Fluorophosphoranes containing the Perfluoropinacolyl Ring System. Part II.[1] Synthesis and Nuclear Magnetic Resonance Studies

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The synthesis of fluorophosphoranes containing the perfluoropinacolyl ring system is reported. The i.r. spectra are reported and mass spectra are discussed. The intramolecular exchange of ligands exhibited by these molecules has been studied. The parent trifluorophosphorane is a strong acceptor and complexes have been synthesised with trimethylphosphine and caesium fluoride.

We have recently reported the synthesis of fluorophosphoranes containing the perfluoropinacolyl moiety by the reaction of fluorophosphines with hexafluoroacetone.[1] We wish to report the extension of this synthetic route to give a number of new perfluoropinacolylfluorophosphoranes, two of which have been prepared by alternate paths by other workers.[2,3,‡]

It was of interest to prepare these derivatives in view of the current development of related dioxyorganophosphoranes as synthetic intermediates[4] and their possible application as models in biochemical systems showing rapid trigonal bipyramidal intramolecular exchange.[5]

The dioxyphosphoranes were prepared by the reaction of hexafluoroacetone with the corresponding fluorophosphines. The reactions invariably produced high yields of the desired fluorophosphorane on warming to room temperature (see Experimental section). The parent perfluoropinacolyltrifluorophosphorane (1), which fumes strongly in air, was prepared as described previously.[1] The compounds are thermally stable, colourless liquids or low-melting solids, and may be distilled without decomposition [apart from compound (6), the rearrangement of which has been previously described [1]]. Compounds (1)—(6) did not display any of the ring opening or rearrangement chemistry that has been noted for similar organophosphorus systems.[6-8]

$$RPF_2 + 2\,(CF_3)_2CO \longrightarrow RPF_2(pfp)$$

(2) R = Me; (3) R = Bu^t; (4) R = Ph; (5) R = Et$_2$N; (6) R = (Me$_3$Si)$_2$N

pfp = perfluoropinacolyl ring moiety [–O–C(CF$_3$)$_2$C(CF$_3$)$_2$O–]

Scheme 1

The chemistry of (1) was investigated, in particular its reactions as a Lewis acid. Thus, combination of (1) with trimethylphosphine in a sealed system produced a surprisingly stable adduct (7), the structure of which was established by ^{19}F n.m.r. spectroscopy. The assigned structure is reproduced in Figure 1. Compound (1) was also found to react with dry caesium fluoride in the presence of acetonitrile to give the ionic product (8). The structure of (8) was also established by ^{19}F n.m.r. spectroscopy; only one isomer of the anion [PF$_4$(pfp)]$^-$ is possible. Reaction with caesium fluoride did not occur in the absence of acetonitrile and separation of (8) from acetonitrile solution as a pure solid was found to be impossible.

$$CsF + \underset{(1)}{PF_3(pfp)} \xrightarrow[20^{\circ}]{CH_3CN} \underset{(8)}{[PF_4(pfp)]^-Cs^+}$$

Scheme 2

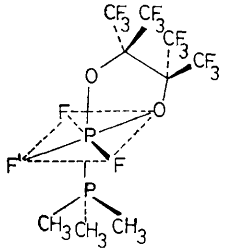

Figure 1 Structure of the adduct between trimethylphosphine and perfluoropinacolyltrifluorophosphorane

Both the adduct (7) and the ionic product (8) appear to be thermally quite stable. Compound (7) may be melted (92 °C) without apparent dissociation and appeared to be at least as stable as $Me_3P{\rightarrow}PF_5$.[9] Compound (7) is the first reported trifluorophosphorane–base adduct and demonstrates the powerful acceptor properties of compound (1) compared with other substituted fluorophosphoranes.

The i.r. spectra of compounds (1) to (7) are presented in Table 1. Frequencies between 1300 and 1190 cm^{-1} are confidently assigned to the very intense CF$_3$ stretching modes. It has been claimed that five characteristic frequencies are found for a perfluoropinacolyl group in a

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‡ Perfluoropinacolyl(diethylamino)difluorophosphorane was described as an adduct, Et$_2$NPF$_2$·2(CF$_3$)$_2$CO, by the authors of ref. 2 although it is clearly a pinacolyl derivative.

[1] Part I, J. A. Gibson and G.-V. Röschenthaler, *J.C.S. Chem. Comm.*, 1974, 694.

[2] G. I. Drozd and S. Z. Ivin, *Zhur. obshchei, Khim.*, 1969, **39**, 1179.

[3] V. N. Volkovitskii, I. L. Knunyants, and E. G. Bykhovskaya, *Zhur. Vsesoyuz. Khim. obshch. im. D. I. Mendeleeva*, 1973, **18**, 236.

[4] F. Ramirez, *Synthesis*, 1974, 90.

[5] D. Marquarding, F. Ramirez, I. Ugi, and P. Gillespie, *Angew. Chem.*, 1973, **85**, 99.

