Fluorophosphoranes containing the Perfluoropinacolyl Ring System. Part III.[1] Carbon-13 Nuclear Magnetic Resonance Studies

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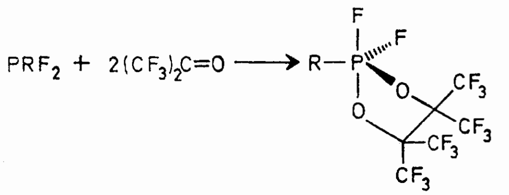
The ^{13}C n.m.r. spectra of fluorophosphoranes containing the perfluoropinacolyl (pfp) ring system are reported: $PRF_2(pfp)$ [R = F, Me, Bu^t, Ph, NEt_2, or $N(SiMe_3)_2$] and $N_2(SiMe_3)_2P_2F_2(pfp)_2$. The results are consistent with previously reported ^{19}F n.m.r. studies and give evidence for a two-stage intramolecular exchange process.

A NUMBER of ^{13}C n.m.r. studies have been made of organophosphorus systems,[2-4] but few investigations have been made of simple monofunctionally substituted phosphoranes,[5,6] particularly of fluorophosphoranes.[7,8] We have recently synthesised and studied, by variable-temperature ^{19}F n.m.r. spectroscopy, fluorophosphoranes containing the perfluoropinacolyl ring system.[1,9] The ground-state structure of these compounds, surmised from the ^{19}F spectra and other considerations, is assumed to be trigonal bipyramidal with the pinacol ring in an axial–equatorial configuration and the substituent group equatorial.



	R		R
(1)	F	(4)	Ph
(2)	Me	(5)	NEt_2
(3)	Bu	(6)	$N(SiMe_3)_2$

SCHEME 1 For the synthesis of (1) and the phosphetidine (7) see ref. 9

Because of the continued interest in the fluxional character of phosphoranes,[10,11] and the availability of ^{19}F decoupling facilities, these compounds presented an interesting opportunity for study by ^{13}C n.m.r. spectroscopy. ^{13}C N.m.r. studies have previously been reported[11] on caged polycyclic phosphoranes containing the perfluoropinacolyl moiety, but shifts and couplings for the monocyclic ring were not observed, presumably due to the complexity of the ^{19}F coupled spectra.

RESULTS AND DISCUSSION

The synthesis and characterisation of the compounds have been reported previously.[1,9] ^{13}C N.m.r. spectra were recorded, when possible, in CD_2Cl_2 solutions, which displayed a carbon signal upfield from those of the pinacolyl carbons; CD_2Cl_2 was used both as a lock and as an internal shift indicator. Shifts were corrected to $SiMe_4$ (see Experimental section). Fluorinated solvents or toluene (a particularly good solvent for many of the compounds) were avoided where possible since (*a*) fluorinated solvents could not provide a spectrometer lock and were perturbed by the ^{19}F broad-band decoupler, producing ill defined signals in the $^{13}CF_3$ region, and (*b*) [$^2H_8$]toluene has strong signals overlaying the $^{13}CF_3$ region. Deuteriated solvents were necessary as an internal spectrometer lock; lack of Overhauser enhancement from ^{19}F decoupling necessitated the use of highly

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concentrated solutions. Studies at very low temperatures were thus limited.

All the pinacolylphosphoranes displayed very similar spectra with highly characteristic $^{13}CF_3$ and ^{13}CO chemical shifts. The ^{19}F decoupler was set at the trifluoromethyl ^{19}F frequency of the compound in question and the modulated broad band was also sufficiently effective to remove any residual $^3J(F{-}P\cdots C)$ and $^4J(F{-}P\cdots C)$ coupling. Random tests with off-resonance settings were made to ensure that spurious results were not produced by inadequate ^{19}F decoupling.

The results of the ambient-temperature spectra are summarised in Table 1. The pertinent features are: (*a*) $^2J(P{-}O{-}C)$ was zero for all the compounds except the alkylphosphoranes (2) and (3) (R = Me and Bu^t respectively); (*b*) $^3J(P{-}O\cdots C)$ was observed for all the compounds and was very similar in all cases (7.3—8.9 Hz). The observation of zero or approximately zero $^2J(P{-}O{-}C)$ couplings is not entirely unexpected since it has been noted by other workers (refs. 2 and 7 and refs. therein) that sign changes are often observed over a series of compounds and values close to zero are frequently given. A typical spectrum [of (4), the phenyl derivative] is shown in the Figure.

