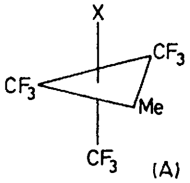
Methyltris(trifluoromethyl)phosphoranes, Me(CF$_3$)$_3$PX. Tetra-alkylphosphoranes with Fluoro-, Chloro-, and Methoxy-substituents

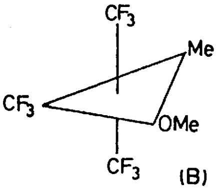
By KWAT I. THE and RONALD G. CAVELL*
(*Department of Chemistry, University of Alberta, Edmonton, Alberta* T6G 2G2 *Canada*)

Summary N.m.r. spectroscopic studies of three new tetra-alkylphosphoranes, Me(CF$_3$)$_3$PX (X = F, Cl, OMe), confirm their true phosphorane character and suggest that the ground state structures observable at low temperatures have a halogen and a CF$_3$ (X = F, Cl) or two CF$_3$ groups (X = Me) in the axial positions of a trigonal bipyramidal framework.

THE only reported tetra-alkylphosphoranes[1] Me$_4$PF and Me$_3$Bu^{n}PF appear to be unstable with respect to the phosphonium salt structure except in an isolated low temperature matrix or in the mass spectrometer. We have found that stable molecular tetra-alkylphosphoranes Me(CF$_3$)$_3$PF (I), m.p. 20—21 °C uncorr. (yield 82%) and Me(CF$_3$)$_3$PCl (II), m.p. 56—57 °C uncorr. (69%), can be easily prepared by the reactions of (CF$_3$)$_3$PX$_2$ (X = F[2] or Cl[3]) with Me$_4$Sn or Me$_4$Pb. A third tetra-alkylphosphorane, Me(CF$_3$)$_3$POMe (III), was obtained in quantitative yield from the reaction of either (I) or (II) with Me$_3$SiOMe at room temperature. Each compound hydrolyses stoicheiometrically in neutral or alkaline aqueous media to give either 2 or 3 mol. of CF$_3$H and the Me(CF$_3$)PO$_2^-$ or MePO$_3^{2-}$ ions[4–6] in solution.



(A)



(B)

(I) X = F
(II) X = Cl

(III)

The strongest supporting evidence for phosphorane character is provided by the observation of all significant nuclear spin coupling interactions in the normal temperature (+ 33 °C) n.m.r. spectra of (I) (wherein the CF$_3$ groups are equivalent) especially the major doublet of 843 Hz, which arises from the single fluorine atom located in the axial position[6] of the trigonal bipyramidal framework.

Low-temperature ^{19}F n.m.r. spectroscopy indicates that both (I) and (II) most likely possess the ground state structure (A). The CF$_3$ portion of the ^{19}F n.m.r. spectrum of (I) at −90 °C showed clearly two chemically shifted resonances in the intensity ratio 2:1. The relatively large value of $^2J_{PF}$ (135 Hz) in the more intense portion of the spectrum suggests[7] that this resonance arises from two equatorial CF$_3$ groups and the low value of $^2J_{PF}$ (35·5 Hz) in the unit intensity portion similarly suggests that this signal arises from an axial CF$_3$ group. The equatorial CF$_3$ signal also showed coupling to the axial F and to the unique (axial) CF$_3$ group. The axial CF$_3$ signal showed coupling to the equatorial CF$_3$ groups but not to the fluorine atom *trans* to it. In neither portion of the CF$_3$ spectrum was the long range F–H coupling resolved. Only the major $^1J_{PF}$ coupling constant was observed in the spectral region arising from the single F atom at low temperatures owing to the low intensity of the signal. All the coupling constants were confirmed by ^{31}P · · · · {^{1}H} n.m.r. spectroscopy. The large positive ^{31}P chemical shift values (*vs.* P$_4$O$_6$)[8] obtained therefrom are suggestive of phosphorane rather than phosphonium salt character.[5]

The parameters obtained for (II) are similar to those of (I) but only partial resolution of the CF$_3$ resonances into two chemically shifted regions with intensity ratio 1:2 could be achieved for (II) at −100 °C. The behaviour of (II) is, however, consistent with the proposed ground-state structure (A).

