Nuclear Magnetic Resonance Studies of 4,4-Bis(trifluoromethyl)-1,2-oxaphosphetans; Through-space Coupling as a Guide to Ground-state Structures of Cyclic Phosphoranes

By **James Andrew Gibson** *,† and **Gerd-Volker Röschenthaler**, Lehrstuhl B für Anorganische Chemie der Technischen Universität, Pockelsstrasse 4, 33 Braunschweig, Germany
Victor Wray, Gesellschaft für Biotechnologische Forschung, Mascheroder Weg 1, Braunschweig, Germany

Hydrogen-1, ^{31}P, ^{19}F, and ^{13}C n.m.r. studies have been completed on three 4,4-bis(trifluoromethyl)-1,2-oxaphosphetans, (1)—(3). A number of interesting features have been observed. Compounds (1)—(3) have chiral centres at phosphorus and consequently induced non-equivalences in trifluoromethyl groups on $(F_3C)_2CHO$ substituents are observed in the ^{19}F n.m.r. spectra. Trifluoromethyl groups in the phosphetan ring system also have the expected non-equivalence. Compound (2) shows observable intramolecular exchange at room temperature in the ^{19}F and ^1H n.m.r. spectra. The chiral centre at phosphorus is eliminated during the intramolecular exchange which probably occurs *via* a bis[bis(trifluoromethyl)methoxy] equatorially substituted intermediate. Long-range couplings [^8J(FF)], interpreted as through-space interactions, have been found in all the compounds; the long-range couplings may be used diagnostically in the assignment of ground-state structures to these trigonal-bipyramidal phosphoranes. Couplings between groups have been assigned on the basis of selective homo- and hetero-nuclear-decoupling experiments.

DURING the course of our work on the synthesis of fluorophosphoranes containing the perfluoropinacolyl (pfp) ring system it was frequently necessary to employ multinuclear n.m.r. investigations in order to understand the ground-state structures and fluxionality of these cyclic phosphoranes.[1-3] Reaction of hexafluoroacetone with tetramethyldiphosphane [4] produced the much more complex products (1)—(3) shown in Scheme 1. We report here the detailed n.m.r. investigations which led to the assignment of structures to (1)—(3). Compounds (1), 2-[bis(trifluoromethyl)methoxy]-2-[(dimethylphosphino)bis(trifluoromethyl)methoxy]-2-methyl-4,4-bis(trifluoromethyl)-1,2-oxaphosphetan, (2), 2,2-bis[bis(trifluoromethyl)methoxy]-2-methyl-4,4-bis(trifluoromethyl)-1,2-oxaphosphetan, and (3), 2-[bis(trifluoromethyl)methoxy]-2-fluoro-2-methyl-4,4-bis(trifluoromethyl)-1,2-oxaphosphetan, are further examples of a number of 1,2-oxaphosphetans that have been described in the literature.[5] These monocyclic phosphoranes are assumed to be trigonal bipyramidal with the four-membered ring in an axial-equatorial configuration. This is supported by *X*-ray crystallographic studies.[6]

---

† *Present address:* Hepworth Iron Company (Research and Development), Hazlehead, Stocksbridge, Sheffield S30 5HG.

[1] J. A. Gibson, G.-V. Röschenthaler, R. Schmutzler, and R. Starke, *J.C.S. Dalton*, 1977, 450.

[2] J. A. Gibson and G.-V. Röschenthaler, *J.C.S. Dalton*, 1976, 1440.

[3] J. A. Gibson, G.-V. Röschenthaler, and R. Schmutzler, *J.C.S. Dalton*, 1975, 918.

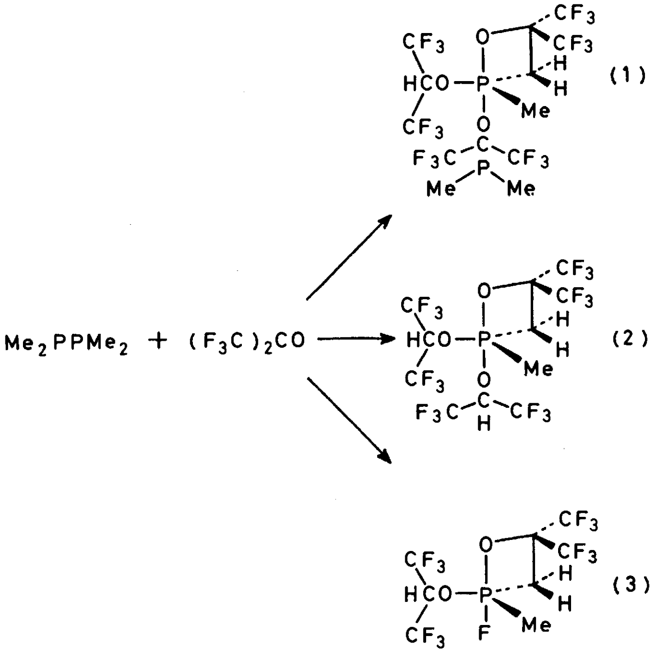
[4] J. A. Gibson, G.-V. Röschenthaler, and R. Schmutzler, *Z. Naturforsch.*, 1977, in the press.

