Fluorophosphoranes containing the Perfluoropinacolyl Ring System. Part 5.[1] Estimates of Two-step Exchange Barriers in some Amino-derivatives

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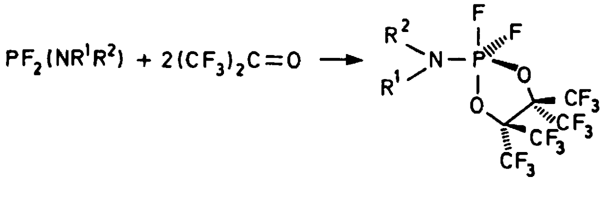
Low-temperature n.m.r. spectra have confirmed the presence of a two-step intramolecular exchange process in aminodifluoro(perfluoropinacolyl)phosphoranes, $PF_2(NR^1R^2)(pfp)$ (R^1 = H, R^2 = H or Bu^t; R^1 = Bu^t or $SiMe_3$, R^2 = $SiMe_3$; R^1 = R^2 = Me or Et; R^1R^2 = $Me_2C[CH_2]_3CMe_2$). Energy barriers for these processes have been estimated. Analysis of the spectra confirms the expected ground-state configurations. Rotational effects are observed in a highly hindered asymmetrically substituted amino-derivative. The compound $PF_2(NH_2)(pfp)$ has been synthesised by cleavage of the bis(trimethylsilyl)amino-precursor with hydrogen chloride. Intramolecular hydrogen-bonding effects are suspected in this compound and in $PF_2(NBu^tH)(pfp)$.

We have recently discussed exchange processes in fluorophosphoranes containing the perfluoropinacolyl (pfp) ring system.[2,3] These compounds were strongly suspected of having a two-step intramolecular scrambling of axial and equatorial substituents, although only one process of 'high energy' had been detected in the ^{19}F and ^{13}C n.m.r. spectra. Mechanistic information, although of considerable importance,[4,5] is not directly retrievable from the spectroscopic data and the choice between Berry pseudorotation (BPR),[6] turnstile rotation,[7] and square-pyramidal intermediates[8] remains problematical. The nature of these monocyclic phosphoranes and their ease of study by ^{19}F, ^{31}P, ^1H, and ^{13}C n.m.r. spectroscopy makes them attractive models for biological systems where phosphoryl and phosphorane intermediates are of paramount importance.[9,10] We have therefore completed exhaustive synthetic and magnetic resonance studies of perfluoropinacolylphosphoranes. This paper reports (*a*) the synthesis of five new aminodifluoro(perfluoropinacolyl)phosphoranes, (*b*) the slowing of the 'low'-energy process in several of the compounds, and (*c*) the estimation of exchange barriers for 'low'- and 'high'-energy processes.

RESULTS AND DISCUSSION

The outline of the preparation of the aminodifluoro(perfluoropinacolyl)phosphoranes, $PF_2(NR^1R^2)(pfp)$ {(1); $R^1 = R^2 = H$; (2) $R^1 = H$, $R^2 = Bu^t$; (3) $R^1 = Bu^t$, $R^2 = SiMe_3$; (5) $R^1R^2 = Me_2C[CH_2]_3CMe_2$; (7) $R^1 = R^2 = Me$} is given in Table 1. Compounds (4; $R^1 = R^2 = SiMe_3$) and (6; $R^1 = R^2 = Et$) have been reported previously.[3] Compounds (3), (5), and (7) were prepared by the reaction of hexafluoroacetone with the corresponding fluorophosphine.[3,11] The reactions gave the usual high yield of the phosphoranes as colourless involatile liquids or low-melting solids.

The chemistry of (4; $R^1 = R^2 = SiMe_3$) continues to excite interest. Thus reaction with anhydrous HCl shows a selective cleavage of the silicon–nitrogen bond (the phosphorus–nitrogen bond appears to be unaffected) to give an equilibrium system driven to completion by removal of chlorotrimethylsilane. The aminophosphorane is a waxy solid melting at 18 °C and having a vapour pressure of *ca.* 0.1 mmHg † at 22 °C. This is considerably less volatile than the parent trifluorophosphorane[3,11] and is analogous to $PF_4(NH_2)$ reported by Cowley and Schweiger[12] but is considerably more stable, being only slightly decomposed after 2 d at room temperature. I.r. spectroscopy was of assistance in the identification of this highly air- and moisture-sensitive compound. Asymmetric and symmetric N–H stretching vibrations were observed at 3 540 and 3 440 cm^{-1}, respectively. Characteristic bands associated with the pfp ring system[3] were observed at 1 118, 995, 958, 874, and 716 cm^{-1}. No P–H or C–H stretching modes were observed.