TABLE 1

^{13}C-{^{19}F} Spectra of fluoro(perfluoropinacolyl)phosphoranes at ambient temperature [a]

Compound [b]	δ(CF_3) p.p.m.	δ(O–C<)	Other	$^2J_{PC}$ Hz	$^3J_{PC}$ Hz	Other
PF_3(pfp) (1) [c]	121.2	82.9		0.0	9.8	
$PMeF_2$(pfp) (2)	121.1	82.7	16.8	3.7	7.3	122 ($^1J_{CH}$), 185 ($^1J_{PC}$)
PBu^tF_2(pfp) (3)	121.3	83.3	27.6 [d]	4.9	8.3	128 ($^1J_{CH}$)
$PPhF_2$(pfp) (4)	121.0	83.6	130—140 [e]	0.0 [f]	7.3	*e*
$PF_2(NEt_2)$(pfp) (5)	122.9	83.9	16.7 (CH_3) 49.8 (CH_2)	0.0	8.5	127 ($^1J_{CH_3}$) 131 ($^1J_{CH_2}$)
$PF_2\{N(SiMe_3)_2\}$(pfp) (6)	121.1	82.1	3.3	0.0	8.6	120 ($^1J_{CH}$)
$N_2(SiMe_3)_2P_2F_2(pfp)_2$ (7) [g]	120.28 [h] 120.52	81.7	0.2	0.0	8.6 [h] 9.6	125 ($^1J_{CH}$)

[a] 35 °C. [b] In CD_2Cl_2 unless otherwise indicated; pfp = perfluoropinacolyl ring system. [c] Immisible in CD_2Cl_2; [$^2H_6$]benzene–methylcyclohexane (1 : 6) was used. [d] δ(CH_3); the tertiary carbon was not clearly resolved. [e] Complex ^1H coupled multiplets due to phenyl-ring carbons, see Figure. [f] Not resolved, *ca.* 0.5 Hz. [g] In $CDCl_3$–CCl_4 (4 : 3) + 5% CD_2Cl_2. [h] Non-equivalent CF_3 groups, shifts from expanded spectra, non-equivalent $^3J_{PC}$ couplings.

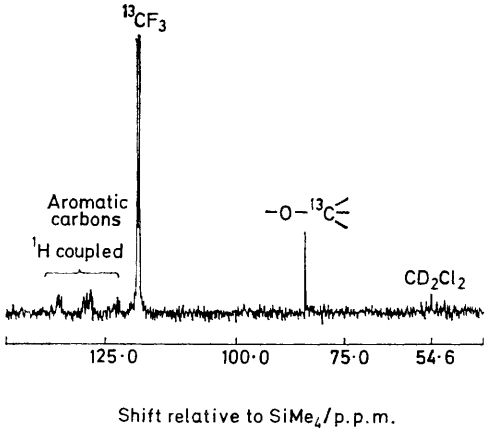


FIGURE ^{13}C-{^{19}F} N.m.r. spectrum of difluoroperfluoropinacolylphenylphosphorane, (4), at 35°C

Compounds (1)—(4) had temperature-independent spectra with only one $^{13}CF_3$ resonance (split into a doublet due to phosphorus coupling) and only one ring-carbon resonance. The possibility of doubling of resonances due to non-equivalence rather than phosphorus coupling was considered but was rejected since the results would be contrary to those found in ^{19}F studies which indicated very rapid equilibration of CF_3 sites for (1)—(4) over a very wide temperature range.[1]

Compounds (5) and (6), the aminophosphoranes, showed a clear temperature dependence. The data from the low-temperature limiting spectra are summarised in Table 2. The $^{13}CF_3$ resonances, doublets at ambient temperature due to phosphorus coupling, broadened on cooling. Maximum broadness was found at −10 and 10 °C for (5) and (6) respectively; on further cooling, resharpening occurred and it was apparent that overlapping doublets of doublets were being resolved. These had the appearance of an asymmetric triplet for (5) and of a poorly resolved doublet of doublets for (6). As it is possible to assign such a doublet of doublets in three ways, the values reported in Table 2 are those most consistent with the 'averaged' spectra at higher temperatures.