[6] V. N. Volkovitskii, I. L. Knunyants, and E. G. Bykhovskaya, *Zhur. Vsesoyuz. Khim. obshch. im. D. I. Mendeleeva*, 1973, **18**, 112.

[7] R. K. Oram and S. Trippett, *J.C.S. Perkin I*, 1973, 1300.

[8] F. Ramirez, *Bull. Soc. chim. France*, 1970, 3497; F. Ramirez, C. P. Smith, and J. F. Pilot, *J. Amer. Chem. Soc.*, 1968, **90**, 6726.

[9] C. W. Schultz and R. W. Rudolph, *J. Amer. Chem. Soc.*, 1971, **93**, 1898.

ring system.[10] These frequencies (which probably include the CF bending modes) are tentatively assigned in Table 1 since a group of five frequencies was found to persist with very little change throughout compounds (1) to (6).

It is extremely difficult to assign P–F frequencies in these molecules, particularly in view of the low (probably C_s) symmetries involved and overlapping with modes from the groups R which may also lie in the 1000—700 cm^{-1} region. Compound (1) which contains no R group has two frequencies in this region which are more confidently assigned to ν_{PF}.

TABLE 1

I.r. spectra * of perfluoropinacolylfluorophosphoranes, RPF$_2$(pfp), and Me$_3$P→PF$_3$(pfp)

R =							
F [a]	Me [a]	Bu^t [b]	Ph [b]	Et$_2$N [b]	(Me$_3$Si)$_2$N [b]	Me$_3$P→PF$_3$(pfp) [c]	Assignment
	3020w	3020m	3100w	3110w	3010m		ν_{CH}
		2980m		2980w	2970m		
		2950w					
		2930w	2910w	2920w	2915w		
2600sh	2620sh						$2\nu_{CF_3}$
2570m	2540m			2550sh	2530m		
2510m		2520m	2500m	2490w			
2490sh					2450w		
	2345w	2370w					
		1484w		1430m			δ_{CH_3}
	1382m	1466w					
	1332m	1408w					
1284sh	1300sh	1296vs		1277sh	1273sh	1273sh	ν_{CF_3}
1264vs	1265vs	1276sh		1263sh			
1234s	1230vs	1243vs	1245vs	1240vs	1245vs	1224vs	
1220m	1200sh	1216vs	1215vs	1217vs	1208s	1196vs	
			1190sh	1190sh			
1198w	1168w	1160m	1163s			1173w	
1144w	1140sh	1136m	1140s	1157w	1152m		
					1134w		
*1113*m	*1120*s	*1118*s	*1120*s	*1126*m	*1113*m		*d*
			1048m	1048m			
*1020*m	*1002*w	*1000*w	*1000*w	*1000*w	*1022*s	*1011*m	*d*
992s [e]					989m		
*974*s	*975*s	*965*s	*967*m	*967*m	*960*s	*978*m	*d*
	945m					956s	
						943m	
900s [e]	910sh	910s			907s		
*880*m	*882*m	*882*m	*882*s	*890*s	*871*s	*874*m	*d*
		846m	840m	866m	858s		
				838s	823m		
	815s	790s	807vs	820s	802w	819m	
					777s	781m	
						756w	
*740*s	*745*s	*742*m	*745*m	*741*m	*735*m	*734*w	*d*
	714vs	718m	720m	719m			
		700w			707s	696m	
		680m	685m	688m			
		640m	602m				

* Frequencies in cm^{-1}; s = strong, vs = very strong, w = weak, m = medium, sh = shoulder.

[a] Gas phase. [b] Capillary film between NaCl plates. [c] Nujol mull between NaCl plates. [d] Modes of the perfluoropinacolyl ring system. [e] ν_{PF}.

The mass spectra of compounds (1) to (7) proved useful in confirming their molecular composition. Molecular ions were not found for (1), (6), and (7) but were observed at very low intensity for (2) and (3). Compounds (4) and (5) had readily detectable molecular ions.

Compound (1), the trifluorophosphorane, had a very intense peak corresponding to $(M - F)^+$, a common observation in fluorophosphoranes.[11] Compounds (2), (3), (4), and (5) all showed a similar characteristic fragmentation pattern $[(M - F)^+, (M - CF_3)^+, (M - R)^+]$. Loss of CF$_3$ produced the base peak for (4) while loss of Et$_2$N gave that for (5). In compounds (1), (2), and (3) the base peak was due to CF$_3$$^+$.

The bis(trimethylsilyl)amino-compound (6) displayed a somewhat different fragmentation, as might be expected for a trimethylsilyl derivative.[12] The peak of highest mass was that formed by loss of Me. Loss of Me$_3$SiF from this ion appeared to be a strongly favoured process giving a peak at *m*/*e* 358. Unfortunately these processes

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[10] M. Allen, A. F. Janzen, and C. J. Willis, *Canad. J. Chem.*, 1968, **46**, 3671.