(3) $R^1 = Bu^t$, $R^2 = SiMe_3$
(5) $R^1R^2 = Me_2C[CH_2]_3CMe_2$
(7) $R^1 = R^2 = Me$

SCHEME 1

$$PF_2\{N(SiMe_3)_2\}(pfp) + 2HCl \rightleftharpoons 2SiMe_3Cl + PF_2(NH_2)(pfp)$$

SCHEME 2

Compound (2; $R^1 = H$, $R^2 = Bu^t$) was synthesised by the action of trimethyl-t-butylaminosilane on the

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† Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa; 1 cal = 4.184 J.

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parent trifluorophosphorane, $PF_3(pfp)$. The rapidity of the reaction demonstrates the high reactivity of

$$SiMe_3(NBu^tH) + PF_3(pfp) \longrightarrow SiMe_3F + PF_2(NBu^tH)(pfp)$$

SCHEME 3

$PF_3(pfp)$, with a chemistry similar to PF_5.[3] Like (1), compound (2) is a relatively involatile liquid having an i.r. spectrum consistent with an N–H containing product [ν(N–H) at 3 455; pfp ring bands at 1 100, 1 005, 970, 890, and 725 cm^{-1}].

The mass spectra of phosphoranes (1)—(7) are consistent with the assigned structures. The highest mass peaks were $[M - F]^+$ or M^+. Compound (1) did not show a molecular ion,[13] but loss of NH_2 was observed.

TABLE 1

Dialkylaminodifluoro(perfluoropinacolyl)phosphoranes, $PF_2(NR^1R^2)(pfp)$ [a]

Compound	Reactants (amount/mol)	Reaction conditions	Yield (%)	B.p. (θ_c/°C) [p/mmHg]	Analyses [b] (%) C	H	F
$PF_2(NH_2)(pfp)$ (1)	HCl (0.025)	r.t.[c]	70	18 [d]	17.4	0.5	64.0
	(4) (0.006)	(see text)			(17.3)	(0.5)	(63.8)
$PF_2(NBu^tH)(pfp)$ (2)	$SiMe_3(NBu^tH)$ (0.005)	*e*	90	22 [d]	25.5	2.2	56.0
	$PF_3(pfp)$ (0.005)	2 h at 20 °C			(25.4)	(2.1)	(56.2)
$PF_2\{NBu^t(SiMe_3)\}(pfp)$ (3)	$PF_2\{NBu^t(SiMe_3)\}$ (0.01)	*e*	95	50—51	28.8	3.4	49.0
	$(CF_3)_2CO$ (0.022)	1 d at 20 °C		[0.01]	(28.6)	(3.3)	(48.8)
$PF_2(\overline{N\cdot CMe_2\cdot[CH_2]_3\cdot C}Me_2)(pfp)$ (5)	$PF_2(\overline{N\cdot CMe_2\cdot[CH_2]_3\cdot C}Me_2)$ (0.01)	*e*	90	39 [d]	34.5	3.8	47.7
	$(CF_3)_2CO$ (0.022)	2 d at 20 °C			(33.3)	(3.4)	(49.2)
$PF_2(NMe_2)(pfp)$ (7)	$PF_2(NMe_2)$ (0.02)	*e*	70	61—62	21.8	1.4	60.2
	$(CF_3)_2CO$ (0.042)	2 d at 20 °C		[12.0]	(21.6)	(1.3)	(59.8)

[a] For $R^1 = R^2 = Et$ and $R^1 = R^2 = SiMe_3$ see ref. 3. [b] Calculated values are given in parentheses. [c] r.t. = Room temperature. [d] Melting point. [e] Warmed from −196 to 20 °C.

