonal bipyramid. It seems reasonable to expect that trends in $^2J_{PF}$ values observed earlier[8] might be paralleled by trends in $^1J_{PC}$ values and that the relatively small magnitudes of $^2J_{PF}$ and $^1J_{PC}$ associated with substituents in the axial positions of the trigonal bipyramid are due to proportionately smaller *s*-character in these bonds relative to equatorial bonds.

The stability of these new penta-alkyl phosphoranes may arise from the electron-withdrawing character of the CF_3 groups. We are now trying to establish whether a minimum number of such groups is necessary for stability.

The static behaviour of these molecules is also not particularly surprising if the relatively high coalescence temperatures found in $(CF_3)_3MePX$ (X=F, OMe)[6] are considered. These variously substituted phosphoranes[9] provide a series of molecules with different barriers to positional interchange which will hopefully yield further insight into the mechanisms of molecular rearrangement of phosphoranes.

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