TABLE 2

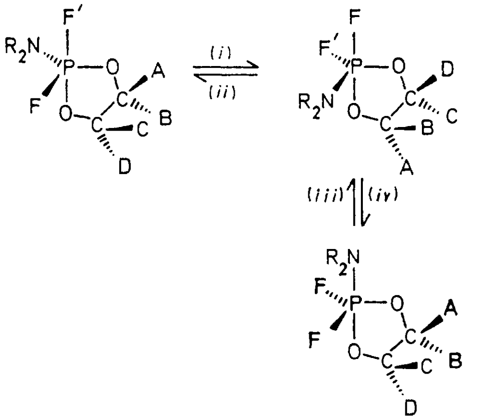
Low-temperature ^{13}C-{^{19}F} spectra of fluoro(perfluoropinacolyl)phosphoranes (5) and (6)

Compound	θ_c/°C	δ(CF_3) [a]	δ(O–C<)	$^2J_{PC}$ Hz	$^3J_{PC}$ Hz
$PF_2(NEt_2)$(pfp) (5) [b]	−30	122.00 (1) 122.31 (1)	83.0 [c]	0.0	9.2 7.8
$PF_2\{N(SiMe_3)_2\}$(pfp) (6) [d]	−25	120.52 (1) 120.78 (1)	81.3 [c]	0.0	8.5 8.7

[a] Relative shifts accurate to ±0.01 p.p.m., absolute shifts to ±0.1 p.p.m., approximate intensities are given in parentheses. [b] Additional resonances assigned to ethyl groups were unchanged at low temperatures. [c] Sharp singlet. [d] Additional resonances assigned to methyl groups were unchanged at low temperatures.

However, while the CF_3 groups were clearly splitting into two environments, the ring carbons for (5) and (6) remained as sharp singlets. Thus a process is occurring which produces two CF_3 environments but which rapidly causes the axial and equatorial ring carbon to equilibrate. Such a process is entirely consistent with the permutational path suggested in our ^{19}F study.[1] A two-step

Berry or turnstile rotation mechanism (BPR or TR) was proposed consisting of a fast TR^1–BPR^1 step and a 'slower' TR^2–BPR^2 step. This is summarised in Scheme 2 (only the discrete trigonal-bipyramidal forms are shown for convenience). The ^{13}C results strongly support our previous arguments. We could not fully stop the exchange for any of the compounds studied since this would have produced, in the ^{13}C spectra for example, four $^{13}CF_3$ resonances and two ring-carbon resonances.



SCHEME 2

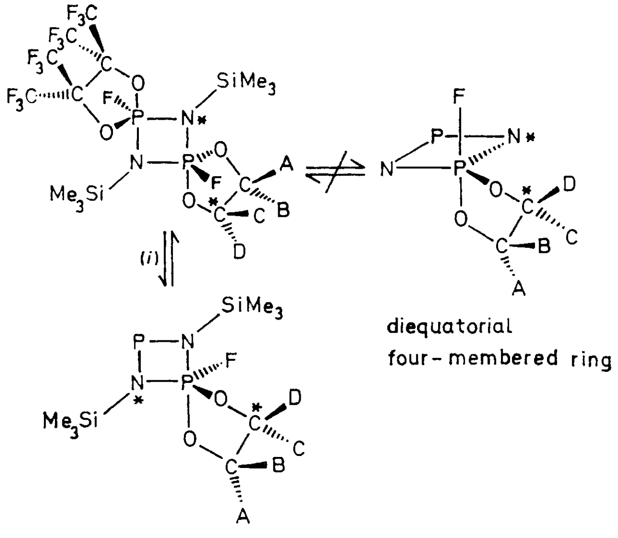
The TR^1 + TR^2 or BPR^1 + BPR^2 gives A≡B≡C≡D; TR^1 or BPR^1 gives A≡C and B≡D; TR^1 or BPR^1 produces equivalent ring carbons. (*i*) TR^1; (*ii*), BPR^1; (*iii*) TR^2; (*iv*), BPR^2. Steps (*i*) or (*ii*) are 'low energy.' Steps (*iii*) or (*iv*) are 'high energy,' slowed on cooling

Again we make no mention of other paths such as a diequatorial pinacolyl-ring intermediate, except to suggest that such forms are highly unlikely due to ring constraints.[12] Also it is not possible from studies of these molecules to deduce any mechanistic data, and thus we continue to include the intriguing possibility of turnstile rotation to explain the apparent very rapid full exchange shown by compounds (1)—(4) and, at elevated temperatures, by (5) and (6) also.

It has been suggested that molecules of these types can undergo intramolecular exchange *via* square-pyramidal intermediates.[13] Careful examination of (1)—(6) reveals that such a mechanism, returning directly to an indistinguishable trigonal-bipyramidal ground state, would produce two CF$_3$ resonances but could not cause all four CF$_3$ groups to be equilibrated unless a formal Berry pseudorotation (or turnstile rotation, of course) occurs to give a new intermediate [with R(axial) following the BPR]. Thus our basic argument is unaffected. In addition, suggestions[14] that P–N bond rotation becomes a factor in the observation of additional CF$_3$ non-equivalence could be ruled out for (5) and (6) since the NEt$_2$ and N(SiMe$_3$)$_2$ ^{13}C resonances showed no effects consistent with rotational freezing and remained unaffected down to the lowest temperatures at which (5) and (6) could be studied.