TABLE 2

Ambient-temperature n.m.r. data for aminodifluoro(perfluoropinacolyl)phosphoranes [a]

Compound	δ(H)	δ(P)	δ(P*F*)	δ(CF_3)	^1J(PF)	^nJ(HP) [b]	^nJ(HF) [b]
$PF_2(NH_2)(pfp)$ (1)	−3.4	50.0	61.5	68.4	837	*c*	*c*
$PF_2(NBu^tH)(pfp)$ (2)	−3.2 (N*H*) [d] −1.4 (CH_3)	48.8	58.6	68.7	872	12.0(2)	14.0(3)
$PF_2\{NBu^t(SiMe_3)\}(pfp)$ (3)	−0.65 ($SiMe_3$) [e] −1.7 (Bu^t)	39.0	35.1 [f] 42.3	68.0	906 925	1.5(4) ($SiMe_3$)	
$PF_2(\overline{N\cdot CMe_2\cdot[CH_2]_3\cdot C}Me_2)(pfp)$ (5)	−1.5 (CH_3) [d] −1.9 (CH_2)	40.1	38.3	67.8	910		
$PF_2(NMe_2)(pfp)$ [g] (7)	−2.82	50.0	58.1	67.8	846	10.5(3)	2.2(4)

[a] For compounds (4) and (6) see ref. 3. N.m.r. studies were carried out at 298 K on pentane–trichlorofluoromethane solutions (20—70%) unless otherwise indicated. Chemical shifts (δ/p.p.m.) are reported as downfield negative. Proton, fluorine, and phosphorus chemical shifts are relative to internal $SiMe_4$, internal $CFCl_3$, and external H_3PO_4 (85%) respectively. Coupling constants (J) are in Hz. [b] Values of n are given in parentheses. [c] Not resolved at ambient temperature. [d] In CCl_4–CH_2Cl_2 solution. [e] In $CFCl_3$ solution. [f] ^2J(FF) 70.5 Hz. [g] In $CFCl_3$–C_6H_5Me.

All the compounds showed the usual fragmentation pattern associated with fluoro(perfluoropinacolyl)phosphoranes.[3] An ion due to $[M - SiMe_3F]^+$ was observed for compound (3).

Compounds (1)—(7) were chosen for the n.m.r. studies since (*a*) they present a wide variety of steric requirements, (*b*) organosilyl and alkyl substituents are directly comparable, (*c*) intra- and/or inter-molecular H · · · F bonding is possible, and (*d*) mixed nitrogen substituents are present. The ambient-temperature n.m.r. data are given in Table 2. Except for compound (3) (see later), at ambient temperature the PF_2 signals were a doublet [^1J(PF)] reflecting a rapid exchange of axial and equatorial environments. The CF_3 signals were singlets (broad for some of the compounds) except for (4; $R^1 = R^2 = SiMe_3$) which had a doublet resonance close to coalescence (see ref. 3). The CF_3 chemical shifts varied only slightly (67.6—68.7 p.p.m.), while δ(P–*F*) varied, as might be expected, over a wide range. The ^{31}P chemical shifts were typical for fluorophosphoranes.[14]

On cooling, a number of effects were noted in the ^{19}F spectra consistent with the two-step exchange process fully discussed in an earlier publication.[3] A typical example is shown in Figure 1. The 2,2,6,6-tetramethylpiperidyl derivative showed, at 40 °C, a sharp singlet for the CF_3 groups and a doublet for the PF_2 [^1J(PF) 920 Hz]. On cooling, the CF_3 singlet broadened and produced a doublet (1 : 1 intensity) with a coalescence temperature of −14 °C while the PF_2 signals remained a doublet. On further cooling the CF_3 resonances rebroadened and emerged as a complex set of signals with three main signals of *ca.* 1 : 2 : 1 intensity. This complex second-order spectrum is almost certainly the result of four different CF_3 environments. Over the same temperature range the PF_2 signals broadened so as to be indistinguishable from the baseline and then resharpened into two doublets of doublets with additional hyperfine interactions also observable. The first process, from −30 °C upwards, corresponds to the high-energy exchange described previously[3] where fluorines directly bound to phosphorus are already rapidly equilibrating and the CF_3 groups have two sets of

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TABLE 3

Fluorine-19 n.m.r. data from variable-temperature studies [a]