[11] T. A. Blazer, R. Schmutzler, and I. K. Gregor, *Z. Naturforsch.*, 1969, **24b**, 1081.

[12] T. R. Spalding, in 'Mass Spectrometry of Inorganic and Organometallic Compounds,' eds. M. R. Litzow and T. R. Spalding, Elsevier, London, 1973, p. 207.

could not be confirmed by metastable ions.* The fragmentation pattern thus appears to be dominated by the presence of reactive Me_3Si groups, this is reflected in the observation of a base peak corresponding to Me_2SiF^+.

TABLE 2

^1H, ^{19}F, and ^{31}P N.m.r. data for perfluoropinacolylfluorophosphoranes and their derivatives at 20 °C

Compound [a]	δ_H	δ_P	δ_{PF_n}	δ_{CF_3}	$^1J_{PF}$	$^3J_{HP}$	$^4J_{HF}$	$^4J_{PF}$	$^5J_{FPF}$
$FPF_2(pfp)$ (1) [b]		+54·3	+65·2	+68·8	935			0·85	2·1
$MePF_2(pfp)$ (2)	−1·83 [c]	+12·8	+44·3	+69·2	973			<0·4	2·3
$Bu^tPF_2(pfp)$ (3)	−1·29	+12·3	+58·6	+69·4	1043	23·4	1·0	<0·3	2·7
$PhPF_2(pfp)$ (4)	−7·8 [d]	+32·4	+49·9	+69·1	959			0·3	1·0
$Et_2NPF_2(pfp)$ (5)	−1·18 (CH_3) [e] −3·42(CH_2)	+48·5	+57·5	+68·3	853	16·5		<0·5 [f]	2·3 [f]
$(Me_3Si)_2NPF_2(pfp)$ (6)	−0·56	+40·5 −20 [j]	+38·6 [g] +46·6 [k]	+68·3 [h]	891 881			<0·5 [f]	1·8 [f]
$Me_3P \rightarrow F_3P(pfp)$ (7) [i]	−1·72	+130	+34·5 +68·4	+66·5	898 726 [m]	12·1	1·6		[l]
$Cs^+[F_4P(pfp)]^-$ (8) [i]		+122·9	+52·2	+67·3	776				

[a] N.m.r. studies were carried out on toluene solutions (30—70%) unless otherwise indicated. Chemical shifts (p.p.m.) are reported as downfield = negative. Proton, fluorine, and phosphorus shifts are relative to internal Me_4Si, internal CCl_3F, and external H_3PO_4 (85%), respectively. Coupling constants are reported in Hz and < is used to denote a maximum value which cannot be determined accurately due to overlapping or similar effects. [b] pfp = Perfluoropinacolyl ring system. [c] $^2J_{HP} = 18·5$ Hz, $^3J_{HF} = 7·5$ Hz, $^6J_{HF} = 0·15$ Hz. [d] Second-order phenyl resonance. [e] $^3J_{HH} = 7·1$ Hz. [f] Not resolved at 20 °C owing to temperature effects, value reported was obtained at 80—100 °C (see text). [g] $^5J_{FH} = 0·6$ Hz, $^4J_{PH} = 0·2$ Hz. [h] Doublet resonance at 20 °C, average shift given (see text). [i] Acetonitrile solutions. [j] Spectra only obtainable by rapid-passage dispersion-mode technique; shifts accurate to ±5 p.p.m., $^1J_{PP} = 710 \pm 20$ Hz. [k] See text, $^2J_{HP} = 16·4$ Hz, $^2J_{PF} = 118$ and 183 Hz, $^2J_{FF} = 71·0$ Hz. [l] Not resolved. [m] $^2J_{FF} = 39·1$ Hz.

Compound (7), the trimethylphosphine adduct, has a peak of highest mass due to $(M - F)^+$ and an intense peak due to $(M - CF_3)^+$ was also observed [the adduct $Me_3P \rightarrow PF_5$ also shows $(M - F)^+$ as the peak of the highest mass[9]]. The base peak was CF_3^+ and a fragmentation pattern attributable to the trimethylphosphine moiety was also observed.

In all the compounds typical ions derived from the fragmentation of the pinacol ring were observed.[10] Hydrolysis products were carefully checked for in the mass spectra but were not observed.

Nuclear Magnetic Resonance Studies.—The so-called Berry pseudorotation and Turnstile rotation pathways have been used extensively in the discussion of intramolecular exchange phenomena.[13,14] Fluorophosphoranes are particularly suited to study by variable-temperature ^{19}F n.m.r. spectroscopy[15] while several reports have also appeared on organophosphorus systems containing the perfluoropinacolyl ring system.[16-18]

The compounds reported here are the first examples of perfluoropinacolylfluorophosphoranes to be investigated by variable-temperature ^{19}F n.m.r. spectroscopy. Thus it was possible to study both CF_3 groups and P*F* groups simultaneously in these compounds.