[5] F. Ramirez, C. P. Smith, and J. F. Pilot, *J. Amer. Chem. Soc.*, 1968, **90**, 6726.

[6] Mazhar-Ul-Haque, C. N. Caughlan, F. Ramirez, J. F. Pilot, and C. P. Smith, *J. Amer. Chem. Soc.*, 1971, **93**, 5229.

RESULTS AND DISCUSSION

The ^{13}C n.m.r. results are summarised in Table 1 and a typical set of ^{13}C n.m.r. spectra is shown in Figure 1. The ^{13}C measurements were made with either protons or fluorines decoupled; thus unequivocal assignments were possible depending on the fine structure observed when a particular nucleus was being decoupled. For example, in compound (1) (see Figure 1) the carbons **5** and **6** have very similar chemical shifts. The proton-decoupled spectrum was very complicated and the assignment of signals is not immediately clear. The fluorine-decoupled spectrum is more amenable to interpretation. The secondary carbon of the $(F_3C)_2CHO$ group, **5**, is a doublet [$^1J(CH)$] of doublets [$^2J(PC)$] while the ring carbon, **6**, is a doublet [$^2J(PC)$] with triplet fine structure [$^2J(CH)$]. Thus, with knowledge of the carbon–phosphorus coupling constants, it is possible to assign the proton-decoupled spectrum as a doublet [$^2J(PC)$] of septets [$^2J(CF)$] overlying a second doublet [$^2J(PC)$] of septets [$^2J(CF)$].

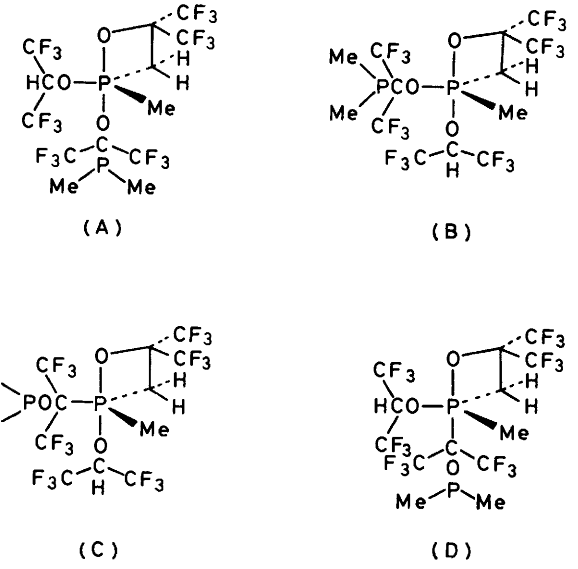


SCHEME 1

All the compounds show methyl carbons with $^1J(PC)$ values characteristic of equatorial placement in the trigonal bipyramid.[7,8] In addition, compound (1) has a second methyl carbon resonance with a smaller $^1J(PC)$ value characteristic of substitution at a phosphorus(III) centre.[9] The resonances of the methylene carbons of the phosphetan ring system lay downfield of the methyl carbons and the large measured $^1J(PC)$ values indicate equatorial placement. The four-membered ring is expected to adopt an equatorial–axial configuration with the oxygen occupying the axial location.[10] The trifluoromethyl carbons had somewhat broader signals, particularly under fluorine broad-band-decoupling conditions, but clearly different trifluoromethyl group environments were being resolved. No attempt was made to assign the shifts listed in Table 1; there does, however, appear to be a rough correlation between shifts and $^1J(CF)$ values.

Problems were encountered during fluorine-decoupling experiments in the ^{13}C n.m.r. investigation of compound (3). The decoupling frequency was set to the average frequency of the trifluoromethyl groups but there was insufficient power to decouple completely the fluorine directly bound to the phosphorus. This fluorine was quite strongly coupled to the methyl and methylene carbons (as is observed in the proton-decoupled spectrum) with the result that the partial decoupling gave ill defined signals for these carbons. The reported $^1J(CH)$ values for (3) therefore have large uncertainties.