Compound [b]	θ_c °C	$\delta(PF_a)$ p.p.m.	$\delta(PF_e)$ p.p.m.	$\delta(CF_3)$ p.p.m.	$\delta(CF'_3)$ [c] p.p.m.	$^1J(PF_a)$ Hz	$^1J(PF_e)$ Hz	$^2J(F_eF_a)$ Hz
$PF_2(NH_2)(pfp)$ (1)	−90	51.8	69.9	*d*	*d*	733	950	67.1 [e]
$PF_2(NBu^tH)(pfp)$ (2)	−80	51.1	67.2	*d*	*d*	790	957	69.3 [f]
$PF_2\{NBu^t(SiMe_3)\}(pfp)$ (3)	−123	35.1	47.4	*d*	*d*	865	969	77.6
	−33 [g]	35.1	47.4	67.1	68.5	906	925	70.5
	90	37.3		68.0		910		
$PF_2\{N(SiMe_3)_2\}(pfp)$ (4)	−130	25.1	53.8	*d*	*d*	772	996	76.0
	−50	38.6		67.0	68.2	920		
$PF_2(\overline{N\cdot CMe_2\cdot[CH_2]_3\cdot C}Me_2)(pfp)$ (5)	−80	31.3	47.4	*d*	*d*	832	1 001	77.6
	−30	39.4		67.0	68.2	920		
$PF_2(NEt_2)(pfp)$ (6)	−20	57.5		67.4	69.2	853		
$PF_2(NMe_2)(pfp)$ [h] (7)	−20	58.1		67.1	68.2	846		

[a] Phosphorus-31 shifts not included; only slight changes with temperature. [b] In C_5H_{12}–$CFCl_3$ solution unless otherwise indicated. [c] $\delta(CF_3)$ and $\delta(CF'_3)$ are the shifts of the doublet resonance; no attempt is made to assign shifts to the complex second-order spectrum from four inequivalent CF_3 groups. [d] Complex second-order spectrum due to four inequivalent CF_3 groups. [e] $^3J(F_aH)$ 39.1 (doublet), $^2J(PH)$ 18.2 Hz. [f] $^2J(F_aH)$ 34.7, $^2J(PH)$ 27.9 Hz. [g] $\delta(PF)\delta(PF')$, $^1J(PF)$ $^1J(PF')$, $^2J(FF')$. [h] In C_6H_5Me–$CFCl_3$ solution.

environments which also equilibrate as the temperature is increased. The second process, from −30 °C downwards, corresponds to the low-energy exchange described previously[3] and is the result of complete stopping of intramolecular exchange on the n.m.r. time scale. Thus axial and equatorial fluorine environments were observed, having characteristic chemical shifts and coupling constants, and four different CF_3 groups were also apparent; the four CF_3 resonances have some characteristics in common with the ^{19}F n.m.r. spectrum of the compound $S(pfp)_2$ at very low temperatures (−150 °C).[15]

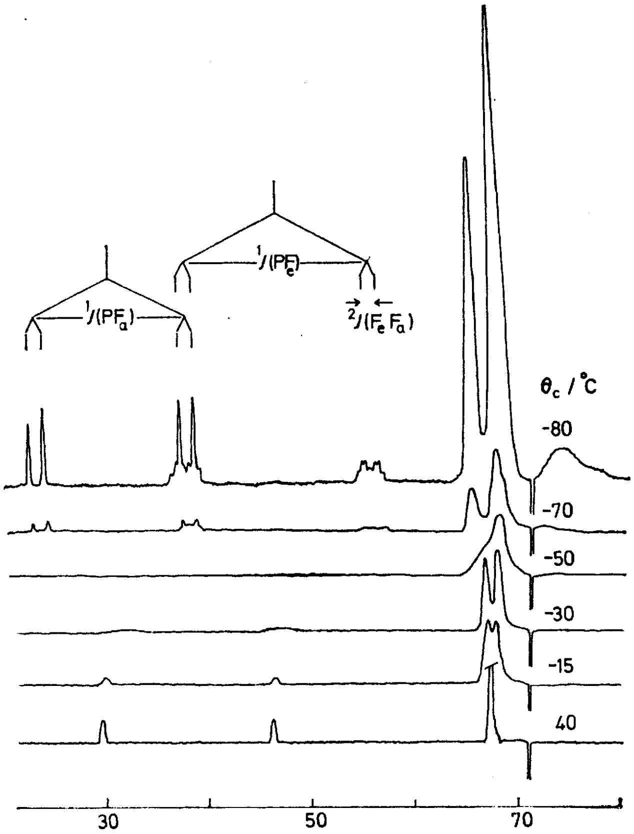

FIGURE 1 Variable-temperature ^{19}F n.m.r. spectra of compound (5). Inverted peaks at 70.9 p.p.m. are 4 000-Hz side bands from $CFCl_3$