Compound (7), a diazadiphosphetidine, requires further comment. The ^{19}F n.m.r. spectrum of this compound has previously been only briefly reported.[9] It consists of a temperature-independent spectrum with two CF$_3$ resonances (shift difference 3.2 p.p.m.) and the low-field CF$_3$ resonance is apparently coupled to the directly bound fluorine on phosphorus more strongly than the upfield resonance. This type of observation has been commented on earlier,[9] *viz.* in the cases of (5) and (6) for which, despite a rapid TR^1–BPR^1, one group of CF$_3$ moieties always lies *cis* to rapidly equilibrating, directly bound, fluorines while the other group lies *trans*. A preliminary *X*-ray study of (7) shows the compound to be trigonal bipyramidal at phosphorus with '*trans*' P–F groups.[15] The PNPN ring is approximately planar (Scheme 2).

The *X*-ray result in itself was mildly surprising since the presence of one five-membered and one four-membered ring on phosphorus could lead to a square-pyramidal structure.[13,16] A static trigonal-bipyramidal structure should give rise to four CF$_3$ resonances (^{19}F or ^{13}C) and two ring-carbon resonances. The ^{13}C spectrum of (7), which is temperature independent, shows only one ring-carbon type and, in the CF$_3$ region, a multiplet is observed [poorly resolved due to the limited solubility of (7)] which has four resonances, *i.e.* a doublet of doublets (see Table 1). The most reasonable exchange path for (7) is shown in Scheme 3. A path with a diequatorial four-membered ring is shown, but is highly unlikely, again due to severe ring constraints. Scheme



SCHEME 3 (*i*), Equilibrates A≡C, B≡D, and ring carbons

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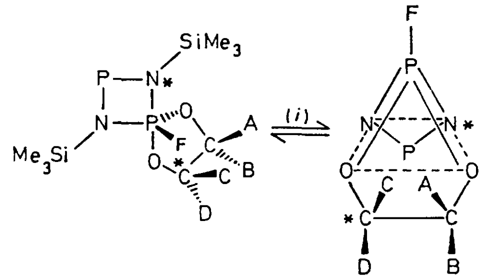
2 is the only one that maintains axial–equatorial four-membered and five-membered rings. It should also be noted that groups A and C always lie ' averaged ' *cis* to the fluorine on phosphorus. Concerted intramolecular exchange at both phosphorus centres is very likely, but has not been depicted for reasons of simplicity.

We suggest, therefore, that (7) is a unique case of a fluorophosphorane centre undergoing an intramolecular exchange where the fluorine on phosphorus remains equatorial at all times. However, it should be pointed out that the presence of low-lying square-pyramidal forms for (7), favourable in view of the four- and five-membered rings,[13,16] could provide an alternative low-energy path through an intermediate of this type (shown in Scheme 4), giving identical results. The fact that the spectra for (7) are temperature independent may be explained by the formal necessity in a BPR of a di-equatorial four-membered ring intermediate for full equilibration to occur and produce spectra similar to those of compounds (1)—(6). This process may also be of high energy in a TR mechanism although, *a priori*, it is not clear why.



SCHEME 4 (*i*), Equilibrates A≡C, B≡D, and ring carbons

EXPERIMENTAL

Spectra were recorded on samples made up in precision n.m.r. tubes (outside diameter, 10 mm). Solvents were purified by trap to trap fractionation and condensed on to the compounds *in vacuo*. Concentrations were maximised in the 30—50% range. ' Ambient '-temperature spectra were recorded at 308 K on a Bruker HX 90 (^{13}C Fourier-transform mode) spectrometer operating at 22.6 MHz. Decoupling frequencies were generated by a HP5110B frequency synthesiser, multiplied three times by the Bruker console prior to amplification by the Bruker broad-band decoupler, and further modulated by imposition of 4 167 Hz sidebands. Internal deuterium lock was used for field–frequency stability. Low-temperature spectra were recorded in the usual manner. Typical settings for data acquisition were 2 000 pulses, pulse width 8 μs, and pulse interval 0.8 s. Spectra were corrected to [^{13}C]tetramethylsilane (0.0 p.p.m.) by use of the relation δ (rel. SiMe$_4$) = δ (rel. CD$_2$Cl$_2$) + 53.6. Downfield shifts are defined as positive.

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