Details of the ambient-temperature spectra of compounds (1) to (8) are given in Table 2. The ^{19}F n.m.r. spectrum of compound (1) is reproduced in Figure 2. Compounds (1) to (6) are fluorophosphoranes and will be considered first. The ^{19}F n.m.r. spectra of (1) to (5) at room temperature consist of one resonance for fluorine attached to phosphorus, split into a doublet ($^1J_{PF}$) and a singlet for the CF_3 groups. Assuming trigonal bipyramidal geometries (see later) and the usual ' rules '

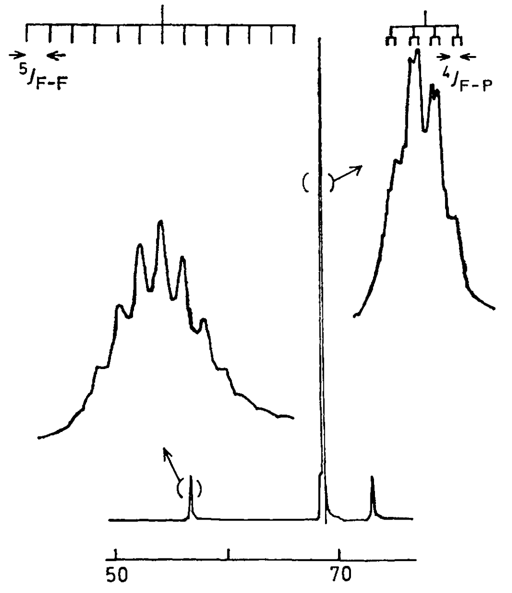

FIGURE 2 ^{19}F N.m.r. spectrum of perfluoropinacolyltrifluorophosphorane

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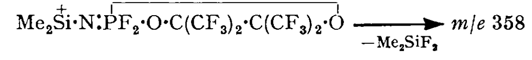
* A tentative fragmentation pattern is:



$$M^+ \xrightarrow[-Me]{} (M - Me)^+ \xrightarrow[-Me_3SiF]{} Me_2\overset{+}{Si}\cdot N\colon PF_2\cdot O\cdot C(CF_3)_2\cdot C(CF_3)_2\cdot O \xrightarrow[-Me_2SiF_2]{} m/e\ 358$$

This process may be associated with the thermal rearrangement characteristics of compound (6) previously reported[1] and is currently under investigation by pyrolysis mass spectrometry.

[13] R. S. Berry, *J. Chem. Phys.*, 1960, **32**, 933.

[14] P. Gillespie, P. Hoffmann, H. Klusacek, D. Marquarding, S. Pfohl, F. Ramirez, E. A. Tsolis, and I. Ugi, *Angew. Chem.*, 1971, **83**, 691.

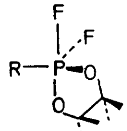
[15] R. Schmutzler, in ' Halogen Chemistry,' ed. V. Gutmann, vol, **2**, p. 31.

[16] F. Ramirez and I. Ugi, *Bull. Soc. chim. France*, 1974, **453**.

[17] I. Ugi, F. Ramirez, D. Marquarding, H. Klusacek, and P. Gillespie, *Accounts Chem. Res.*, 1971, **4**, 288.

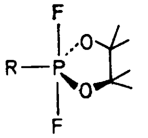
[18] S. Trippett and P. J. Whittle, *J.C.S. Perkin I*, 1973, 2302.

for substitution of alkyl groups on fluorophosphoranes[15] such spectra can only be explained by rapid intramolecular exchange in structure (a) or by a static structure (b).



(a)

or

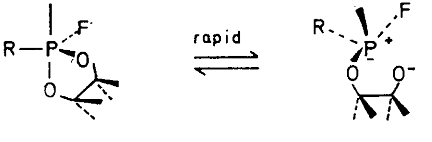


(b)

We do not favour (b) as the ground state for a number of reasons. Five-membered rings, particularly those containing electronegative substituents, prefer an axial–equatorial configuration because of ring strain in the diequatorial arrangement.[16,19,20] Diequatorial substitution has only been found in certain cases where an alkyl ring is involved.[21] The P*F* chemical shifts and $^1J_{PF}$ coupling constants[15] all support structure (a). It is interesting that the $^1J_{PF}$ values reported are closer to those for tetrafluorophosphoranes than for difluorophosphoranes[15] and are close to those reported for perfluoroalkoxy-substituted fluorophosphoranes.[22] As might be expected compound (1), the trifluorophosphorane, has the highest P*F* shift at 65·2 p.p.m. Compound (6) has a broad doublet for the CF_3 resonances at room temperature, despite a sharp P*F* doublet, while compound (5) has a broad singlet for the CF_3 groups. If structure (a) were rigid two P*F* resonances would be expected and four separate CF_3 signals [except for compound (1) which would only have two sets of non-equivalent CF_3 groups].