We had previously only been able to slow the high-energy process in compounds (4) and (6) and had not observed stopping of the low-energy process. This was achieved for compounds (1), (2), (4), and (5) by the use, surprisingly, of n-pentane–trichlorofluoromethane mixtures whereas most other low-temperature solvents were unsuitable. The results confirm our proposed ground-state structures shown in Scheme 1. In an attempt to estimate the barriers to high-energy exchange, the coalescence temperatures of the CF_3 groups in the ^{19}F spectra were determined. In contrast, in order to estimate the barriers to the low-energy exchange we determined the coalescence temperatures of the centre doublet in the ^{31}P spectra arising from the non-equivalence of $^1J(PF_a)$ and $^1J(PF_e)$ (see Figure 2). Free-energies of activation at the coalescence temperature were determined by normal methods.[16] The method is not entirely accurate in the CF_3 region since the two sets are, in fact, coupled[3] and rigorous treatment would involve analysis of an exchanging $A_3A'_3B_3B'_3$ spin system. However, since δ/J is large and good estimates of δ were possible, we feel the $\Delta G_{T_c}^{\ddagger}$ values calculated are good guide-lines to the ordering of the energy barriers. The Kubo–Sack exchange matrix for the ^{31}P spectrum indicates that the centre resonance can be treated exclusively as the collapse of a simple doublet with the outer lines remaining unchanged (see Figure 2). The $\Delta G_{T_c}^{\ddagger}$ values calculated by these techniques are given in Table 4.

In the case of compounds (1) and (2) the two processes are of relatively similar energy and separation of the CF_3 singlet into a doublet was not complete before the second, low-energy, process caused distortion of the CF_3 signals and prevented the accurate determination of the coalescence temperature. The low-energy barriers for (1) and (2) were determined in the usual manner and the barriers for the high-energy process must be within

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1—3 kcal mol^{-1} of the values shown in Table 4. Both energies were calculable for compounds (4) and (5), while only the high-energy processes were observed in the spectra of (6) and (7). This is probably due to the combination of low barriers (estimated <7 kcal mol^{-1}) and the tendency for (6) and (7) to crystallise rapidly from solution as the temperature is lowered below −50 °C.

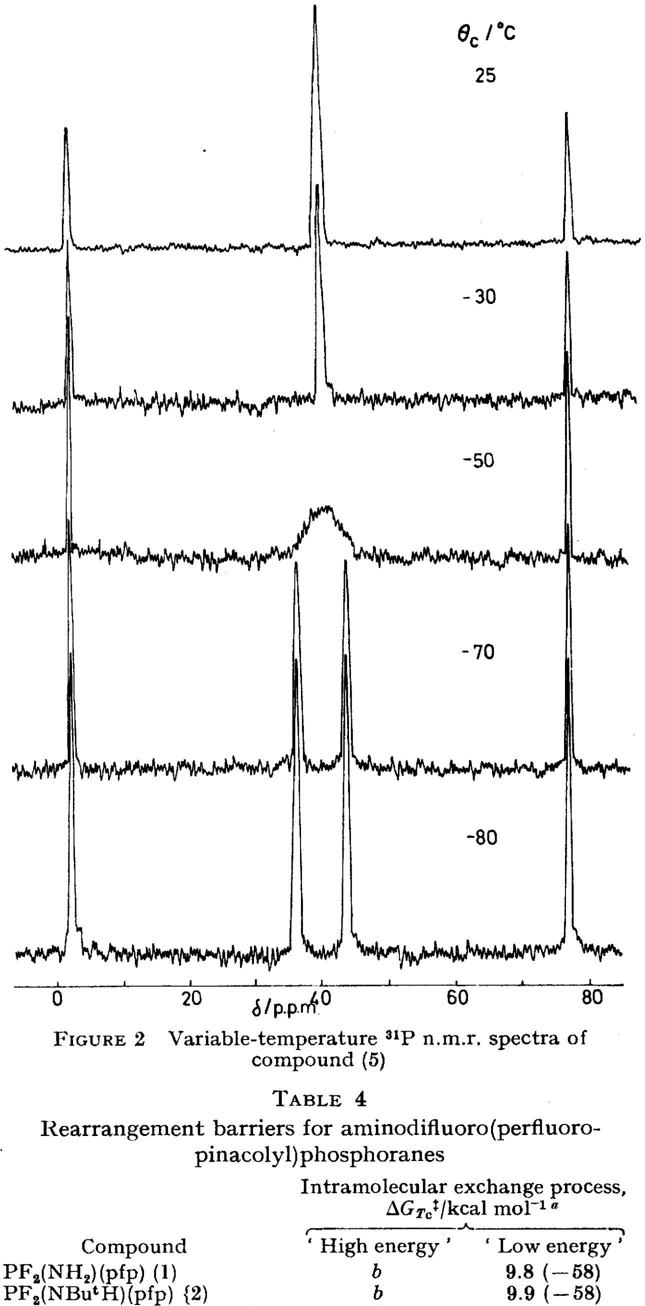


FIGURE 2 Variable-temperature ^{31}P n.m.r. spectra of compound (5)