Despite the information gained from ^{13}C n.m.r. studies there remained, for example, four possible structures for (1) consistent with the data. These are shown in Scheme 2: (A) and (B) are stereoisomers as are (C) and (D). Structure (D) need not be considered further as it violates the 'apicophilicity' rules in that an alkyl group is placed axial in preference to an alkoxy-group. Such a structure would be expected to be strongly destabilised with respect to (A), (B), or (C).[10,11] Structures such as (C) must be considered, however, since there was no prior knowledge of the mode of insertion of hexafluoroacetone into the P–P bond. The choice between (A), (B), and (C) was made on the basis



SCHEME 2

---

[7] K. I. The and R. G. Cavell, *J.C.S. Chem. Comm.*, 1975, 716.

[8] H. Dreeskamp, C. Schumann, and R. Schmutzler, *Chem. Comm.*, 1970, 671.

[9] B. Mann, *J.C.S. Perkin II*, 1972, 30.

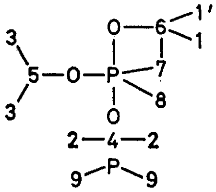
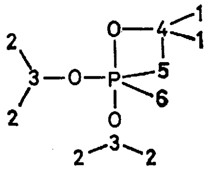
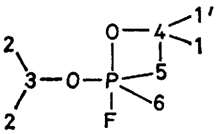
[10] R. Luckenbach, 'Dynamic Stereochemistry of Pentacoordinated Phosphorus and Related Elements,' Georg Thieme, Stuttgart, 1973.

[11] I. Ugi, and F. Ramirez, *Chem. in Britain*, 1972, **8**, 198 and refs. therein.

of the fluorine spectra and in particular the selective-decoupling experiments.

TABLE 1

Carbon-13 n.m.r. data for (1)—(3) [a]

Compound		Chemical shift [b]/p.p.m. [Carbon number]				Coupling constants/Hz [Carbon number]					
		CF_3 [c]	$(F_3C)_2CO$	CH_2	CH_3	$^1J(CF)$ [c]	$^2J(CF)$	$^1J(CP)$	$^2J(CP)$	$^1J(CH)$	$^2J(CH)$
	(1)	121.4 [1] 123.1 [1′] [2] 123.7 [3]	85.2 [4] 72.2 [5] 71.6 [6]	50.6 [7]	24.2 [8] 9.9 [9]	282 [1] 285 [1′] [2] 289 [3]	29.1 [4] 35.3 [5] 32.7 [6]	52.5 [4] 130.1 [7] 133.3 [8] 19.9 [9]	23.2 [4] 8.0 [5] 16.6 [6]	153.1 [5] 140.0 [7] 132.4 [8] 130.5 [9]	2.5 [6]
	(2)	123.5 [1] 122.1 [2]	72.5 [3] 72.3 [4]	50.8 [5]	22.9 [6]	285 [1] 284 [2]	34.4 [3] 33.0 [4]	124.9 [5] 128.8 [6]	10.3 [3] 16.8 [4]	151.5 [3] 140.2 [5] 131.7 [6]	2.7 [4]
	(3)	122.4 [1] [1′] 122.8 [2]	71.5 [3] 71.4 [4]	47.0 [5]	21.0 [6]	283 [1] [1′] 289 [2]	35.0 [3] *d* [4] 45.3 [5] 26.5 [6]	123.1 [5] 134.9 [6]	6.2 [3] 21.0 [4]	152 [3] 140 [5] 132 [6]	*d* [4]

[a] Spectra were recorded at 25.16 MHz under ^1H or ^{19}F decoupling conditions; (1) and (3) in C_6D_6, (2) in CD_2Cl_2. [b] Measured relative to the solvent (downfield positive) and corrected to tetramethylsilane by the relations $\delta_{rel.}(SiMe_4) = \delta_{rel.}(C_6D_6) + 128$ p.p.m. and $\delta_{rel.}(SiMe_4) = \delta_{rel.}(CD_2Cl_2) + 54.2$ p.p.m. [c] Shifts not assigned to particular CF_3 groups. [d] Not clearly resolved.