Arguments concerning the path of the intramolecular exchange will be based on the assumption of trigonal bipyramidal geometry although the possibility in some compounds of distortions towards, for example, square pyramidal structures is intriguing.* *X*-Ray investigations of organophosphorus systems containing the perfluoropinacolyl moiety indicate some distortions are produced and it is claimed that these distortions ' assist ' the turnstile mechanism of exchange.[16] The structure is still fundamentally trigonal bipyramidal however. Other studies have shown that spiro-phosphoranes may be sufficiently distorted as to be close to square pyramidal.[23]

The possibility of equilibration of sites by an ionisation process was considered, *viz*:



A mechanism of this type cannot be discounted despite the long range ($^5J_{PFF}$) coupling observed even at elevated temperatures (see Table 2). A P–O bond cleavage would cause, in certain circumstances, a loss of the coupling mentioned.† In addition due consideration must also be given to other factors such as solvent or catalytic effects[24] or the effect on the exchange barrier of low-lying square pyramidal isomers.[20]

The temperature dependent ^{19}F n.m.r. spectra of compounds (1) to (6) was investigated in the hope of throwing more light on the mechanism of exchange. Toluene–CCl_3F was found to be the best solvent system but nevertheless studies were restricted to *ca.* —90 °C due to crystallisation occurring.

Compounds (1) to (4) had spectra that were completely independent of temperature while compounds (5) and (6) had temperature-independent P*F* signals but the CF_3 resonance split into two signals on cooling. The spectra of compound (6) are shown in Figure 3.

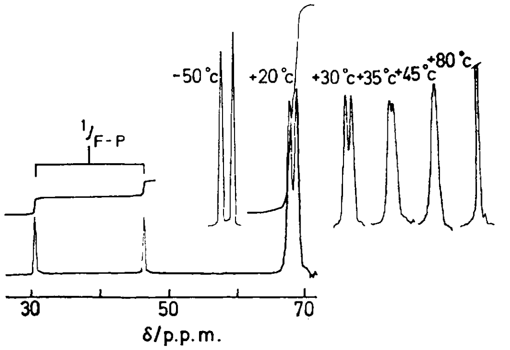


FIGURE 3 ^{19}F N.m.r. spectrum of [bis(trimethylsilyl)amino]-perfluoropinacolyldifluorophosphorane; effect of temperature upon CF_3 resonances

At *ca.* —50 °C the CF_3 signals had the appearance of the spectrum previously observed for $\mathrm{O{=}\overline{S{-}O{-}C(CF_3)_2{-}C(CF_3)_2{-}O}}$.[25] The low-field CF_3 signal was further split by what appeared to be long-range ($^5J_{FPF}$) coupling to the fluorine on phosphorus. The coupling was approximately twice that found at high temperature when the CF_3 resonances average to one sharp signal. The high-field CF_3 signal showed no additional coupling.

We believe that the results of the variable-temperature studies may best be explained by the processes depicted in Figure 4. The sequence of exchanges is similar to that described by Trippett and co-workers[7,18] but is

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* An *X*-ray crystallographic investigation of the phosphetidine in Part I[1] is underway and will provide data as to the extent of such distortions.

† See footnote of ref. 16, p. 458.

[19] F. H. Westheimer, *Accounts Chem. Res.*, 1968, **1**, 70.

[20] R. R. Holmes, *Accounts Chem. Res.*, 1972, **5**, 296.

[21] N. J. De'ath, D. Z. Denney, D. B. Denney, and C. D. Hall, *Phosphorus*, 1974, **3**, 205.

[22] D. E. Young and W. B. Fox, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 1033.

[23] H. Wunderlich, D. Mootz, R. Schmutzler, and M. Wieber, *Z. Naturforsch.*, 1974, **29b**, 32; M. Eisenhut, R. Schmutzler, and W. S. Sheldrick, *J.C.S. Chem. Comm.*, 1973, 144.

[24] M. Eisenhut, H. L. Mitchell, D. D. Traficante, R. J. Kaufman, J. M. Deutch, and G. M. Whitesides, *J. Amer. Chem. Soc.*, 1974, **96**, 5385; J. A. Gibson, D. G. Ibbott, and A. F. Janzen, *Canad. J. Chem.*, 1973, **51**, 2853.

[25] M. Allen, A. F. Janzen, and C. J. Willis, *Chem. Comm.*, 1968, 55; J. A. Gibson and A. F. Janzen, unpublished work.

more easily visualised by taking projections in the plane of the pinacol ring looking towards the phosphorus atom. The depicted relationship of the groups R, F, and F′ is only approximate but is equally valid for both the trigonal bipyramidal and turnstile forms shown.

By inspection it is clear that step *1* (TR^1 or BSR; TR^1 = turnstile rotation *1*; BSR = Berry pseudo-rotation) will produce the equilibration A≡C and B≡D but not A≡B and C≡D, while step *2* equilibrates all four sites, A≡B≡C≡D (when taken with step *1*). Steps *1* and *2* both equilibrate F and F′. Steps *1* and *2* correspond to the low-energy and high-energy processes, respectively, as described by Trippett.[7,18] The appearance of the spectra thus depends on whether steps *1*, *2*, or both are operating (or the symmetry related steps *3*, *4*, *etc.*).