TABLE 4

Rearrangement barriers for aminodifluoro(perfluoropinacolyl)phosphoranes

Compound	Intramolecular exchange process, $\Delta G_{T_c}^{\ddagger}$/kcal mol^{-1} [a] ' High energy '	' Low energy '
$PF_2(NH_2)(pfp)$ (1)	*b*	9.8 (−58)
$PF_2(NBu^tH)(pfp)$ {2)	*b*	9.9 (−58)
$PF_2\{NBu^t(SiMe_3)\}(pfp)$ [c] (3)	12.7 (−11)	*d*
$PF_2\{N(SiMe_3)_2\}(pfp)$ (4)	15.0 (35)	6.5 (−127)
$PF_2(\overline{N\cdot CMe_2\cdot[CH_2]_3\cdot C}Me_2)(pfp)$ (5)	12.5 (−14)	9.4 (−68)
$PF_2(NEt_2)(pfp)$ (6)	13.0 (−1)	
$PF_2(NMe_2)(pfp)$ (7)	11.7 (−28)	

[a] Values of T_c (in °C) are given in parentheses. [b] Not distinguishable. [c] Barrier to P–N rotation = 13.5 kcal mol^{-1} (T_c = −8 °C). [d] Not calculable.

General comments may be made about the $\Delta G_{T_c}^{\ddagger}$ values in Table 4. It appears that substitution of organosilicon for alkyl groups on nitrogen may increase the exchange barrier marginally, but this may not be statistically significant. A compound with an exceedingly bulky substituent such as 2,2,6,6-tetramethylpiperidyl still has a relatively small ' high-energy ' exchange barrier (12.5 kcal mol^{-1}), and we find it increasingly difficult to visualise a process which places this group in an axial position and has a free energy of activation of this magnitude. The Berry mechanism requires axial placement of the amino-group in the high-energy process, as discussed in Parts 2 and **3** of this series.[2,3] Aminotetrafluorophosphoranes,[14] with similar barriers, are assumed to rely on the amino-substituent acting as a ' pivot ' in a BPR process and there is no necessity for axial placement of the nitrogen. This situation cannot apply in compounds (1)—(7).[2]

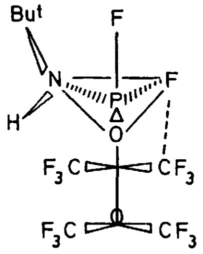
The presence of hydrogen on nitrogen appears to increase the exchange barrier despite a marked reduction in the steric bulk. For example, the low-energy process in $PF_2\{N(SiMe_3)_2\}(pfp)$ (4) has a $\Delta G_{T_c}^{\ddagger}$ value considerably lower than that found in (1), $PF_2(NH_2)$-(pfp). Other workers have commented [12] on the high barrier to exchange displayed by $PF_4(NH_2)$ and attributed the behaviour to the presence of intramolecular hydrogen–fluorine bonding. The involatility of compound (1) is remarkable in comparison to the parent trifluorophosphorane and corresponds to a similar relation between PF_5 and $PF_4(NH_2)$, and may be due to intermolecular HF bonding. We thus believe that there are strong arguments in favour of intra- and intermolecular H–F bonding in fluorophosphoranes containing NH groups.