The ^{19}F n.m.r. spectrum of (III) at +33 °C also indicated averaged CF$_3$ environments. At −40 °C, two chemically shifted CF$_3$ regions were observed; a doublet of septets with a large $^2J_{PF}$ arising[7] from an equatorial CF$_3$ group and an incompletely resolved doublet of quartets of twice the intensity with a smaller $^2J_{PF}$ which arises from two axial CF$_3$ groups. Both regions showed a coupling of 13·6 Hz due to $^4J(F_{ax}F_{eq})$. Proton-decoupled ^{31}P spectra at −50 °C confirmed the presence of two $^2J_{PF}$ values. In keeping with our previous suggestion,[7] CF$_3$ groups occupy

TABLE. N.m.r. data

		Chemical shifts				Coupling constants						
Compound	Temp. /°C	τ[a]	φ(CF$_3$)[b] p.p.m.	φ(PF)[b] p.p.m.	δ(p)[c] p.p.m.	$^2J_{PH}$	$^3J_{FH}$	$^4J_{FH}$	$^1J_{PF}$	$^2J_{PF}$	$^3J_{FF}$	$^4J_{FF}$
Me(CF$_3$)$_3$PF .. (I)	.. +30	7·89	62·3	13·3	+164·1	15·4	8·7	0·6	843	102·5	17·3	—
	−90		59·7[d,e]		+166·4[l]				827	135·0	16·0[h]	12·5
			68·2[f,g]							35·0		12·5
Me(CF$_3$)$_3$PCl .. (II)	.. +30	7·48	63·3		+165·8	12·8		0·8		101·2		
Me(CF$_3$)$_3$PMe .. (III)	.. +30	8·10[i]	67·0[k]		+171·3	11·2		0·9		75·5		
		5·97[j]				12·8		0·9				
	−40		60·0[d,g]		+169·9[l]					108·5		13·6
			66·9[f,e]							62·0		13·6

[a] τ relative to Me$_4$Si. [b] φ in p.p.m. from CFCl$_3$ as internal standard, +ve indicating resonance to high field . [c] p.p.m. *vs.* P$_4$O$_6$[8] + ve indicating resonance to high field. [d] Equatorial CF$_3$. [e] Relative intensity 2F. [f] Axial CF$_3$. [g] Relative intensity 1F. [h] Value for ^3J (FPCF$_{eq}$); the coupling ^3J (FPCF$_{ax}$) was not observed. [i] Me group on P. [j] MeO group. [k] At 80 °C. [l] ^{31}P · · · {^{1}H} spectrum.

axial positions of a trigonal bipyramid in preference to the Me and OMe groups; thus the ground-state structure of (III) is (B). Any alternative assignment requires $^2J_{PF}$ to vary widely with substitution on phosphorus without apparent reason and we think that this is unlikely since $^2J_{PF}$ appears to be a consistent and predictable indicator of the position of the CF_3 group on phosphorus.

All three compounds clearly behave as molecular phosphoranes at ordinary temperatures making these the first truly stable tetra-alkylphosphoranes to be obtained. It seems reasonable to suggest that the replacement of alkyl groups by strongly electron-withdrawing trifluoromethyl groups has favoured the formation of the stable five-co-ordinate structure.

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[1] H. Schmidbaur, K-H. Mitschke, and J. Weidlein, *Angew. Chem. Internat. Edn.*, 1972, **11**, 144.

[2] W. Mahler, *Inorg. Chem.*, 1963, **2**, 230.

[3] H. J. Emeléus, R. N. Haszeldine, and R. C. Paul, *J. Chem. Soc.*, 1955, 563.

[4] R. G. Cavell and K. I. The, unpublished results.

[5] V. Mark, C. H. Dungan, M. M. Crutchfield, and J. R. Van Wazer, *Topics Phosophorus Chem.*, 1967, **5**, 227.

[6] E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, 1963, **2**, 613.

[7] R. G. Cavell, D. D. Poulin, K. I. The, and A. J. Tomlinson, *J.C.S. Chem. Comm.*, 1974, 19.

[8] A. C. Chapman, J. Homer, D. J. Mowthorpe, and K. T. Jones, *Chem. Comm.*, 1965, 121. The chemical shift of 85% H_3PO_4 is +112 p.p.m. (to high field) of P_4O_6.