The fluorine n.m.r. data for (1)—(3) are summarised in Table 2 and the spectrum of (1), at 94.13 MHz, together with various decoupling experiments, is reproduced in Figure 2. The trifluoromethyl groups in all the compounds had highly characteristic chemical shifts. For example, all the compounds had resonances at 72.4—74.5 and 76.4—78.3 p.p.m. assigned to the $(F_3C)_2CHO$ and ring trifluoromethyl groups, respectively.[5] This could be directly confirmed in the case of (2) since, at room temperature, signals of relative intensity 2 : 1 were

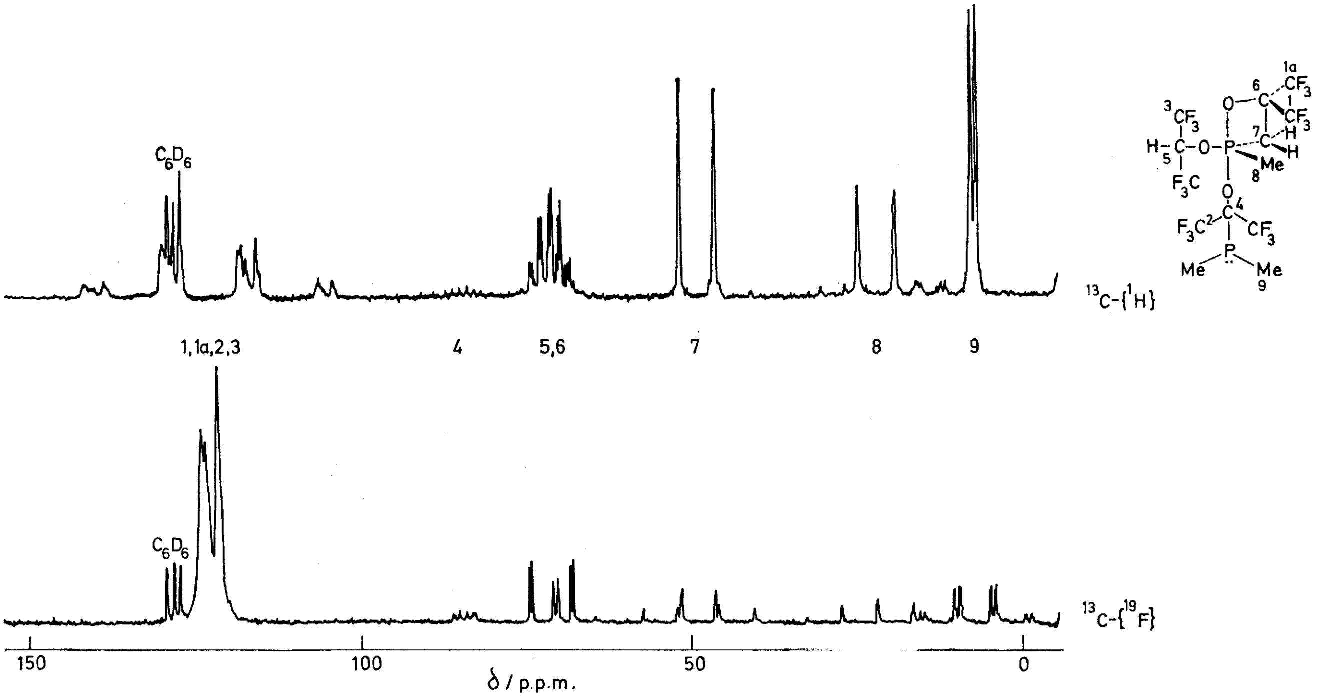


FIGURE 1 Carbon-13 n.m.r. spectrum of (1) at ambient temperature under fluorine- and proton-broad-band-decoupling conditions

observed at 74.5 and 78.0 p.p.m., respectively. The signal of intensity 2 must belong to the rapidly intramolecularly exchanging $(F_3C)_2CHO$ groups.

TABLE 2

Fluorine-19 n.m.r. data for (1)—(3) [a]

		Chemical shifts/p.p.m.				Coupling constants/Hz			
Compound	θ_c/°C	$(F_3C)_2CO$	$OCH(CF_3)_2$	$C(CF_3)_2$ [b]	PF	^1J(PF)	^3J(FF) [c]	^8J(FF)	^3J(HF)
(1)	Ambient	67.0	72.4	76.5			9.0	9.0	6.0 [d]
		67.7	73.1	78.3					
(2)	50		74.5	78.0					5.0
	−60		74.1 [e]	77.3			8.8	8.5	5.2 [e]
			74.4						6.0
			74.5	78.7					
			74.9						
(3)	Ambient		72.9	76.4	29.6	832	8.0 [f]	7.0 [f]	5.6
			73.5	77.0					