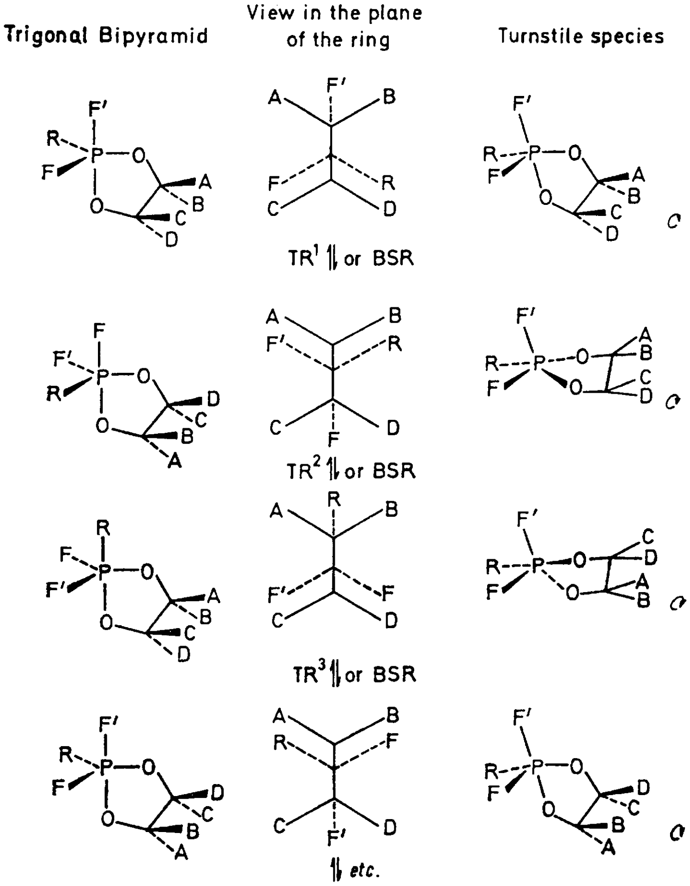

FIGURE 4 Intramolecular exchange processes in perfluoropinacolylfluorophosphorane

For compounds with temperature-independent spectra [(1)—(4)] steps *1* and *2* are operating, even at -90 °C, while for (5) and (6) step *2* is slowed at lower temperature but step *1* is still rapid.* By inspection it is also obvious that the long-range coupling observed in only one of the CF$_3$ signals of compounds (5) and (6) at low temperatures is not unexpected since one set of CF$_3$ groups always lie *cis* to rapidly equilibrating F and F′ while the other CF$_3$ groups lie *trans*. The coupling is averaged at high temperatures when step *1* and *2* are operating.

It is interesting that when the discrete trigonal bipyramidal forms are considered step *2* must involve the placing of R in the axial position (and therefore the term ' high energy process ' [7]). Construction of molecular models for compound (3; R = Bu^t) indicates strong steric interactions with the three ligands at 90° when the Bu^t group is axially substituted. It is of considerable surprise therefore that step *2* is still operating even at -90 °C for this species. For this reason we have included the turnstile rotation forms in Figure 4 as the placing of R in a formal axial position is avoided. Turnstile rotations can be effected by holding F, F′, and R as the trio and rotating the pinacol ring through successive arcs of 60°.[14] As has been pointed out by others [14] the pair may continue to rotate through high-energy forms before relaxing to a stable trigonal bipyramid. We do not consider that our results in any way offer proof of a turnstile mechanism but the possibility should be considered in the light of the very low barrier to step *2* for compounds (2)—(4) [compound (1) is, of course, a special case where step *1* and *2* are identical].

The P–N-rotation freezing effects described by Trippett [18] were not observed in compounds (5) and (6). Although various forms with the pinacol ring lying diequatorial (as a high-energy form) have not been considered here the conclusions reached are essentially identical. Finally it should be pointed out that the characteristics of exchange for compounds (2)—(4) are very similar to RPF$_4$ compounds (R = alkyl or aryl). The low barriers observed in the RPF$_4$ compounds are thought to be possible because R can remain equatorial during the exchange.[26] This explanation is clearly not applicable in the case of the compounds reported here.

The structures of compounds (7) and (8) were also assigned on the basis of their ^{19}F n.m.r. spectra. Compound (8) had a phosphorus shift of +122·9 p.p.m. indicating six co-ordinate geometry,[9,27] while the ^{19}F n.m.r. spectrum showed, in addition to the CF$_3$ signal, two doublets of triplets indicating two types of coupled fluorine in a 2 : 2 ratio. The structure is therefore octahedral with C_{2v} symmetry, only one isomer being possible since the pinacolyl ring must be *cis*-substituted.