Compound (3), $PF_2\{NBu^t(SiMe_3)\}(pfp)$, has interesting spectra worthy of additional comment. At ambient temperature the ^{19}F spectrum consisted of one signal for the CF_3 groups but two P–*F* resonances. However, the $^1J(PF)$ values were very similar (906 and 925 Hz) and did not fall satisfactorily into axial and equatorial types.[14] On warming the P–*F* resonances collapsed and eventually resharpened into a simple doublet (910 Hz). The energy for this process was estimated from the ^{31}P spectrum as 13.5 kcal mol^{-1}. On cooling, the CF_3 signal split in the usual manner ($\Delta G_{T_c}^{\ddagger}$ 12.7 kcal mol^{-1}) while the appearance of the P–*F* portion of the spectrum was not substantially altered. However, on further cooling, the CF_3 resonances became complex (*i.e.* four environments), but in addition the P–*F* resonances initially broadened and eventually resharpened into an ABX spectrum (X = P) [$^1J(PF_a)$ 865 and $^1J(PF_e)$ 969 Hz]. The energy for this process could not be determined since the ^{31}P spectrum was already a doublet of doublets. We believe that these results may be explained by the ' normal ' two-stage exchange process but with the superimposition of a hindered rotation about the asymmetrically substituted nitrogen–phosphorus bond with respect to the two rapidly equilibrating (at intermediate temperatures) axial and equatorial fluorines. This is only observed in the case of compound (3). The exact nature of the hindered rotation with respect to the rapidly exchanging phosphorane is difficult to visualise. Trippett and Whittle[17] commented on the observation of what was believed to be a hindered P–N rotation in similar phosphoranes containing the pfp ring system. Unfortunately the nitrogen in question was symmetrically substituted and, in view of other data provided and the lack of similar observations in symmetrically substituted derivatives reported here, we believe that a total stopping of intramolecular exchange was being observed rather than the effects of a hindered rotation. This is not to say that hindered rotation does not occur in symmetrically substituted amino-derivatives, but that such a process does not affect the PF_2 or CF_3 signals.

Of the three exchange mechanisms available none satisfactorily or entirely explains the effect of the hindered rotation on the PF_2 or CF_3 signals. The least problems are encountered when a detailed examination of the turnstile mechanism is made, since rotation of the two fluorines and the alkylamino-group as a fixed trio could give non-equivalent P–F resonances. Additional non-equivalences should be induced in the pfp CF_3 groups but such effects may be small. A Berry process explains the observations poorly, particularly if a single energy minimum (in the axial plane) for the P–N rotation is assumed, since pseudo-rotation and P–N rotation become inextricably coupled, and during a pseudo-rotation the P–N bond would re-establish its low-energy conformation which should give total equilibration of P–F environments.

Finally, hyperfine couplings observed at very low temperatures are useful diagnostic tools in the determination of static ground-state structures. For example the fluorine spectrum of (1) at −90 °C showed the axial fluorine strongly coupled to one proton only. A similar effect is noted in (2), where at low temperatures the axial fluorine is strongly coupled to the proton on nitrogen. Assuming that the ground-state trigonal bipyramid of (2), for steric reasons, has a Bu^t group *cis* to F_a, then the coupling must be transmitted by a 'zig-zag' path. Compound (2) does not, despite having an asymmetrically substituted nitrogen, show the effects already discussed for (3), presumably due to a lower P–N rotational barrier.

The other hyperfine interactions that are of interest are those involving equatorial fluorines. Although not unequivocably resolved in many of the compounds, it is interesting to note that in the fully stopped ^{19}F spectra of (2) and (5) (see Figure 1) the equatorial fluorine signal consists basically of a doublet [$^1J(PF_e)$] of doublets [$^2J(F_eF_a)$] of quartets [J 14.1 and 19.7 Hz for (2) and (5), respectively]. We believe the clue to the origin of the quartet interaction lies in the X-ray crystallographic analysis of a related diazadiphosphetidine.[2,11,18] One CF_3 group lies exceptionally close to the equatorial fluorine (average F···F distance *ca.* 3 Å), while the other CF_3 groups are at considerably greater distances. Therefore the origin of the coupling may be a through-space interaction. This has previously been observed in other trifluoromethyl systems.[19] The ground-state structure and spacial orientation of the CF_3 group in compound (2) are shown in (A). Thus from a detailed knowledge of the exchange processes, couplings, and chemical shifts it is possible to confirm unequivocable ground states for phosphoranes (1)—(7). We have confirmed the axial–equatorial ring placement, one axial and one equatorial fluorine on phosphorus, and, finally, the presence of a two-step exchange path in these molecules.



(A)

EXPERIMENTAL

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

Hydrogen-1, ^{19}F, and ^{31}P n.m.r. spectra were recorded on a JEOL 60 JNMC instrument at 60, 56.4, and 24.3 MHz respectively. An external H_2O lock system with generation of 4 000 Hz side bands was used to locate resonances accurately. Low-temperature spectra were recorded using the JEOL temperature controller in the usual manner. Stability was ±1 °C with an absolute accuracy (from methanol calibration) of, probably, ±3 °C. Infrared spectra were recorded on a Beckman IR 20A spectrometer 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 (1), particularly sensitive to the atmosphere, was examined by condensing a small quantity in the 'cold arm' of the gas cell and depositing on the NaCl plates by gentle warming of the cell. Compound (5) was examined as a Nujol mull. Mass spectra were recorded on an A.E.I. MS 9 (direct-inlet or reservoir system) instrument.