[a] Spectra were recorded at 56.4 or 94.13 MHz relative to internal $CFCl_3$ (downfield negative); (1) in C_6D_6, (2) and (3) in $CFCl_3$–CD_2Cl_2. [b] Downfield shifts are assigned to a CF_3 group *cis* to equatorial methyl (see text). [c] Coupling between CF_3 groups on the phosphetan ring. [d] $^3J(P^{III}F)$ 3.0 Hz. [e] Assignment into axial and equatorial types not made. [f] Poorly resolved, quoted values are only approximate. ' ^8J(FF) ' refers to the through-space coupling (see text).

Additional resonances were observed in the case of (1), assigned to the $(Me_2P)(F_3C)_2CO$ group, and (3) [a doublet, ^1J(PF) 832 Hz], assigned to the axial [12] fluorine directly bound to phosphorus. The resonances assigned to the ring trifluoromethyl groups were the only signals to have clearly discernable fine structure, the nature of which will be discussed later. The other resonances were broad and generally featureless at 56.4 MHz, but at 94.13 MHz were split into two distinct environments for each CF_3 type. Thus compound (1) showed six CF_3 signals of three types (Figure 2) and (3) showed four CF_3 signals of two types. Since the phenomena are strongly field dependent the doubling of CF_3 environments must be a chemical-shift rather than a spin–spin coupling effect. We interpret these observations as being the result of a chiral centre at phosphorus which induces chemical-shift non-equivalence in the diastereotopic trifluoromethyl groups.[13] The phosphorus centres in all the three compounds are chiral provided the ground states are shown in Scheme 1. Indeed it is not possible in the case of (1) and (3) to propose stereoisomers which do not have a chiral centre. Compound (2) is quite different and is discussed below.

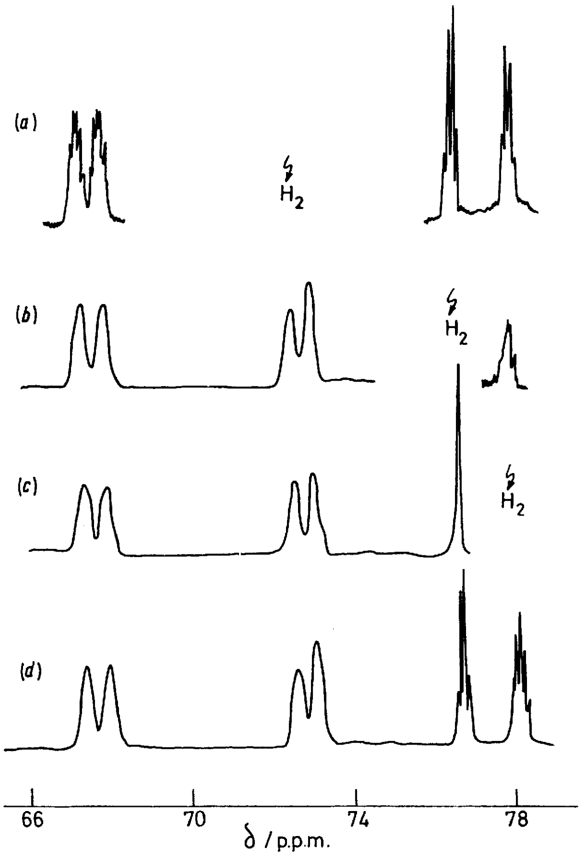


FIGURE 2 Fluorine-19 n.m.r. spectrum of (1) recorded at 94.13 MHz at ambient temperature. H_2 represents the applied decoupling frequency

Although the non-equivalence of trifluoromethyl groups in the $(F_3C)_2CHO$ and $(Me_2P)(F_3C)_2CO$ moieties can be explained by stopped rotation we do not favour this explanation. Such a proposal is unnecessary [13] and, in addition, there is no evidence in the literature indicating high barriers to P–O rotation. Small changes in the magnitude of non-equivalence were noted on varying the temperature and these may be explained by changes in rotamer populations.[13] The shift differences of the CF_3 sets decreased by less than 0.2 p.p.m. over a 60 °C temperature range (ambient to 85 °C).