Compound (7) is interesting in that two isomers are possible. A phosphorus shift of +130 p.p.m. again indicated six-co-ordinate geometry while a second phosphorus signal was observed at -20 p.p.m., in the correct range for four-co-ordinate phosphorus.[27] Unfortunately accurate phosphorus spectra were not

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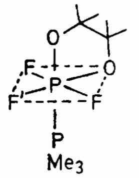
* Compound (6) showed some additional broadening of the CF$_3$ doublet at -90 °C and the P*F* signal also showed similar effects; unfortunately it was not possible to complete studies below this temperature.

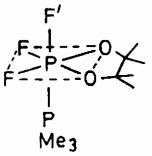
[26] E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, 1963, **2**, 613.

[27] M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. van Wazer, *Topics Phosphorus Chem.*, 1967, **5**, 173.

available since the limited solubility of (7) in acetonitrile necessitated the use of the fast sweep, high R_f power, dispersion-mode technique.[28] Many of the individual lines were not clearly resolved but with the coupling constant data available from ^1H and ^{19}F n.m.r. spectra it was possible to simulate spectra which were in good agreement to that observed. The $^1J_{PP}$ coupling obtained by this technique was 710 Hz which compares very favourably with the very high value of 720 Hz reported for $Me_3P{\rightarrow}PF_5$.[9] The two possible structural isomers for $Me_3P{\rightarrow}PF_3$(pfp) are:



' oxygen-*trans* '



' fluorine-*trans* '

The ^{19}F n.m.r. spectrum of (7) in the P*F* region consisted of a doublet of doublets of triplets and a doublet of doublets of doublets, with relative intensities of 1 : 2, respectively. In addition there is long-range HF coupling, more clearly resolved in the ^1H n.m.r. spectrum which consists of an apparent doublet of doublets of quartets ($^4J_{HF}$ and $^4J_{HF'}$ being equal at 1·6 Hz). The relevant coupling-constant data are given in Table 2. The results can only be explained by the formation of the ' oxygen-*trans* ' isomer in preference to the ' fluorine-*trans* ' isomer since there is adequate literature [9,29,30] available indicating that both $^4J_{HF'}$ and $^2J_{PF'}$ should be *ca.* 0 Hz for the ' fluorine-*trans* ' isomer. With $^4J_{HF'} = 1{\cdot}6$ Hz and $^2J_{PF'} = 118$ Hz the ' oxygen-*trans* ' structure is indicated. Observed vicinal coupling constants are strongly a function of the dihedral angle at phosphorus and approach zero for angles of 180°.[9,29,30]

EXPERIMENTAL

The appropriate precautions in handling moisture-sensitive products were observed throughout this work. Solvents for n.m.r. studies were dried by standard procedures.

^1H, ^{19}F, and ^{31}P Spectra were recorded on a JEOL 60 HL instrument at 60, 56·4, and 24·3 MHz respectively. An external H_2O lock system with generation of 4000 Hz side bands was used to locate resonances accurately. Coupling-constant data were taken from ^1H and ^{19}F spectra in preference to ^{31}P spectra as the former were considered more accurate. The average of several forward and reverse sweeps was used to determine the ^{31}P shifts in the rapid-passage dispersion-mode spectra necessary for compound (7).

I.r. spectra were recorded on a Beckman IR 20A in the gas phase in a 10-cm cell, fitted with Kel-F wax-sealed NaCl plates, or as liquid films between NaCl plates [compound (7) required mulling in Nujol]. Spectra were calibrated with polystyrene film.

Mass spectra were recorded on an A.E.I. MS 9 and a A.E.I. MS 30 instrument (direct-inlet system).

The fluorophosphines were synthesised by literature procedures [31] except for $(Me_3Si)_2NPF_2$ [32] (see Acknowledgement). Hexafluoroacetone was purified by trap-to-trap distillation to remove traces of the hydrate. Trimethylphosphine was prepared by standard methods.[33] Caesium fluoride was dried by heating under high vacuum for 9 h. Phosphorus pentafluoride (Matheson) was used as received.

Preparation of Perfluoropinacolylfluorophosphoranes.—Data pertinent to the preparation of these compounds, including analyses, are listed in Table 3. For i.r. and n.m.r. data see Tables 1 and 2. The following preparation is typical for compounds (2)—(6).

Perfluoropinacolylphenyldifluorophosphorane.—Into a thick-wall glass tube containing phenyldifluorophosphine (7·3 g, 0·05 mol) at −196 °C was condensed hexafluoroacetone (16·6 g, 0·1 mol). The tube was flame-sealed and allowed to warm slowly to +20 °C during 2 h; it was then shaken for 2 days.

The tube was opened *in vacuo* at −196 °C and traces of unchanged hexafluoroacetone were removed at 0 °C by gentle pumping. The crude product (22·7 g, 95%) was distilled *in vacuo* to give 20·3 g (b.p. 63—64 °C, 2·6 mmHg) of a clear colourless liquid.