Hydrogen chloride gas was purified and dried by careful trap-to-trap condensation on the vacuum line. The compound $SiMe_3(NBu^tH)$ was prepared by the action of chlorotrimethylsilane on NBu^tH_2 and purified by distillation.[20] (Dimethylamino)difluorophosphine was prepared by the literature method.[21] The new fluorophosphines

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PF_2(tmp) (tmp = 2,2,6,6-tetramethylpiperidyl) and $PF_2\{NBu^t(SiMe_3)\}$ were prepared by normal procedures and will be reported in another publication.[22,23] Compounds (4), (6), and PF_3(pfp) were prepared as reported previously.[3] Compounds (3; $R^1 = Bu^t$, $R^2 = SiMe_3$), (5; $R^1R^2 = Me_2C[CH_2]_3CMe_2$), and (7; $R^1 = R^2 = Me$) were prepared by the reaction of hexafluoroacetone with the corresponding fluorophosphine (see Table 4). The following preparation is typical.

(Dimethylamino)difluoro(perfluoropinacolyl)phosphorane, (7).—Into a thick-walled glass tube, fitted with a Teflon screw tap and containing (dimethylamino)difluorophosphine (1.13 g, 0.01 mol) at −196 °C, was condensed hexafluoroacetone. The tube was removed from the vacuum line and allowed to warm slowly to room temperature. A rapid reaction was observed which appeared complete in 2—3 h. The tube was allowed to stand for 2 d at room temperature before being opened to the vacuum line when excess of hexafluoroacetone was removed. The product, a colourless viscous liquid, was redistilled and gave a 70% yield of (7) (3.1 g), b.p. (12 mmHg) 61—62 °C.

Preparations.— *Aminodifluoro(perfluoropinacolyl)phosphorane*, (1). Into a thick-walled glass tube, fitted with a Teflon screw tap and containing (4) (3.37 g, 0.006 mol) at −196 °C, was condensed dry hydrogen chloride. The tube was carefully warmed to room temperature and shaken for 1 h. A reaction was observed and small quantities of an unidentified white solid were produced. Initial results indicated the establishment of an equilibrium with starting material, cleavage product, HCl, and chlorotrimethylsilane. The reaction was driven to completion by pumping off HCl and $SiMe_3Cl$, detected by i.r. spectroscopy, and by introducing fresh HCl. Three successive 0.008-mol treatments by HCl produced a quantitative yield of $SiMe_3Cl$. The crude product was purified by trap-to-trap fractionation under high vacuum and the pure material was trapped at −15 °C. I.r.: 3 540m (NH_2), 3 440m (NH_2), 1 562m (NH_2), 1 260vs (CF_3), 1 225vs (CF_3), 1 185m, 1 158m, 1 143m, 1 118s (pfp), 1 025s, 995m (pfp), 958s (pfp), 927s, 874m (pfp), 828s, 740m, 716m (pfp), and 695m cm^{-1}.

Difluoro(perfluoropinacolyl)-t-butylaminophosphorane, (2). Into a thick-walled glass tube containing $SiMe_3(NBu^tH)$ (0.73 g, 0.005 mol) at −196 °C was condensed PF_3(pfp) (2.1 g, 0.005 mol). The tube was sealed *in vacuo*, allowed to warm to room temperature, and then left for 2 h. The tube was opened to the vacuum line and trap-to-trap distillation produced $PF_2(NBu^tH)$(pfp) (2.1 g, 90%), $SiMe_3F$ (0.4 g, 100%), and PF_3(pfp) (trace) in traps at 0 and −78 °C, respectively. I.r.: 3 455m (NH), 2 980m (br, CH_3), 1 472w, 1 438m (CH_3), 1 404m (CH_3), 1 378m (CH_3), 1 250vs (CF_3), 1 220vs (CF_3), 1 190s, 1 165s, 1 130s, 1 100vs (pfp), 1 040m, 1 005m (pfp), 970s (pfp), 917s, 890m (pfp), 835s, 810m, 752m (pfp), 725m, 705m, and 631s cm^{-1}.

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