The trifluoromethyl groups on the ring are, of course, non-equivalent because of a lack of plane of symmetry in the ring. The non-equivalence is of greater magnitude than the diastereotopic effects in the CF_3 groups of $(F_3C)_2CHO$ except in the case of (3) where the shift differences are approximately the same. All the compounds, including (2) at low temperatures, had very similar ring CF_3 resonances consisting, at 94.13 MHz, of a quartet and a multiplet. Thus the CF_3 groups are strongly coupled [^4J(FF) *ca.* 9 Hz] while the upfield resonance was additionally coupled to other nuclei. Phosphorus or proton decoupling failed to reduce the upfield resonance to the expected quartet and the additional coupling must arise from a long-range fluorine–fluorine interaction.

---

[12] R. Schmutzler, in ' Halogen Chemistry,' ed. V. Gutmann, Academic Press, New York, 1967, vol. 2.

[13] W. B. Jennings, *Chem. Rev.*, 1975, **75**, 307.

The homonuclear-decoupling experiments carried out on compound (1) are shown in Figure 2. Irradiation of the downfield pair of resonances, assigned to the (Me_2P)-$(F_3C)_2CO$ group, had no significant effect on the other signals and is not included. Irradiation of the centre resonances [see Figure 2(*a*)] sharpened the downfield resonance slightly and, more importantly, removed the residual coupling in the extreme upfield ring CF_3 resonance to give a quartet. Observation of the proton spectrum while under decoupling condition (*a*) confirmed the assignment of the central resonances to the $(F_3C)_2CHO$ group as loss of $^3J(HF)$ coupling occurred. Irradiation of the downfield half of the ring CF_3 group resonances, (*b*), produced a multiplet of ' quartet ' appearance for the upfield half, while irradiation of the upfield multiplet, (*c*), reduced the downfield quartet to a singlet and had a small effect on the $(F_3C)_2CHO$ resonances (particularly the upfield part). The results may only be reasonably interpreted as due to the spin–spin interaction of *one* of the ring CF_3 groups with, predominantly, one of the CF_3 groups of the $(F_3C)_2CHO$ group. This coupling [$^8J(FF)$ *ca.* 9 Hz] can be accounted for by a through-space mechanism. Construction of molecular models indicates that a close interaction between the CF_3 groups is possible only when the $(F_3C)_2CHO$ group is equatorial.

TABLE 3

Hydrogen-1 and ^{31}P n.m.r. data for (1)—(3) [a]

	Chemical shifts/p.p.m.				Coupling constants/Hz			
Compound	P	CH_3	CH_2	OC*H*	$^2J(PCH_3)$	$^2J(PCH_2)$	$^3J(PH)$	$^3J(FPCH)$
(1)	6.8 P^{III}	−1.20	−4.11 [b]	−5.60 [c]	6.0	13.1 [b]	15.7 [c]	
	9.4 P^{V}	−2.10	−4.39		16.5	29.0		
(2)	10.0	−1.90	−3.83 [d]	−5.15 [e]	16.5	20.7 [d]	13.0 [e]	
(3)	2.1	−2.35	−4.30 [f]	−5.50 [c]	17.6	*f*	15.6 [c]	11.4 (CH_3) [d]

[a] Phosphorus-31 spectra measured at 24.3 or 40.5 MHz relative to external H_3PO_4 (downfield negative); (1) in C_6D_6, (2) and (3) in $CFCl_3$–CD_2Cl_2. Hydrogen-1 spectra measured at 60.0 or 100.06 MHz relative to internal tetramethylsilane (downfield negative). [b] ABX spectrum, iterated values, $J(AB)$ 17.6. [c] Doublet of septets. [d] A_2X spectrum above room temperature; at −60 °C an ABX spectrum with $\delta(AB)$ *ca.* 6 Hz. [e] Values at 50 °C; at −60 °C two $(F_3C)_2CHO$ groups at −4.71 and −5.57 p.p.m. [$^3J(PH)$ 12.0 and 12.5 respectively]. [f] ABXY spectrum, coupling constants not determined, $\delta(AB)$ between the values for (1) and (2).

Interaction from an axial position appears highly unlikely. Thus isomers (B) and (C) are ruled out for compound (1), and (A) is confirmed as the ground-state structure. We previously observed[2] couplings from equatorial fluorines to CF_3 groups in the perfluoropinacol ring system, and believe that through-space spin–spin interactions of this type are a general phenomenon in bulky perfluorocyclophosphoranes.[14] The features observed for (1) were also found in (2) (at low temperatures) and (3). In each case, therefore, the upfield portion of the ring CF_3 resonances is assigned to the trifluoromethyl group *trans* to the equatorial methyl group and *cis* to the equatorial $(F_3C)_2CHO$ group. The observation of coupling predominantly to one of the CF_3 groups of the $(F_3C)_2CHO$ moiety is surprising and must reflect a highly preferred rotamer, but we still do not favour restricted rotation as an explanation.