Preparation of Perfluoropinacolyltrifluorophosphorane.—Into a thick-wall glass tube containing (6) (11·2 g, 0·02 mol) at −196 °C was condensed phosphorus pentafluoride (2·5 g, 0·02 mol). The tube was flame-sealed and allowed to warm slowly to +20 °C during 36 h; it was then left for 4 days. The crystalline compound (6) was observed to react during this period to give a cloudy viscous liquid mixture.

The tube was opened *in vacuo* at −196 °C and the volatile materials were removed on warming. The crude volatile materials were separated by trap-to-trap distillation on the vacuum line with bath temperatures of −196, −78, and −30 °C. The −196 °C trap was found to contain traces of PF_5 and some Me_3SiF (identified by i.r. and n.m.r. spectroscopy) while the −78 °C trap contained pure Me_3SiF. The combination of the −196 and −78 °C traps indicated a close to quantitative yield of trimethylfluorosilane (0·039 mol). The −30 °C trap contained a microcrystalline material that melted sharply at −10 to −11 °C to give a clear liquid having a vapour pressure of 13 mmHg at +20 °C and *ca.* 1 atm at +55 °C. The yield of (1) was 5·9 g (0·014 mol).

Preparation of the Adduct of Trimethylphosphine with (1).—Trimethylphosphine (0·08 g, 0·001 mol) and (1) (0·42 g, 0·001 mol) were combined at −196 °C *in vacuo* in a glass tube fitted with a Teflon high-vacuum valve. When the mixture was warmed to +20 °C a rapid reaction occurred giving an off-white solid. Traces of volatile materials were removed by gentle pumping and the product was very carefully recrystallised from acetonitrile to give 0·45 g of air-stable colourless crystals, m.p. 95—96 °C.

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Preparation of Caesium Perfluoropinacolyltetrafluorophosphate (8).—Compound (1) (0·84 g, 0·002 mol) was condensed at −196 °C onto caesium fluoride (0·3 g, 0·002 mol) in a glass tube fitted with a Teflon high-vacuum valve and magnetic stirrer. No reaction occurred until acetonitrile (3·5 ml) was condensed onto the mixture when the caesium fluoride was observed to dissolve with stirring during 12 h at +20 °C. When acetonitrile was pumped off a sticky solid product was left which apparently contained acetonitrile.

TABLE 3

Perfluoropinacolylfluorophosphoranes, $RPF_2(pfp)$, and their derivatives

Compound	Reactants, mole		Reaction conditions	Yield (%)	B.p. (t/°C) [p/mmHg]		Analyses (%)			
							C	H	F	P
$PF_3(pfp)$ (1)	(6)	0·02	Warmed up from −196 to 20 °C; 4 days at 20 °C	70	55	Calc.	17·2		56·5	7·4
	PF_5	0·02			−11 [c]	Found	17·2		56·8	7·3
$MePF_2(pfp)$ (2)	$MePF_2$	0·05	Warmed up from −196 to 20 °C; 3 days at 20 °C	85	44				[b]	
	Hfa [a]	0·01			[21]					
$Bu^tPF_2(pfp)$ (3)	Bu^tPF_2	0·05	Warmed up from −196 to 20 °C; 12 h at 20 °C	100	17—18 [c]	Calc.	26·4	2·0	57·9	6·7
	Hfa	0·1				Found	26·4	2·0	58·3	6·6
$PhPF_2(pfp)$ (4)	$PhPF_2$	0·05	Warmed up from −196 to 20 °C; 2 days at 20 °C	85	63—64	Calc.	30·3	1·1	55·9	6·5
	Hfa	0·1			[2·6]	Found	30·3	1·1	55·8	6·3
$Et_2NPF_2(pfp)$ (5)	Et_2NPF_2	0·05	Warmed up from −196 to 20 °C; 12 h at 20 °C	95	47—48	Calc.	25·5	2·1	56·5	6·6
	Hfa	0·1			[2·2]	Found	25·5	2·1	56·8	6·6
$(Me_3Si)_2NPF_2(pfp)$ (6)	$(Me_3Si)_2NPF_2$	0·05	Warmed up from −196 to 20 °C; 12 h at 20 °C	100	30—31 [c]	Calc.	25·8	3·2	47·4	5·5
	Hfa	0·1				Found	25·7	3·3	47·5	5·7
$Me_3P{\rightarrow}PF_3(pfp)$ (7)	Me_3P	0·001	Warmed up from −196 to 20 °C	90	95—96 [c]	Calc.	21·8	1·8	57·4	12·5
	$PF_3(pfp)$	0·001				Found	21·1	1·8	57·1	12·1
$Cs^+[PF_4(pfp)]^-$ (8)	CsF	0·002	Stirring in CH_3CN for 12 h				See text.			
	$PF_3(pfp)$	0·002								

[a] Hfa = Hexafluoroacetone. [b] See ref. 3. [c] M.p.

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