The ^1H and ^{31}P n.m.r. spectra of compounds (1)—(3) were unexceptional, showing the expected hyperfine interactions. The data are given in Table 3. [The data for (2) are from the low-temperature spectra.] All the three compounds had ABX spectra for the methylene protons, but iterative fitting was only possible for (1) since the A — B shift difference for (2) is small and results in an approximate A_2X spectrum. In addition the spectra for (3) were further complicated by coupling from the fluorine directly bound to phosphorus. The methylene protons are more correctly described as an ABXY spin system and a full analysis was not undertaken. The phosphorus spectra contained the expected coupling constants extracted from the fluorine and proton spectra, with compound (2) giving a doublet [$^1J(PF)$ 832 Hz]. Compound (1) showed two types of phosphorus and the downfield resonance was assigned to the P^{III} on the basis of spin–spin splitting and decoupling experiments. A phosphorus–phosphorus coupling was observed [$^3J(PP)$ 3.0 Hz].

Intramolecular Exchange.—Trigonal-bipyramidal phosphoranes often display intramolecular scrambling of axial and equatorial ligands.[10,15] This effect is clearly displayed by (2) which has two $(F_3C)_2CHO$ groups, axially and equatorially substituted in the trigonal bipyramid. At room temperature and above only one signal due to the $(F_3C)_2CHO$ group was observed in the ^1H and ^{19}F n.m.r. spectra. The fluorine spectrum consisted of a singlet (intensity 2) for the $(F_3C)_2CHO$ group and a singlet (intensity 1) for the ring CF_3 groups. A process is thus occurring which causes simultaneous equilibration of axial and equatorial $(F_3C)_2CHO$ groups and, secondly, the two ring CF_3 groups.

The effect of temperature on the ^1H n.m.r. of (2) is pronounced. On cooling below 0 °C two proton environments were observed for the $(F_3C)_2CHO$ groups and at −60 °C fine structure was observed [$^3J(HF)$ and $^3J(HP)$]. It is not possible to assign unequivocably the resonances to axial or equatorial types. The coupling constants observed at 50 °C were the averages of those observed at −60 °C and therefore couplings to axial and equatorial groups must have the same sign. Also observable in the proton spectrum was the strong skewing of the doublet due to the ring methylene hydrogens at −60 °C. The spectrum at higher temperatures is very close to a simple 1 : 1 doublet. The low-temp-

---

[14] J. A. Gibson and G.-V. Röschenthaler, unpublished work.

[15] W. G. Klemperer, in ' Dynamic N.M.R. Spectroscopy,' eds. F. A. Cotton and L. M. Jackman, Academic Press, New York, 1975.

erature spectrum can be simulated as an ABX spectrum with a shift difference between A and B of *ca.* 6 Hz.

The variable-temperature fluorine spectra showed similar effects. At −60 °C two $(F_3C)_2CHO$ groups were resolved, complete with chirality-induced non-equivalences, as a complex overlapping set of multiplets. In addition the ring CF_3 groups were non-equivalent and very similar in appearance to those of compounds (1) and (3) at room temperature (see Figure 2).

A model for the intramolecular-exchange process must take into account both the scrambling of the axial and equatorial $(F_3C)_2CHO$ groups, the elimination of the chiral centre at phosphorus with respect to the CF_3 groups, and the establishment of a plane of symmetry through the ring. Since diequatorial ring placement (particularly a four-membered ring containing oxygen) is thought to be a high-energy process [5,10,11] the exchange path envisaged must place two $(F_3C)_2CHO$ groups simultaneously equatorial. Such an exchange scheme is depicted in Figure 3. We have limited the discussion to the description of trigonal-bipyramidal forms and formalised Berry pseudorotational processes,[16] although the arguments would not significantly differ for the discussion of a turnstile exchange process.[2,3,17] Irregular bond-breaking intermolecular processes may be ruled out by the observation of spin–spin coupling to phosphorus in the fast-exchange spectra.

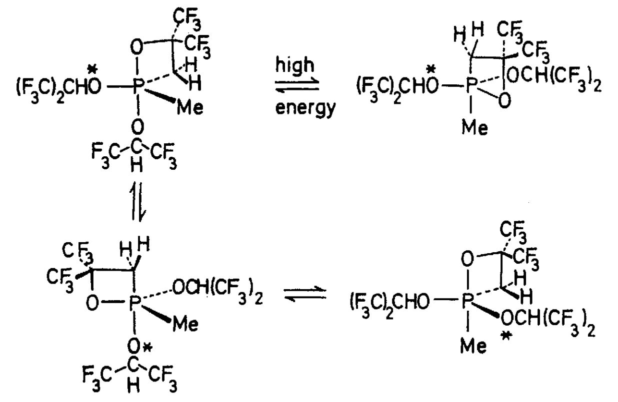


FIGURE 3 Two-step and one-step intramolecular-exchange paths for (2) *via* trigonal-bipyramidal intermediates

Of the two schemes outlined in Figure 3 the one-step process involves simultaneous axial placement of two ' alkyl ' groups which should be of higher energy than either of the two intermediates depicted in the two-step process.[10] Similar two-step exchange mechanisms have been proposed to explain the intramolecular-exchange processes in trifluoromethylphosphoranes $PMe(CF_3)_3X$ ($X = Cl$, OMe, *etc.*),[18] and two-step processes have actually been observed in fluoro(perfluoropinacolyl)-phosphoranes.[3] Although exchange *via* square-pyramidal intermediates [19] is attractive, we cannot envisage any simple sequence from the ground-state structure that will achieve the desired equilibration of groups. With two equatorial $(F_3C)_2CHO$ groups the chiral centre at phosphorus is eliminated [10] and a plane of symmetry in the phosphetan ring is established.

Similar sequences of exchange can be postulated for compounds (1) and (3), indeed the energies required must be of similar magnitude to that for (2). However, exchange processes, even if rapid, could not equilibrate any of the groups as found in (2) and it is not possible to write any intermediate stereoisomer with no chiral centre at phosphorus and a plane of symmetry in the phosphetan ring. However, concentrations of other stereoisomers must be small or significant perturbations of the through-space couplings would be observed. We found no evidence of stable structural isomers for (1) and (3) and therefore suspect that there are relatively large differences in the apicophilicities of F, (Me_2P)-$(F_3C)_2CO$, and $(F_3C)_2CHO$.

EXPERIMENTAL

Compounds (1) and (2) were prepared by the reaction of hexafluoroacetone with tetramethyldiphosphane as described elsewhere.[4] They were purified by trap-to-trap condensation on the vacuum line, samples for n.m.r. study having purities generally >97%. Compound (3) is also produced in the reaction of hexafluoroacetone with tetramethyldiphosphane but the yield is low and the material is extremely difficult to purify. Samples for n.m.r. study were prepared by fluorination of the corresponding chlorophosphorane with SbF_3 and purified by trap-to-trap condensation.[20] Samples of the compounds were condensed into the n.m.r. tubes (5 mm, ^{19}F, ^{1}H; 8 mm, ^{31}P; 10 mm, ^{13}C) containing the solvent (see Tables) at −196 °C and flame sealed. The tubes were warmed to room temperature and shaken to facilitate mixing.

Hydrogen-1, ^{19}F, and ^{31}P n.m.r. spectra were recorded at 60, 56.4, and 24.3 MHz on a JEOL JNM C-60 HL spectrometer or at 100.06, 94.13, and 40.50 MHz on a Varian XL-100-12 spectrometer. Carbon-13 n.m.r. spectra were obtained at 25.16 MHz in the Fourier-transform mode on the Varian instrument. Ambient-temperature spectra were recorded at 25 (JEOL) and 37 °C (Varian). Variable-temperature spectra were obtained in the usual manner. Decoupling frequencies were generated by a Varian Gyrocode synthesiser.

We thank the Alexander von Humboldt-Stiftung for the provision of a Research Fellowship (to J. A. G.), the Deutsche Forschungsgemeinschaft for support, and Professor R. Schmutzler (T. U. Braunschweig) for his co-operation in the provision of facilities for this work and for valuable discussions.

[7/071 *Received, 14th January,* 1977]

---

[16] T. S. Berry, *J. Chem. Phys.*, 1960, **32**, 933.

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

[18] R. G. Cavell, J. A. Gibson, and K. I. The, *Inorg. Chem.*, submitted for publication.

[19] R. R. Holmes, *J. Amer. Chem. Soc.*, 1974, **96**, 4143.

[20] J. A. Gibson, G.-V. Röschenthaler, and R. Schmutzler, *Chem. Ber.*, in the press.